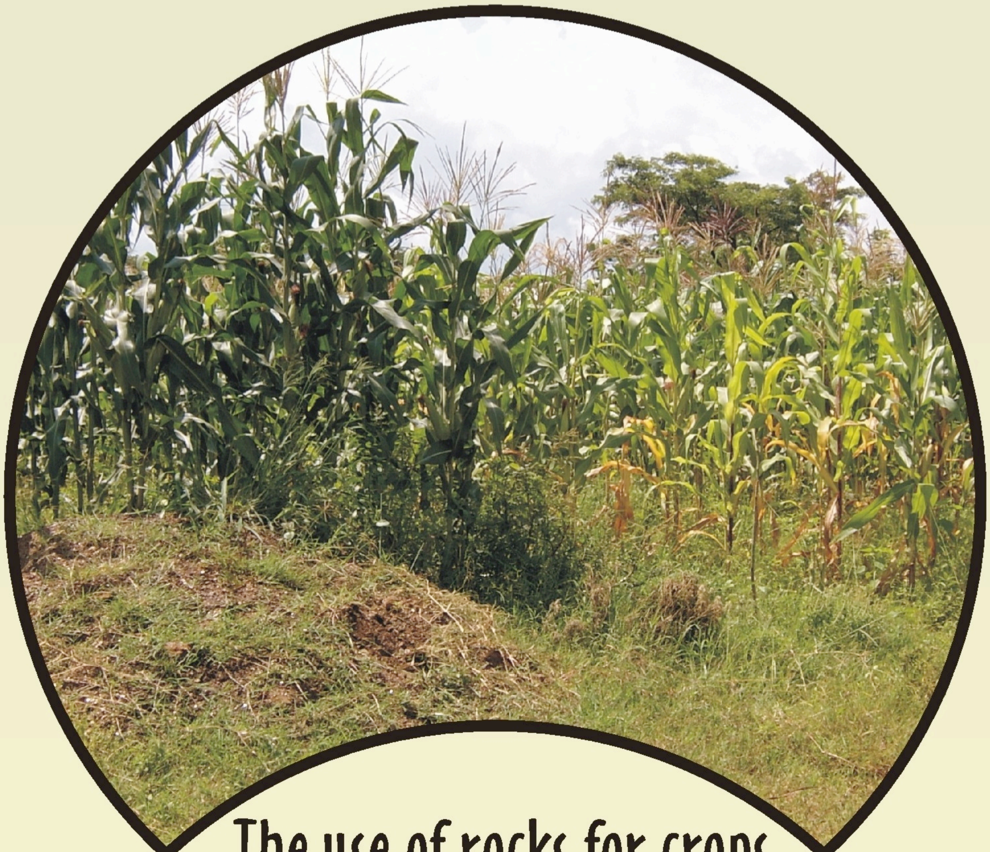
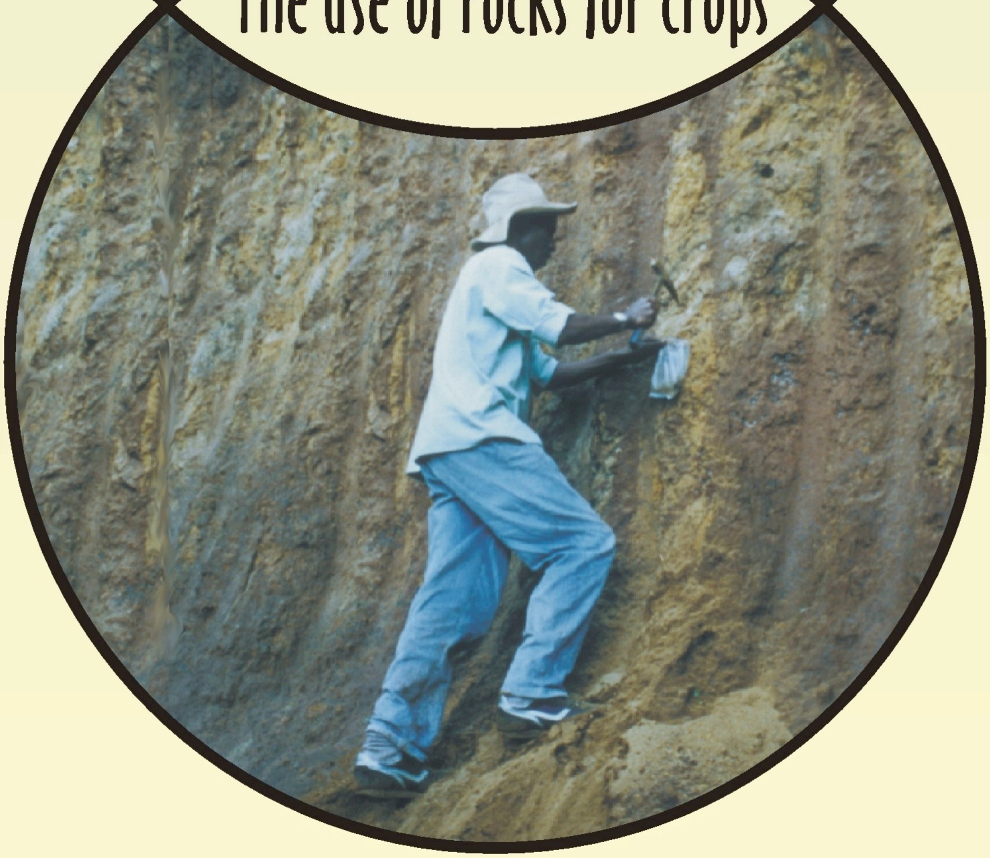
Agrogeology



The use of rocks for crops



Peter van Straaten

Agrogeology: The use of rocks for crops

By

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Agrogeology

The use of rocks for crops

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Foreword

Increasing agricultural production is particularly urgent in regions of the world such as sub Saharan Africa where populations are rapidly growing but food production is not keeping pace with it, thus leading to millions left hungry and malnourished. In these regions, the quality of the environment is also deteriorating as areas under forests and wetlands or areas preserved for wildlife conservation are continuously threatened by the expansion of land under agriculture. This is not sustainable. To reduce and reverse this phenomenon, increasing food production will require intensive agriculture that increases the productivity of land under production. This will require the use of modern technologies that integrate the use of fertilizers (both organic and inorganic), improved seeds and planting materials, and better access to markets especially for smallholder farmers. Fertilizers, when the appropriate types and amounts are used, provide a rapid means of improving soil fertility and production. However, their high costs especially in Africa where they currently go for between 3 and 4 times the world price, limits their use. Under these conditions, the agronomic potential of agrominerals that are locally and regionally available needs to be explored. They can be integrated with organic fertilizers (manure, cover crops, and agroforestry practices) and whatever amounts of commercial fertilizers that farmers can afford or be assisted with by government and their development partners.

This book, *Agrogeology: The use of rocks for crops,* by Dr. Peter van Straaten, provides excellent background information on the pathway of nutrients from rocks to soils to plants as well as on formation and global distribution of agrominerals. There are, for instance, large phosphate rock deposits that could be useful in correcting the phosphorus deficiencies in many soils of Africa, South America and Asia. Several recent studies, especially from Africa, indicate that some of the rock phosphate deposits are agronomically as effective as the commercially available phosphatic fertilizers. Rock phosphates have also liming benefits, thus reducing soil acidity where this is necessary. This book also provides information on the geological provenance of other major plant nutrients and micronutrients. In addition, information is provided from other agrominerals such as vermiculite that can improve the physical conditions of soils, especially their water holding capacity. Improvements in soil nutrients and water holding capacity has the additional benefits of improving soil biology, a property that often declines with declining soil fertility and land degradation.

There is no doubt that our knowledge base on the use and management of agrominerals for improved agricultural production is growing fast. There is also growing global research and development partnerships, including the Rock for Crops network. This book brings together information on many nutrient replenishing practices using geological materials. It provides an extensive and valuable compilation of these materials and appropriate methods for their utilization in land-based food production systems. It supplements well the earlier book, *Rock for Crops: Agrominerals of sub-Saharan Africa* by the same author, that created tremendous interest in the use of rocks, especially phosphate containing ones, in integrated soil fertility management.

The author deserves congratulation for a very useful contribution towards improving agricultural production through the practical application of geology. The book will certainly be useful to many students, teachers, geologists, soil scientists, agronomist, farmers and policy makers especially in developing countries. It will also make a significant contribution towards achieving the Millennium Development Goals of reducing the number of hungry and poor people globally. But this will only happen, at least at a significant operational scale, if governments and their development partners make the necessary investments in research and development to get the increased utilization of agrominerals in agriculture.

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December 17, 2006.

Preface

Students of agricultural sciences are commonly introduced to only a small segment of geology, usually on aspects of minerals in soils as well as mineral and rock weathering. Similarly, students of geology normally get only very small exposure to soil science and the use of minerals in soil fertility enhancement. This book is intended for undergraduate and graduate university and college students in geology, soil science and agricultural sciences in general as well as interested agricultural practitioners and agricultural advisors in government and developing agencies. It provides linkages between earth science, soil science and plant nutrition. It intends to enhance scientific knowledge of the rock-soil-plant continuum in a systematic and holistic way. The focus on using rock and mineral resources for agriculture is in response to the urgent need to increase food production in parts of the world where food security is still a major challenge.

This book offers a basic understanding of the geology of plant nutrients and provides information on processes that are involved in the release of nutrients from rocks to soils, for the growth of plants. The reader will become aware that 'crops need rocks as nutrient stocks'. The reader will also find out more about the raw materials and processes necessary to make conventional and low-cost geological fertilizers and soil amendments, and on ways to utilize these geological resources directly or through processing. In addition, the reader will become sensitized on environmental issues related to the extraction of geological nutrient resources and the use of these resources in agriculture.

The beginning chapters of this book provide background information on weathering and on the relationship between rocks, soils and plants. Subsequent chapters focus on plant nutrients, on the way these nutrients are taken up by plants from soils. Except nitrogen, all plants nutrients are derived from rocks and minerals, and the reader will find out more about the origins, transformations and uptake of these nutrients by plants in Chapters 3 to 8. Chapter 4 (Phosphorus) is extensive; in this chapter the reader will see details of one of the most important geological nutrient resources, phosphate rocks. Next to nitrogen, phosphorus deficiencies are the most limiting factors for crop production systems in the world. The principal phosphate mineral is apatite and it is hoped that the reader will develop an 'appetite for apatite'. In addition, a general overview on the geology of the phosphate rocks will be provided and on the principal pathways to transform and modify mineral-bound, inorganic phosphorus into plant available phosphorus. Moreover, the reader will learn about environmental issues related to the extraction and use of this resource. The length of this chapter reflects the large amount of scientific work by geologists on the origins of phosphates and phosphate accumulations, and the work of many soil scientists and industry to develop this crucial mineral group and plant nutrient for agricultural use. Chapter

9 provides information on the use of whole rock fertilizers, and chapter 10 on other minerals, such as vermiculite, perlite, pumice and zeolite to enhance physical properties of soils and growth media for the horticultural industry. The text will also provide some information on some unconventional materials (for example: reservoir sediments), that are tested on their potential to enhance soil fertility, and on techniques utilized in some arid and semiarid regions of the world, using naturally occurring rocks, for example volcanic scoria and pumice as rock mulch, to reduce evaporation from soils.

For the author the involvement with agrogeological research and development has come a long way. The initial field experiments in Dodoma, Tanzania, in 1984, were followed by agrogeology projects in Tanzania, Ethiopia, Zimbabwe, Sri Lanka. These projects were supported by the International Development Research Centre (IDRC), Canada. The reaction to the publication of the first book on ‘Rocks for Crops - Agrominerals of sub-Saharan Africa’ (van Straaten 2002) showed the great interest and apparent relevance of this subject matter. In 2002, the Indonesia Agrogeology Centre was opened and, in 2004, the First International Conference on ‘Rocks for Crops’ was held, in Brazil. The Second International Conference on ‘Rocks for Crops’ will be held in Kenya in 2007. Agrogeology courses are now taught at several universities, and numerous agrogeological research and development projects are presently conducted around the world. There is an active ‘rocks for crops’ discussion network on the web with participants from many countries. It is obvious, the interdisciplinary science of agrogeology has come of age.

Acknowledgements

I want to thank the many friends and colleagues in Africa, South and North America, Asia and Europe, who encouraged me to write this book. My special thanks go to those who assisted me directly with the preparation of this book. Steve Sadura was instrumental in starting with me on the first draft of a course manual for the undergraduate course ‘Agrogeology’ at the University of Guelph, Canada. Over the years, I gradually changed and extended the manual into a comprehensive compilation and finally into this monograph. Critical reading of earlier versions of the course manual by Chris Roosenboom, Susan Roberts, Jo Passmore, Jessica Stevenson and Heidi Braun and comments from students of previous agrogeology classes resulted in clarifying some aspects and cleaning up the manuscript. Many thanks go to Mary-Catherine (M-C) Lanning, who has been the ‘anchor’ for most of this project, the person who assisted with the illustrations and who pulled all the information and corrections together and transformed them into the current book form. Dr. Steve Stockton of ‘Naturestock’ was of great assistance in the final stages of the book, with reorganizing parts of the book, editing and putting everything together in the current book form. Thanks Steve! The author is also indebted to Dr. Peter Kevan, Enviroquest, to get the book published in a form and price that is affordable to most readers.

I am also grateful to my colleagues Drs. Les Evans, Richard Heck, and Paul Voroney from the Department of Land Resource Science, University of Guelph, for critical comments and suggestions.

My greatest thanks go to my wife ‘twiga’ Ellen and our two sons Oliver and Jos for their patience and encouragement, and for their understanding for me being up at odd hours of the night to orchestrate the ‘symphony of agrominerals’ and work on the manuscript for this book.

Conversion factors

P_2O_5	x	0.44	➜	P
P	x	2.29	➜	P_2O_5
K_2O	x	0.83	➜	K
K	x	1.20	➜	K_2O
CaO	x	0.71	➜	Ca
Ca	x	1.40	➜	CaO
MgO	x	0.60	➜	Mg
Mg	x	1.66	➜	MgO

Chapter 1

Introduction to Agrogeology

Food security depends to a large extent on biophysical factors and resources such as water and soil. Good quality soil and available water are the two most important natural resources to support terrestrial life. Soil and water enhance and maintain key biological activities such as plant growth and many ecological functions on the surface of the earth. Important functions of soils, apart from storage and cycling of nutrients and water for plant growth, include the maintenance of other organic life in soils, as well as the regulation of flow of water in the landscape, the ability to filter water, and the capacity to transform and degrade organic and inorganic materials such as municipal and animal wastes. Soils also provide support for socioeconomic structures such as buildings for habitation and structures such as dams and roads. In addition, soils are vital repositories for other elements and compounds such as the greenhouse gas carbon dioxide, which is stored in the form of organic matter. The management of soil organic matter can have profound effects on the sequestration of CO_2 and the exchange of greenhouse gases such as CH_4 and CO_2 from the soil to the atmosphere and of CO_2 to the soil pool (Lal *et al*. 1997).

Humans try to enhance the vital, life-supporting properties of soils with the principal objective of enhancing crop production and safe food supplies for their consumption. While these interventions are successful in many parts of the world, many soils have been badly managed by humans. Soil degradation often occurs through poor or inappropriate agricultural management practices such as poor tillage, poor cropping practices, overgrazing, deforestation, poor management of animal manure and other organic residue resources, poor irrigation, excessive use of fertilizers and pesticides, as well as poor management of municipal or industrial ‘wastes’.

There are three main types of soil degradation: physical, chemical and biological. Physical degradation includes compaction and hard-setting of soils, desertification and erosion, as well as soil nutrient depletion and degradation of soil structure through actions of water and wind. Poor water management can lead to the drawdown of water tables and subsequent drying effects on soils. Chemical degradation includes nutrient depletion through leaching and excessive soil nutrient extraction, as well as through salinization and acidification. Salinization is often the result of poor irrigation management. Biological degradation, such as the decline of macro- and micro-organisms, the decline of organic matter cycling, or the increase in soil pathogens in soils, can lead to the decline in natural soil fertility.

Historically, long-lasting civilizations established and developed on fertile soils along rivers and flood plains and in volcanic areas. The annual flooding and sedimentation of fertile mud and silts derived from the upstream volcanic highlands of Ethiopia contributed to fertile alluvial soils of the River Nile, which in turn supported the civilizations of ancient Egypt. Other cradles of civilization were established on fertile soils along river systems and on flood plains, including the ancient civilizations along the Tigris and Euphrates in ancient Mesopotamia, civilizations in the plains of the Indus and Ganges in Pakistan and India, and civilizations along the Yangtse River (Cháng Jiãng) and Yellow River (Huáng Hé) in China. However, when forests in the catchment areas were cut down, when land was overgrazed, when irrigation systems were not maintained and soils were not cared for, resources started to deteriorate, which ultimately caused the downfall of complex and long-lasting civilizations.

The combination of temperate climates, high availability of water and fertile volcanic soils provided favourable conditions for the production of crops for early Greek, Roman and Etruscan civilizations in parts of the Mediterranean area. Other suitable areas for early agriculture and civilizations were parts of Central and South America with fertile volcanic soils and sufficient available water. But these very fertile areas were also areas at risk from volcanic eruptive activities, from volcanic flows to catastrophic destruction by volcanic ashes and volcanic gases.

Violent volcanic events accompanied by eruptions and the spread of large amounts of volcanic ash and gases have had disastrous effects on land and human populations, for example the volcanic events associated with the eruption of Thera/Santorini in the Aegean Sea around 1,650 BC and at the foot of Vesuvius in Italy where thick piles of pumice covered Pompeii in 79 AD. Although known to be very fertile, these areas are prone to high-risk volcanic events that can destroy fertile lands and lives.

Learning from these historic experiences and events we have to recognize the fragility of the vital resources of land and soils, as well as water, air and energy resources. Concerted and more ecologically focused actions are needed to manage soils, water and energy resources to meet human needs, not only today but also for future generations and to confront the dangers of land and soil degradation. Human intervention is required to protect soil and water resources and processes that contribute to food security for humans. It is anticipated that environmental changes including climate change will not only have enormous economic and social implications, but also serious effects on natural ecosystems, on land and water use, as well as biodiversity.

The International Panel on Climate Change (IPCC) forecasts milder winters, extended growing seasons and higher yields of some crops in areas with temperate climates, while countries in areas of tropical and subtropical climates, mainly developing countries, will experience net losses of crop production due to higher temperatures and droughts. The effects of climate change on water availability will seriously affect developing countries located in arid and semi-arid areas through extended drought periods. Other parts of the world will be affected by increased flooding. The changes in global climate, changing hydrological regimes and increased climatic variability are expected to have significant effects on food supply and food security in large parts of the world.

Healthy and well maintained and managed soil and land, water and energy resources are crucial for long-lasting economic, social and cultural development. In the following sections we will focus on soil resources and their management. We will specifically study nutrient resources within soils and their management to meet human needs through enhanced and safe food production.

Soils are complex blends of minerals, organic compounds, living organisms, water and air that interact in response to biological, chemical, and physical processes. Soils are unconsolidated materials made up of weathered rock and organic matter covering large parts of the land surface of our planet. Some 45–50% of a common soil's volume is made up of solids, of weathered rock fragments and minerals or secondary minerals formed in the soil. The rest of the soil is made up of air, water, and only 3-5% organic matter. However, this organic matter has special functions in soils, which include the bonding together of rock fragments and minerals as well as supporting many varieties of soil organisms.

Directly or indirectly, rocks and minerals support plant growth, provide shelter for small organisms and microorganisms, and release plant nutrients into the soil solution for plant uptake from weathering. When rocks and minerals weather, they become part of the soil itself. But not all rocks and minerals are of equal value to soil. Minerals like quartz are virtually inert and release no (or only very small concentrations of) essential plant nutrients. Other minerals contain and release one or more of the essential nutrients needed for plant life, for example P, K, Ca, Mg, S, and trace elements. In fact, all plant nutrients, with the exception of nitrogen, are ultimately derived from geological resources.

In many countries, natural accumulations of these geological nutrient resources are industrially transformed into soluble fertilizer mainly for use in agriculture and horticulture. Fertilizers, apart from N-fertilizers, are derived from geological resources, from rocks and minerals that contain high plant nutrient concentrations. The nutrients from these rocks and minerals are physically and chemically processed into fertilizers, made up of highly soluble nutrient compounds.

Highly soluble and concentrated nutrient resources in the form of synthetic fertilizers are mostly used by plantation farmers and by those farmers who can afford them. Many farmers in developing countries however cannot afford expensive and largely imported fertilizers. They have to rely on locally available sources of nutrient resources for their soils and here the role of geologists can become important. Geologists are expected to know how to find, delineate and extract geological nutrient resources from rocks and minerals that are useful for farmers. A specialized group of geologists, agrogeologists, put their geological knowledge and experience into the service of agriculture with the explicit aim to increase food production for resource poor farmers.

Soils and water are crucial for sustaining human, animal and plant life. Managing these resources wisely will contribute to improved land use and to an enhanced level of long lasting rural development. A major challenge for many countries has been adequate production of quality food, given the demands of an increasing population. Although the world as a whole has enough arable land to produce food for the present and future generations, there are unequal distributions of fertile soils, land and water resources, and food production inputs. As a key agricultural entry point, we will discuss the major biophysical factors that limit agricultural productivity, specifically inherent low soil productivity and human induced soil nutrient depletion, as well as means of understanding and overcoming these barriers.

Water resources, important for lasting agricultural production will be dealt with only marginally in this text. Although many nutrient replenishing practices using geological materials have already been recognized for a considerable amount of time, there is a need to compile these materials and appropriate methods for their utilization in land-based food production systems.

1.1 The basic need: food

Agriculture is the engine of economic growth in most countries of the world. Unlike many developed countries, rural agriculture in developing countries commonly employs or involves more than 70 percent of the population in one way or another. And yet, poor living standards and outright poverty, with incomes of less than US $1 a day, are still prevalent in large parts of the world. There are many causes for the low living standards and rural development in many developing countries. One crucial internal factor that contributes to the problem is low crop productivity. External factors like weak markets, high agricultural input prices, limited access to information and credit, and low crop prices in times of surpluses have also hampered rural development. On top of these factors, government investment into rural infrastructure and education, (as well as extension services), has generally been low. Only rarely can those who are the main players in rural development, the farmers, influence these conditions and limiting factors.

Providing appropriate and inexpensive ways to increase food production is especially important in those developing countries where agricultural output is struggling to keep pace with population growth. ‘There is no shortage of food on the planet,’ UN Secretary General Kofi Annan told the delegates at the opening of the World Food Summit in 2002. However, while many countries produce more food than they need, other countries struggle to find and manage their resources to grow or buy their own food.

From the world's 6 billion people, almost half (2.8 billion) live on less than two dollars a day, and 1.2 billion exist on one dollar or less per day. In 2003, more than 800 million people did not have enough to eat. Almost one in seven people continue to go hungry in a world of plenty, a quarter of them in sub-Saharan Africa. Hunger and malnutrition kill approximately 10 million people a year. This is a staggering 25,000 per day, one life is lost due to malnutrition and hunger every five seconds! The hot spots of hunger in the world are depicted in Figure 1.1. Major recent initiatives to reduce poverty include the Millennium Development Goals, which aims to reduce the proportion of people living on less than US$ 1 per day before the year 2015.

To increase food production, the farmer needs sufficient water and fertile soils for crop production or good grazing land for farm animals. The fundamental role of soils as medium to grow crops and support life cannot be overestimated. Poor soils produce poor crops, which in turn result in poor health and finally outright hunger.

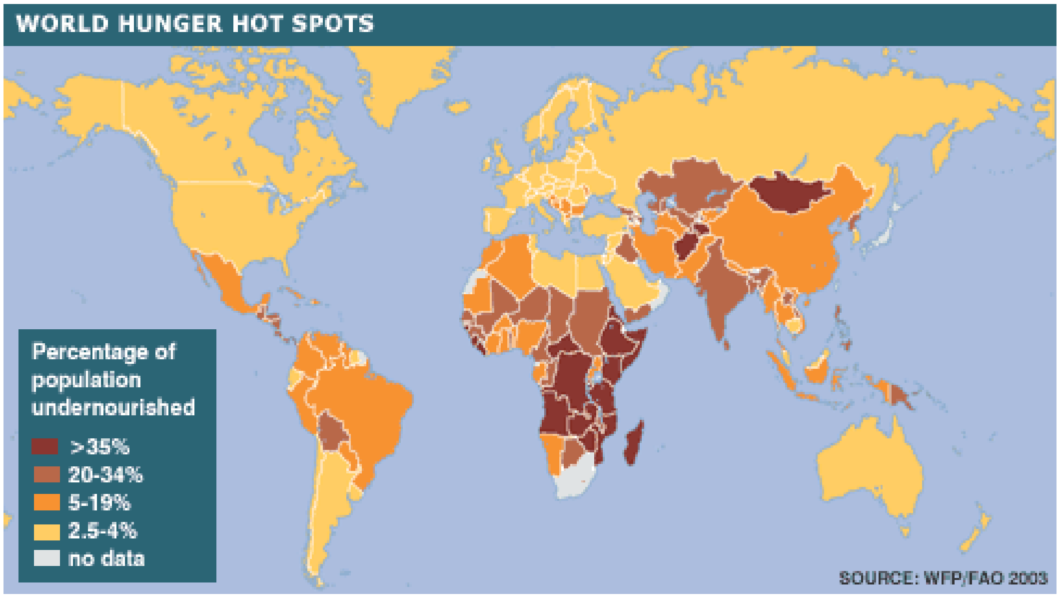


Figure 1.1. *The World hunger hot spots (source: World Food Programme/FAO, 2003).*

Among the strategies employed to overcome soil fertility problems are the use of artificial fertilizers, materials that have been processed chemically into highly soluble and concentrated forms from various geological resources, for example phosphate rocks. Other processes for fertilizer production involve the 'mining' of nitrogen from air, which requires substantial energy inputs and non-renewable resources like natural gas. More sustainable, low-cost methods and materials include the use of natural rock and mineral fertilizers, which are materials formed in nature and used in agriculture with little or no processing.

There are also critical biophysical factors that form barriers to agricultural development in these areas. These are mainly climatic barriers, largely out of our immediate control, but also inherent and human-induced, anthropogenic, factors that control soil and food productivity. One of the critical inherent factors limiting crop production lies in the nature of the soils and the rocks underlying them. In most cases, low inherent soil fertility barriers reflect the underlying rocks and minerals, the parent materials, and their origin and state of weathering. The anthropogenic factors, on the other hand, are related to changing agricultural management practices like shortening of fallow periods, intensification of cropping on decreasing land area, decreasing soil organic matter maintenance, overgrazing, and soil nutrient depletion.

Soil nutrient-depleting practices extract more nutrients than are replenished, in other words 'nutrient mining' (Stoorvogel *et al.* 1983; Van der Pol 1993; Smaling *et al.* 1997). But soil depletion is practiced largely for lack of alternatives and due to pressures on land and resources. These soil nutrient-depleting practices have been widely responsible for the drop of the per capita food production in sub-Saharan Africa, the region most affected by this decline (Sanchez *et al.* 1997; Sanchez 2002). Other losses of mineral nutrients by wind and water erosion also contribute in a measurable way to the decreasing soil quality and quantity (Buerkert and Hiernaux 1998; Stocking 2003). But not only soil nutrient depletion and erosion are reasons for concern. If no major actions are taken, salinization and water scarcities due to the changing climates will continue to negatively affect land use, leading to a decline in crop production and ultimately food security.

1.2 Agrogeology as part of 'Geology for Development'

Geologists not only play a major role in understanding the physical, chemical and biological processes that are responsible for the formation and history of planet earth, but are also instrumental in searching for and developing geological materials for humankind including metals, hydrocarbons, and non-metallic minerals. Geologists contribute to society and development by delineating and helping in the development of natural resources including those that are essential for our basic needs, principally water, shelter and food. Geology can also play a major role and become a constructive tool for agricultural development, especially through exploration and development of fertilizer raw materials used either directly or in modified forms for the production of one of our most basic needs, food.

The use of rocks to improve soil fertility has a long history. The Egyptians, Greeks and Romans knew the value of certain rocks to increase crop production. Pliny (62-113) recommended the use of marl and limestones, as well as saltpetre (potassium nitrate). After the decline of the Roman an Empire there were few recorded contributions to the use of rocks for soil fertility improvement until the 1700s.

In the late 1700s, one of the leading founding fathers of the United States, Benjamin Franklin (1706-1790) observed that French farmers used gypsum as soil conditioner, and introduced the use of gypsum, imported from Canada, as ‘land plaster’ to the United States.

The German chemist Justus von Liebig (1803-1873), widely regarded as one of the founding fathers of modern plant nutrition and fertilizer chemistry, recognized that:

- nutrients are taken up from soils through the roots,
- soils are fertile only if nutrients removed by the plant are replenished,
- each kind of plant species requires different nutrients.

Liebig also developed the ‘Law of the Minimum’, which has been a major principle in plant nutrition.

In 1840, the first phosphate rocks were mined and processed with sulphuric acid into superphophates. By 1842, Sir J.B. Lawes (1814-1900), the founder of the Rothamsted Experimental Farm, England, produced the first commercial superphosphate fertilizers. In Germany, the discovery in 1857 of potassium-rich salts (‘potash’) started the first production of K fertilizers.

The use of whole rocks for agriculture started in the late 19th century when Hensel (Hensel 1890, 1894: ‘bread from stones’) used finely ground rocks and minerals as low-cost, locally available geological nutrient resources for agricultural development. The study of using ground rocks without chemical modifications for beneficial agricultural purposes was re-started by Keller (1948), Fyfe and co-workers at the University of Western Ontario, Canada, and Chesworth and van Straaten at the University of Guelph, Canada. In 1984, the first interdisciplinary ‘agrogeology’ project receiving major funding from the International Development Research Centre (IDRC) in Ottawa, Canada, began evaluating Tanzania’s phosphate resources and other rock materials and conducted field experiments on their agronomic effectiveness.

In the latter project, geologists and soil scientists got together and began jointly to work with farmers on the use of locally available agromineral resources with the stated goal of improving soils for the benefit of smallholder farmers.

1.2.1 What Can Geologists Contribute?

The classical role of geologists is to find out how the earth works, to find and develop mineral-based raw material resources needed in our modern world for daily material and technical requirements and comfort. But the role of geologists is well beyond this classical picture. Some of the roles of geologists including the role of agrogeologists in society are illustrated in Table 1.1.

Table 1.1. *Branches of geology*

Need	Geoscientific Discipline	Activity
General knowledge	Geology, Geophysics, Geochemistry, Palaeontology	Study of physical, chemical and biological processes that lead to the formation of rocks and the evolution of our planets
Metallic and non-metallic mineral raw materials	Exploration geology, Economic geology	Search for and development of metallic and non-metallic resources for daily technical necessities and comfort
Energy raw materials	Energy resource geology	Search for and development of coal, oil, gas, uranium and other naturally occurring energy resources
Food	Agrogeology	Search for and development of agrominerals to maintain and enhance sustainable soil use for agricultural food production systems
Water	Hydrogeology, Engineering geology	Search for and management of ground and surface waters
Shelter and infrastructure	Engineering geology	Search for and development of rock materials for buildings and infrastructure
Environmental protection	Environmental geology, Engineering geology	Study of environmental issues related to mineral resource extraction and processing, monitoring and prediction of natural hazards, e.g. volcanic and earthquake activities
Community health	Environmental Geology, Medical Geology	Monitoring ground and surface water quality, contaminations and other environmental pollution; study of geochemical aspects of deficiencies, toxicities and diseases in food, water and soil

1.2.2 What is Agrogeology?

The term agrogeology was used widely in the 1870s and 1880s in Germany. It was the preferred term for soil science (or soil knowledge) and marked the geological roots of soil science and the importance given at that time to weathering processes. Agrogeology, the weathering aspect of soil science, was considered a branch of geology (Yaalon 1997; Simonson 1999). The Russian school of soil science under Dokuchaiev (1846-1903) however realized that soil formation was not only a function of rock weathering but represented far more complex interactions and interrelationships between ‘dead’ rocks and other factors and biophysical and chemical processes. It is the Russian school under Dokuchaiev and other schools in Germany and the United States (especially Hilgard) that founded the new school of soil investigations and advanced the new science of pedology.

The geological roots of soil science were still evident in the first and second International Agrogeology conferences in Budapest (1909) and Stockholm (1910). But with widening acceptance of the more complex nature of soil formation the label of agrogeology was changed into agropedology during the third international conference in Prague, in 1922. Two years later in Rome, the conference was called the Fourth International Pedological Conference (Simonson 1999). This change over time from agrogeology to pedology marked the growing understanding of other pedogenic processes. The term agrogeology in the 1880s reflected the close relationship of soil science and geology and marked the breakaway of soil science from geology.

The usage of the term agrogeology today represents a new use of this term as a branch of geology that deals with geological materials and processes that are used to improve the chemical, physical and biological productivity of soils. Agrogeological studies not only investigate unprocessed and processed raw materials that are used to enhance the fertility status of soils, but also emphasize the geological processes that are responsible – on various scales – for the distribution of parent materials that are at the base of soils and involved in soil formation.

The classical geologist sees the soil as ‘overburden’, something that must be removed to get to the rocks below. The engineering geologist defines soil as anything that can be moved by a bulldozer. The typical North American views soil simply as ‘dirt’ or ‘mud’. To the farmer or the agronomist however, soils are viewed as a ‘life support system’ for plants, without which there would be no agricultural production or food. Food is ultimately derived from the organic and inorganic constituents of the earth.

Soil scientists and geologists tend to speak different scientific languages, have different priorities, occupy different buildings and often work for different government ministries. As a result, communication between them is often difficult. It is obvious that multi-disciplinary and interpersonal skills and expertise are needed to tackle the challenges of soil degradation and declining food security related to soil nutrient depletion in many parts of the world. Agrogeology is an attempt to bridge this apparent gap between soil scientists and geologists in order to effectively manage our natural resources in a more sustainable, longer-lasting way.

Agrogeological intervention requires a practical, problem-solving approach. For this, the agrogeologist needs to understand the rock-soil system, as well as the soil-plant system.

1. The rock-soil system:

    - What nutrients can rocks and minerals provide for soils and plants?
    - How are nutrients released from rocks to soil solution and plants?

2. The soil-plant system

    - What do plants need for optimal growth?
    - How do plants take up nutrients and when do they need nutrients for optimal growth?
    - What can the growth media (e.g. soils) provide for plants?
    - What are the soils limiting factors and needs?

If the soil system cannot provide the nutrients that the plants need for optimum growth, which agrogeological intervention should be envisaged? What is the most appropriate agrogeological material to enhance and maintain crop/tree/animal production in a sustainable way?

To be effective, the agrogeological material to be applied to the soil should:

- Match specific soil and crop requirements,
- Be practical, requiring low maintenance (appropriate technology),
- Be socially acceptable and socially desirable,
- Be cost effective.

This book is designed to provide information for an integrated approach towards land management in developed and developing countries. It stresses the need to utilize locally available organic and inorganic resources for soil fertility enhancement and sustainable soil management. Traditional uses of agrominerals for fertilizer production are also described. This book should contribute to a better understanding of soil and land management practices and geological resources that can enhance soil conditions and crop/animal production. The book will also provide information on environmental issues related to the chemical properties of agrominerals themselves, on pathways and losses of agrominerals during extraction and processing, and finally issues related to their application to soils and crops.

Land tenure issues and mining rights are beyond the scope of this text, but are very important for the practical implementation of the principles of agromineral resource management. It is obvious that these barriers have to be addressed and overcome by the local and government stakeholders before one can make practical use of agrominerals to replenish and enhance soil fertility.

The geology of naturally occurring geological nutrient resources for crop production, agrominerals, will be discussed in this book along with methods and techniques of how to find these resources and how to process them. This book will provide some background knowledge for the development and use of rocks and minerals for making fertilizers and soil amendments, as well as contributing to alternative rock and organic interventions to suit local soil conditions and be used by crops preferred by the farmers. Options of agromineral use also include modification techniques and direct application options with discussions on technical strength and weaknesses of these applications.

Agrogeology is an interdisciplinary, applied science. It brings together researchers and practitioners from soil science, geology, engineering and rural extension to try to find practical solutions to reduce soil nutrient depletion and soil degradation. Agrogeology also addresses the potential of making physical and chemical improvements to soils and growth media in horticulture. In the joint agrogeological approach, scientists, farmers and practitioners learn from each other (Where do nutrients originate from? What do soils and plants need? How can we improve soils and other growth media?) and put this newly acquired knowledge and understanding into practice.

Agrogeology is a promising scientific approach that specifically aims at making use of rocks and minerals to improve soil fertility for the benefits of farmers, making use of rocks for crops.

Chapter 2

From Rocks to Soils to Plants

The distribution and abundance of geological nutrient resources, the release of these nutrients into the soil, and the uptake of these nutrients by plants is described as the rock-soil-crop pathway, the principal nutrient transfer from rocks to soils to crops. This transfer of nutrients from rocks to soils to crops is the natural path for plant growth and essential for the understanding of crop production using naturally available nutrient resources.

2.1 From Rocks to Soils

Soil, one of the essential life support systems of our planet earth, is formed from common rocks on the surface of the earth by various processes. Fertile agricultural soils are not evenly distributed on the earth's surface; some areas are endowed with fertile soils, while other areas are infertile. In order to understand the reasons for the uneven distribution of soils, it is necessary to understand the environmental conditions in which these soils developed, and how long they took to develop. To a large extent, the chemical, physical and biological composition of soils reflect the underlying rock materials, the climate, the time of exposure at the surface, as well as the biological activities and physical and chemical processes to which they have been exposed.

2.2 Rocks

Rocks are divided into three main groups based on their modes of origin:

- igneous,
- sedimentary and
- metamorphic.

Igneous rocks (from Latin 'ignis' meaning 'pertaining to fire') are formed by cooling from hot, molten material from magma. These hot, molten materials are formed at great depths in the earth. On their way to the surface of the earth they may reach the upper part of the earth's crust and crystallize into the earth's crust, forming intrusions. They may also reach the earth's surface in the form of extrusive igneous rocks, for example as volcanic lava or as forcefully ejected particles and ashes called pyroclastic materials (from Greek 'pyros' meaning fire and 'klastos' meaning broken) from volcanic eruptions. Principal igneous rocks in the continental crust include granite and gabbro (both intrusive rocks), as well as basalt and andesite (extrusive volcanic rock types). Sedimentary rocks (from Latin 'sedimentum' meaning 'settle') are formed at or near the earth's surface by the sedimentation and subsequent cementation of pre-existing individual particles of sand, silt and clay particles to form sandstone, mudstone, shale, or from chemical mineral precipitation, or deposition of organic sources (biological limestones, sedimentary phosphates, coal).

Metamorphic rocks (from Greek ‘meta’ meaning ‘change’ and ‘morphos’ meaning ‘form’) are igneous, sedimentary or even older metamorphic rocks, that have been changed by heat, pressure and by chemically active fluids within the earth. Typical metamorphic rocks of the continental crust are schists, gneisses and amphibolites. The metamorphic rock ‘greenstone’, referred to below, is a greenish-coloured metamorphosed volcanic rock, mainly of basaltic composition.

2.2.1 Minerals

Rocks are made up of aggregates of minerals. A mineral can be defined as a solid inorganic substance having an orderly and regular arrangement of elements such as oxygen, silicon, aluminium, magnesium, iron etc. A mineral has a defined chemical composition, which can vary only between fixed limits. It has characteristic physical and chemical properties such as hardness, melting point, shape, etc. By far, the most abundant minerals in the crust are silicates: quartz, feldspars, micas. Other common minerals include amphibole, pyroxene, olivine and clay minerals. The principal rock forming minerals of the upper continental crust are shown in Table 2.1.

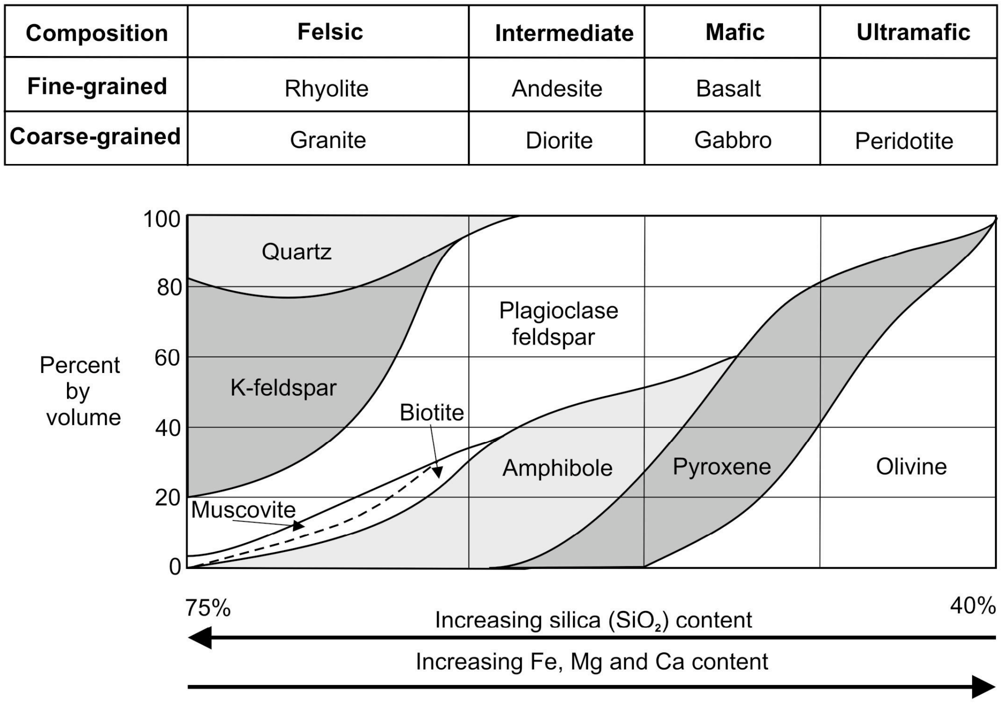
Table 2.1. *Principal rock forming minerals of the upper continental crust (Nesbitt and Young 1984)*

Name of Mineral	Percent in Continental Crust (by volume)
Plagioclase feldspar	39.9
Quartz	23.2
K-feldspar	12.9
Biotite (mica)	8.7
Muscovite (mica)	5
Others	3

Minerals occur in various proportions in rocks. Sedimentary rocks contain many different silicate minerals, mainly clay minerals but also other transported and newly formed silicates, as well as carbonates, sulphates, sesquioxide minerals, phosphates, and organic complexes. Igneous rocks are composed of many different minerals, but there are only a few main rock-forming minerals, such as quartz, two types of feldspars (plagioclase and alkali feldspars), ferromagnesian minerals (e.g. olivine, pyroxene, amphibole) and micas. The distribution of these minerals in common igneous rocks is illustrated in Figure 2.1. Felsic rock types like rhyolite or granite (the coarse-grained equivalent to rhyolite) are rich in silica, mostly in the form of quartz (SiO_2). The chemical compositions of the most common rock-forming minerals are shown in Table 2.2.

Table 2.2. *Chemical composition of main rock-forming minerals (in percent).*

Mineral	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**FeO**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**P_2O_5**
Quartz	100								
Orthoclase	62-66	18-20			0-3		9-15	9-4	
Albite	61-70	19-26			0-9		0-4	6-11	
Anorthosite	40-45	28-37			10-20		0-2	0-5	
Muscovite	44-46	34-37	0-2	0-4		0-3	8-11	0-2	
Biotite	33-36	10-13	3-17	5-17	0-2	2-20	6-9		
Hornblende	38-58	0-19	0-6	0-22	0-15	2-26	0-2	1-3	
Augite	45-55	3-10	0-6	1-14	16-26	6-20			
Olivine	35-43		0-3	5-34		27-51			
Epidote	35-40	15-35	0-30		20-25				
Apatite					52-55				36-42
Tourmaline	35-40	30-37	0-10	0-10	0-6	0-12		0-6	
Magnetite			69	31					



Composition	**Felsic**	**Intermediate**	**Mafic**	**Ultramafic**
Fine-grained	Rhyolite	Andesite	Basalt	
Coarse-grained	Granite	Diorite	Gabbro	Peridotite

Figure 2.1. *Classification of common igneous rocks.*

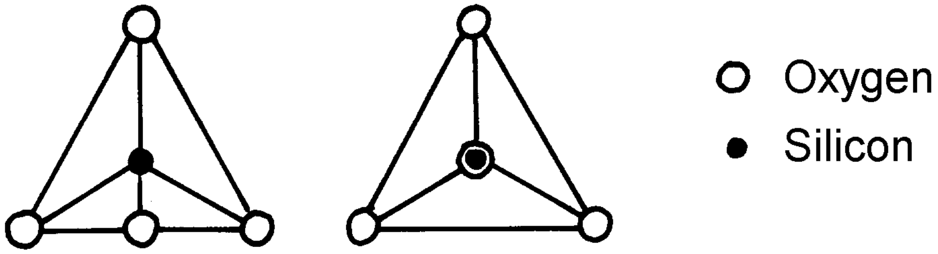


Figure 2.2. *Diagrammatic representation of the silicon tetrahedron with a small silicon ion in the centre surrounded by four oxygen atoms. Left: side view. Right: top view. The tetrahedron is a geometric shape with four sides. It resembles a three-sided pyramid when placed on a flat surface.*

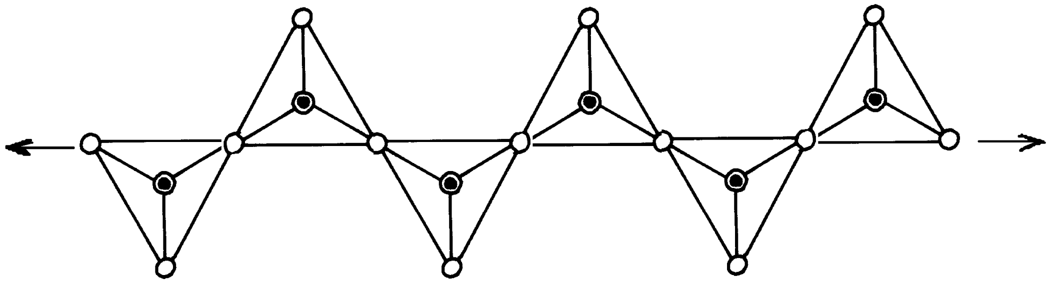


Figure 2.3. *A single chain of silicon tetrahedra joined to each other by one corner oxygen atom. In pyroxene each single chain is joined to the next via ionic bonds through Fe and Mg.*

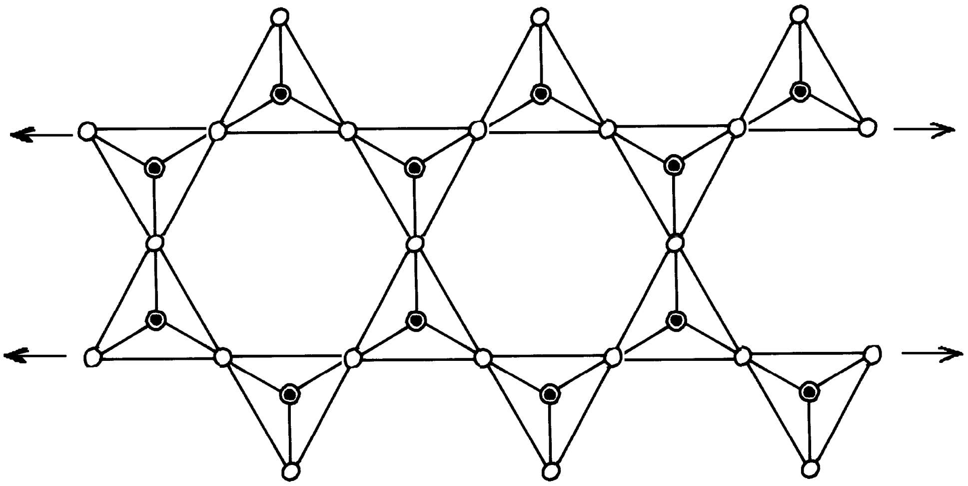


Figure 2.4. *A double chain of silicon tetrahedra. In the mineral amphibole, each single chain is joined to the next via ionic bonds through magnesium and iron.*

The basic building block of all silicate minerals is the silicon tetrahedron (Figure 2.2). In common silicate minerals, the silicon tetrahedra are linked directly to one another via strong 'covalent' bonds. In this type of bond, oxygen atoms at the corner of the tetrahedron share their outermost electrons with the adjacent tetrahedron. Pyroxenes are typified by single chains of silicon tetrahedra (Figure 2.3), amphiboles have double chains (Figure 2.4), clay minerals as well as micas form sheet structures (Figure 2.5) and feldspars and quartz have a three-dimensional framework of tetrahedra.

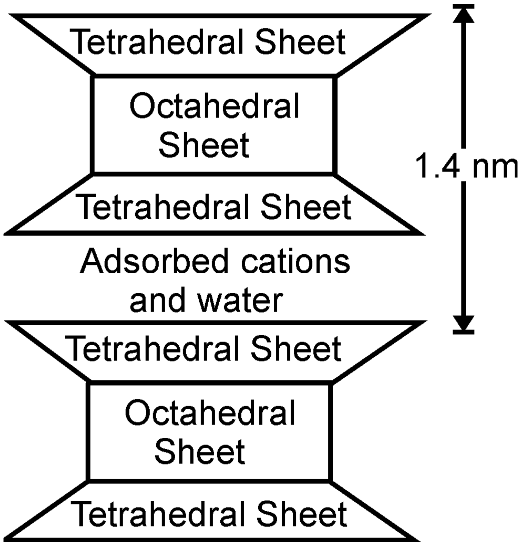


Figure 2.5. *Two sheets of mica with interlayer cations bonding them together. Each sheet consists of two sheets of Si-tetrahedra and one Al-octahedral sheet giving a 2:1 structure much like a 2:1 clay mineral, for example smectite.*

As the number of strong covalent bonds increase, so do the stabilities of the minerals. In contrast, olivine does not possess covalently bonded tetrahedra; instead they are linked to one another by relatively weak ionic bonds through iron and magnesium ions. During weathering, these weak bonds are severed. Therefore the most easily weathered common silicate mineral is olivine, and the most resistant mineral is quartz.

2.3 New Rocks and Sediments

In geological time scales, the earth's surface is constantly changing. Mountains rise and erode, oceans open and close, continents drift apart or towards each other and global climate changes. Figure 2.6 is a cross section of the earth's crust and upper mantle showing, in a very generalized way, the distribution of rock types and their ages as related to potential soil fertilities. In areas where new or relatively unweathered material is brought to the surface, soil fertility tends to be higher than in areas where land surfaces are old and have been subjected to extensive weathering and leaching processes (Fyfe *et al.* 1983; Fyfe 1989).

Fresh, nutrient rich geological material is brought to the land surface in specific zones of the earth, for example in areas where two extensive and relatively rigid portions of the crust and the upper mantle ('plates') collide, or where compressional stress shortens and thickens the earth crusts into mountains. These zones of colliding plates, known as convergent plate margins, are also frequently zones of volcanic eruptions (Figure 2.6). The famous 'Ring of Fire' with extensive zones of volcanic activity surrounds the Pacific Ocean. Volcanic eruptions and release of new nutrient rich rocks can also occur where the crust is under tensional stress and reacts with the formation of rift valleys (e.g. the East African rift system) or 'basin and ranges'.

Other zones where fresh rocks from lower parts of the earth's crust or mantle reach the surface of the earth are at 'divergent' plate boundaries. In oceanic environments, volcanic rocks of mainly basaltic composition come to the surface of the earth at diverging plate boundaries (mid-ocean ridges). Most of the mid-ocean ridges are under water with a few exceptions, notably Iceland, which lies on the Mid-Atlantic Ocean ridge.

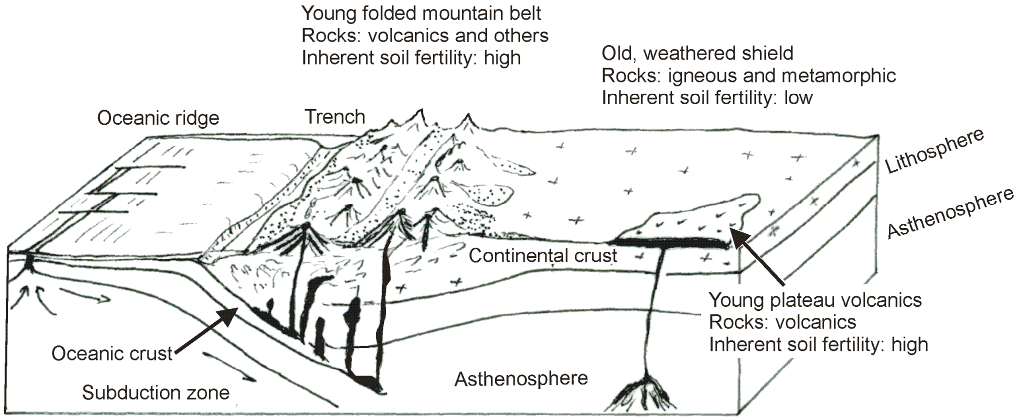


Figure 2.6. *Generalized section across a continent (eg. South America) with inherently different soil fertilities developing on different parent materials (van Straaten 2006).*

Large volumes of volcanic rocks may also be released as flood basalts related to deep-seated mantle plumes. The voluminous outpouring of lavas in parts of western India, the Deccan traps, and the Columbia River flood basalts in parts of Washington, Oregon and Idaho in the United States are the surface expressions of thermal instabilities deep in the earth, at the core-mantle boundary.

In addition to the emergence of new rock material from beneath the earth's crust, fertile soil also arises from nutrient-rich river sediments. The main areas that accumulate these sediments consist of flood plains and deltas, for example the deltas and flood plains of the Euphrates and Tigris, the Yangtse (Cháng Jiãng) and Yellow River (Huáng Hé) in China as well as the Mississippi River and the banks and delta of the River Nile. Other fertile areas occur through the accumulation of airborne and fluvial materials liberated and transported by glacial processes. However, many stable continental interiors (especially at low latitudes) have, by-and-large, not received the benefits of these processes and as a result generally have lower soil fertility and soil productivity (Figure 2.6).

2.4 Weathering

For rocks to become soils they must weather. This means physical, chemical and mineralogical changes of rocks and minerals under conditions of relatively low pressure and temperature, at or near the surface of the earth. Many of these processes are mediated by micro-organisms and other biota through biological weathering processes.

Physical weathering occurs predominantly in cold or temperate climates, but also in arid environments. It involves the physical breaking-up and disintegration of minerals and rocks by water, salt, fire and other factors.

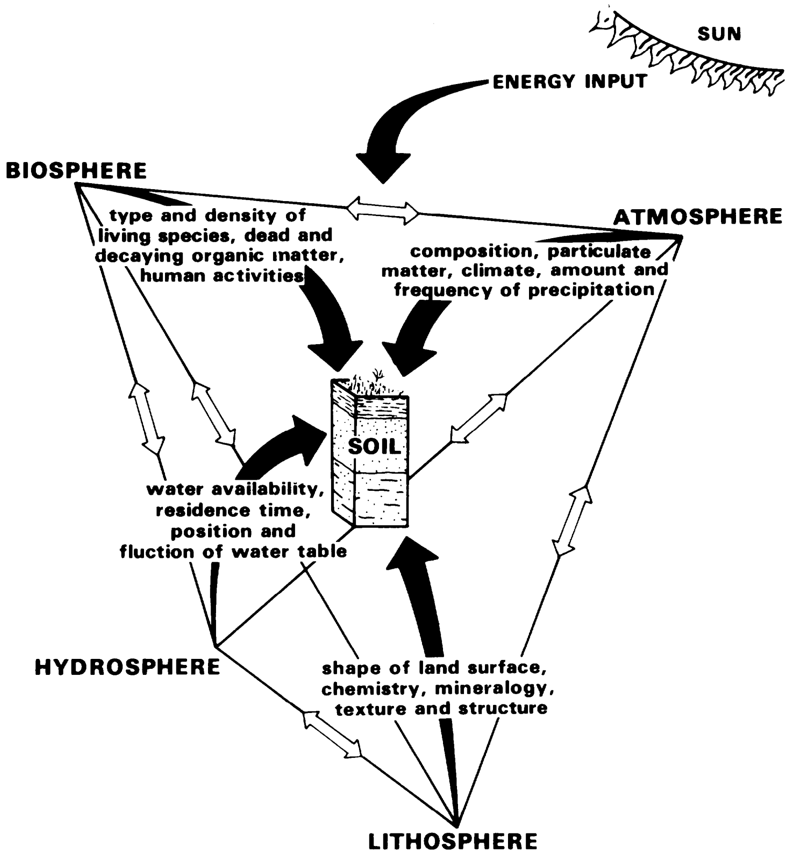


Figure 2.7. *Soils are the result of the interaction of the four spheres of the earth's surface (atmosphere, hydrosphere, lithosphere and biosphere) with energy inputs from the Sun (from Chesworth 1982, with permission).*

Chemical weathering of minerals and rocks is the predominant form of weathering in warm, humid climates. Water provides a medium for the movement of ions and other dissolved materials and high temperatures increase the rate of chemical reactions of rocks and minerals. There is a substantial loss of nutrients from rocks and minerals due to chemical weathering. Once the nutrients are released into solution they leach into ground water or pass into surface waters or are taken up by plants growing in the soil. Some of the nutrients are reconstituted into secondary minerals such as clays.

Physical and chemical weathering along with the changes induced by biological action, for example plant roots that wedge rocks apart, and microbiological chemical modifications at the soil-rock interface, are often interconnected. For example, the chemical processes involved in the immediate surroundings of roots, the rhizosphere, play a significant role in biological weathering (Hinsinger 1998). Figure 2.7 illustrates the way in which the atmosphere, hydrosphere, biosphere and lithosphere interact to form our life-support system - the soil. The lithosphere or geosphere plays a crucial role in the formation of soils and in the following section this specific 'sphere' will be highlighted.

2.4.1 Physical Weathering

Physical weathering involves the physical breaking-up and disintegration of rocks and minerals. Fires can heat up the outer 'skin' of rocks causing them to expand and fracture. Water can cause physical disintegration of rocks and minerals by entering cracks and pores and subsequently freezing (water expands about 9 percent when it freezes). Similarly, salt minerals growing in cavities and along grain boundaries of minerals can exert enormous pressures on rocks leading to rupture and disintegration.

Mechanical disintegration of rocks and minerals occurs without profound changes in mineralogy and chemistry. In addition, as physical weathering takes place a reduction of the bulk specific gravity occurs. Rocks typically have a specific gravity somewhere between 2.6-3.0 g cm^{-1}, but soils have a specific gravity of only 1.0-1.4 g cm^{-1}, with considerable space for soil water, for air and for microorganisms to grow and roots to penetrate.

2.4.2 Chemical Weathering

Chemical changes are characterized by leaching and depletion of some elements and residual accumulation of others. Newly formed (authigenic) minerals like clays and alteration products of rocks and minerals are usually the result of chemical weathering. The thermodynamic stability of minerals and rocks in soils is a function of temperature, total pressure and the activity of aqueous species in the soil solution. Some mineral species are more stable in aqueous solutions than others. Compact silicate minerals, such as amphibole and feldspar, are transformed to more open structured minerals such as clays. In contrast, minerals like quartz are very resistant to weathering, and are therefore often concentrated in the soil.

The highest rate of chemical weathering takes place in warm humid conditions. In areas with these conditions, chemical weathering results in the leaching of alkali and earth alkali elements together with a portion of silica. Iron and aluminum, on the other hand, concentrate under these conditions in the form of oxides and hydroxides. Kronberg *et al.* (1987) report that soils in the Amazon Basin of Brazil develop into hydrated refractory oxide assemblages of quartz, kaolinite, goethite and hematite, in some cases also gibbsite. Concentrations of alkali and earth alkali elements like Na, K, Mg and Ca have been reduced in these soils to trace amounts (Kronberg *et al.* (1987). Elements like B, Cl, Mo, As, Se and I are enriched in soils relative to the parent rock concentrations, while oxides of elements like Zr, Nb and others are resistant to weathering (Kronberg *et a*l. 1979).

Common chemical weathering reactions include:

- ○ Solution of solid material,
- ○ Hydrolysis,
- ○ Hydration,
- ○ Oxidation/reduction reactions.

Solution

A solution involves the reaction of minerals with water molecules. Water is essential for the weathering of rocks and minerals as well as for soil development. For effective weathering to take place, water must percolate through the minerals, rocks, and soils and translocate soluble weathering products. The simplest process of solution is that of dissolving salts by water and the dissolution of carbonates by acids. Because water molecules are dipolar (they have a positive and a negative end), they can attach themselves to ions (electrically charged elements) on the surface of the mineral removing ions. All minerals undergo some degree of solution upon weathering but those with an increased number of strong chemical bonds (covalent) are typically more resistant than those with weak ionic bonds.

The chemistry of aqueous solutions is important for the dissolution of minerals. Rainwater is a weak acid; mainly carbonic acid formed from the reaction of CO_2 with water, according to: $H_2O + CO_2 \rightarrow H_2CO_3$. This weak acid (pH 5.7) reacts with minerals and releases ions into solution. In fact, the weathering system of minerals contributes to regulating atmospheric CO_2 and can be seen as a carbon sink. The ions released during weathering of minerals are either released into the hydrosphere, or they are adsorbed by other mineral and organic complexes or taken up by plants. Warmer and wetter climates have generally high chemical weathering rates (Table 2.3).

Table 2.3. *Weathering rates from various places in the world under different environmental conditions (compiled by Macias and Chesworth 1992).*

Location	Type of rock or mineral	Rate of weathering (μm per 1000 years)
Baffin Island, Canada	Hornblende	0.1-0.5
Montana	Hornblende	<1
Western U.S.A.	Basalts	10-20
Southern Alps (N.Z.)	Arenites	1,000
Central Europe	Granites	6,000-13,000
Chad	Granite, Gneiss	13,500
New Caledonia	Acid rocks	10,000-16,000
New Caledonia	Ultrabasic/basic rock	29,000-47,000
Ivory Coast	Granites	5,000-50,000
West Africa	Volcanics	10,000- 50,000

Hydrolysis

Hydrolysis is the reaction between dissociated water molecules (H^+ and OH^- ions) and minerals. It is one of the principal reactions of weathering and most silicate minerals are susceptible to it. A typical hydrolysis reaction illustrates the breakdown of Na-plagioclase feldspar into kaolinite, Na-ions, bicarbonate and silicic acid (equation 2.1).

$$\underset{\text{Na-feldspar}}{2NaAlSi_3O_3} + 2H_2CO_3 + 9H_2O \rightarrow \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 2Na^+ + 2HCO_3^- + \underset{\text{Silicic acid}}{4H_4SiO_4} \quad \text{(equation 2.1)}$$

Hydration

Hydration involves the emplacement of water molecules within the structure of minerals. An example of this is the conversion of anhydrite to gypsum (equation 2.2).

$$\underset{\text{Anhydrite}}{CaSO_4} + 2H_2O \rightarrow \underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O} \quad \text{(equation 2.2)}$$

Oxidation

Oxidation reactions involve the loss of electrons. The reason that most weathered soils appear reddish or brown is that they contain the oxidized remains of iron-rich minerals. The oxidation of the divalent iron is oxidized to the trivalent form of iron, in this case FeOOH, as shown below.

$$2FeO + 2H_2O \rightarrow 2FeOOH + 2H^+ + 2e^- \quad \text{(equation 2.3)}$$

2.5 The Five Principal Soil Forming Factors

There are five major factors that influence soil formation. These are:

I. Parent material,
II. Climate,
III. Relief,
IV. Organisms (living and dead),
V. Time.

Soils are dynamic, living systems, in which several soil forming processes commonly interact with each other. Rarely is only one factor alone responsible for the formation of soils. The unravelling of the formation of soils is intricate and complex, providing a challenge for scientists to understand the changing interaction of the five factors and related processes.

2.5.1 Parent Material

Parent materials are unconsolidated, chemically weathered, mineral materials and/or organic matter from which the A and B horizons (the upper part of the soil profile) develop by soil forming processes. Another description of parent material is "the initial state of the soil system" (Jenny 1941).

One of the questions repeatedly asked by geologists is: why are soil scientists often unsure of the underlying parent material? According to the American Soil Taxonomy, the lower limits of soils are "the lower limit of biological activity, which generally coincides with the common rooting depth of perennial plants". It is beneath this zone that one eventually finds the weathered parent material and then the unweathered rocks. Soil scientists who dig out test pits for soil characterization and classification often do not reach much below the rooting depth of perennial plants, and even with great efforts it may be impossible to reach the weathered bedrock at depth.

Different parent materials weather differently not only as a function of mineral stability but also as a function of their grain size and texture and related drainage. Different rock types weather differently even when the environmental conditions are the same. They weather into different types of soil, each exhibiting different chemical and physical properties.

Minerals, which form at high temperature and high pressure, break down relatively quickly under earth surface conditions of low pressure and low temperature. In his ground-breaking work, Goldich (1938) established that rocks and minerals, which formed at lower temperatures, are more resistant to weathering and largely influence the formation of secondary products.

The process of weathering follows the sequence of the so-called 'Bowens Reaction Series' (Figure 2.8) showing the same order as described by Goldich (1938), but expressed as stability in relation to temperature. Weathering rate follows the sequence of minerals in the modified Bowen reaction series, with olivine and Ca-rich plagioclase weathering faster than biotite and Na-rich plagioclase feldspar and muscovite and quartz. It should be noted that micas (for example: biotite) weather more quickly than indicated because their sheet structure can become de-laminated, thus increasing the surface area of the mineral available for chemical weathering, as well as oxidising the ferrous iron (II) to ferric iron (III).

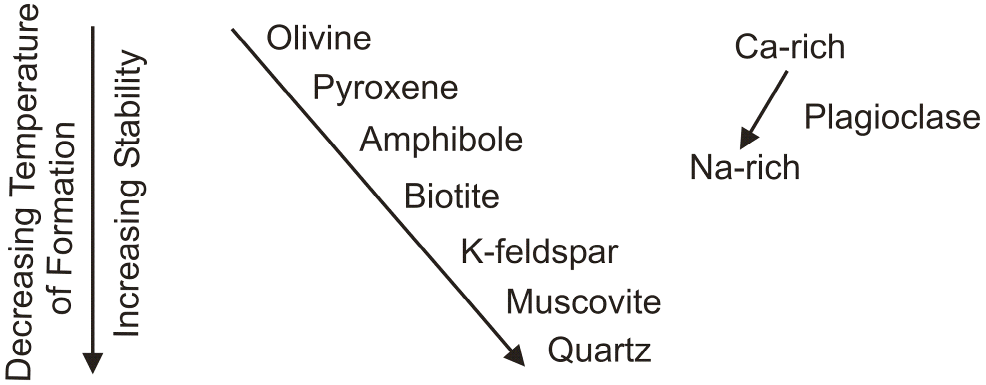


Figure 2.8. *Modified Bowen reaction series showing silicate mineral stability related to temperature of formation.*

Many studies of dissolution kinetics have been carried out under ultra-clean controlled laboratory conditions on single minerals (Busenberg and Clemency 1976; Berner and Holdren 1977, 1979; Berner 1978; Siever and Woodford 1979; Holdgren and Berner 1979; Berner *et al.* 1979, Schott *et al.* 1981, Schott and Berner 1985; Brantley and Chen 1995; Nagy 1995; Oelkers 2001) but also on rocks, for example volcanic glass (e.g. White 1983; Oelkers and Gislason 2001). The results of these fundamental studies on the surface chemistry and kinetics of the breakdown of minerals provide us with data and insights into the processes, on the speed of reaction and resultant mineral assemblages at mineral surfaces of many of the common rock-forming minerals. These findings are especially useful when studying the effects of the application of multi-nutrient silicate rocks as ‘rock fertilizers’ to soils (see chapter 9). The rate of dissolution of minerals is commonly measured as a function of aqueous Si, Al concentrations, pH, temperature, pressure, redox (for Fe and Mn containing minerals), and time.

The mechanism of mineral dissolution is, in general, very complex. It can be either dissolution of the total mineral without leaving a residue (congruent dissolution), for example olivine, or, more complex, partial dissolution with intermediary mineral formation and leaving a residue behind (incongruent dissolution). Dissolution commonly begins at mineral cleavage sites, at cracks and imperfections, and at sites with structural defects in the minerals (Banfield and Eggleton 1990). At the mineral surface, reactions and exchange processes are controlled by the proton (H^+) concentration in soil solution as well as the rates at which these protons exchange for cations at the mineral surface and diffuse through newly formed surface layers into the mineral. The often reddish surface layers of minerals are formed as a result of leaching and oxidation of Fe minerals. The surface coatings can act as 'armour' to further dissolution of minerals and can determine the rate of further dissolution of the minerals.

Most published data indicate that, upon fresh exposure of minerals to aqueous solutions under ambient climatic conditions, there is an initial very rapid detachment and flow of ions from mineral and glass surfaces into soil solution followed by a steady flow of released ions (Silber *et al.* 1999). As expected, mafic minerals like olivine and pyroxene as well as volcanic glass release nutrient elements relatively fast in contrast to nutrient ions released from pure feldspar or quartz, as well as feldspar-rich and quartz-rich rocks.

But these laboratory data should not be looked at in isolation. Antweiler and Drever (1983) drew attention to the fact that laboratory experiments do not always reflect the complexities of actual natural systems. They noted that laboratory data and field data substantially differed and that soluble organic compounds derived from vegetation seem to greatly enhance the breakdown of minerals.

At the time, Huang and Keller (1970) had already drawn attention to the influence of organic acids on the weathering of clays. Research in subsequent decades focused on the effects of organic acids on the release of nutrient elements from minerals into soil solution (Boyle *et al.* 1974; Schnitzer and Kodama 1976; Tan 1980; Song and Huang 1988; Barman et al. 1992; Welch and Ullman 1993; Drever 1994; Berner and Cochran 1998; Hinsinger *et al.* 2001) and the intricate interaction between microorganisms, organic and inorganic solutes and minerals in the rhizosphere (Robert and Berthelin 1986; Banfield and Hamers 1997; Hinsinger *et al.* 2001). The data show that organic compounds play a considerable role in aqueous soil chemistry and the weathering of minerals and rocks in terms of increasing or decreasing nutrient release and in the mobilization and immobilization of potentially toxic elements like Al. The potentially toxic Al is precipitated as secondary minerals in soils above a pH of 5 and below a pH 5 Al is immobilized through organic complexation.

Obviously, it remains difficult to mimic very complex and rapidly changing biophysical and geochemical systems and mineral weathering in soils. A special challenge is to predict and model dynamic natural multi-component systems and their kinetics in soils, where inorganic mineral and organic components interact with microorganisms under changing conditions.

2.5.2 Climate

Although parent material often controls soil formation on a local scale, a very important influence on the continental or even global scale, is climate. Climate plays a major role in soil formation and differs from region to region, the extremes being cold and polar desert environments described by Ugolini (1986) to weathering regimes in hot tropical countries as described by Nahon (1986).

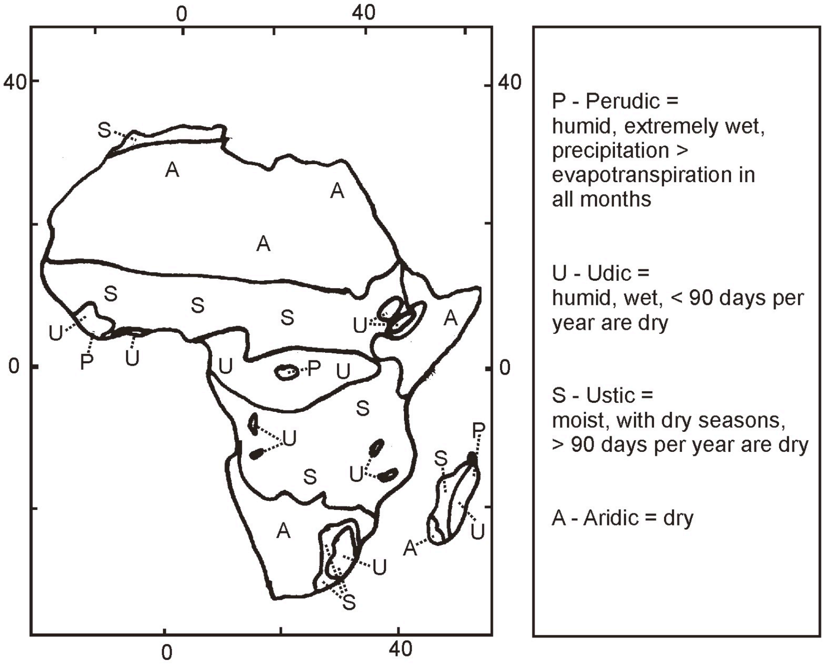


Figure 2.9. *Soil moisture regimes in Africa (source: Van Wambeke 1982).*

Climate factors such as precipitation and temperature affect not only the rate of physical and chemical weathering of rocks, they also affect biological acquisition of nutrients for soils. Precipitation rates and temperature regimes play a major role in processes of soil formation. The rate of weathering (and therefore the rate of soil formation) is faster in warm climates with high rates of precipitation and slower in cool climates, such as those in areas of high altitudes and high latitudes.

In many regions of the humid tropics, the soils are very deep and rich in chemically resistant minerals as well as newly formed clays and iron and aluminum oxides and hydroxides. Deep leaching over long periods of time has leveled out most but not all differences from the underlying geological rock formations. In areas of high rainfall, high temperatures and low relief, it is often difficult to find bedrock, as the area is usually deeply weathered and covered by thick blankets of soil.

Soil development in temperate climates differs from tropical climates as it is generally less intensive in terms of chemical weathering. The environment favours physical weathering and other processes instead.

Figure 2.9 illustrates the different soil moisture regimes in Africa, showing climatic conditions from very dry in the North and the South to very humid and wet in the central part. This climatic East-West zonation correlates with the latitudes: hot and wet at the equator and gradually drier towards the North and the

South. Deviation from this general East-West latitude controlled pattern occurs in the Northeast and the Southeast, where high mountains modify the climatic conditions.

Soil moisture regimes refer to the presence or absence of plant available water related to precipitation and evapotranspiration. Under aridic moisture conditions the soil is dry for at least half of the growing season and moist for less than 90 consecutive days. Ustic soil moisture conditions are found in areas where soil moisture is sufficient except for the dry seasons. More than 90 consecutive days per year are dry under this moisture regime. Udic soil moisture regimes are characterized by wet soil conditions and less than 90 days per year are dry. Perudic soil moisture regimes denote soil conditions that are extremely wet, with precipitation exceeding evapotransporation at all times.

2.5.3 Relief

Both large and small-scale topographic features can have profound effects on the distribution of rainfall. Topographic highs such as ridges and mountain ranges influence the climate, and subsequently affect soil formation and productivity. Commonly, the orographic shadow (leeward) sides of mountains receive less precipitation than the windward sides. On a global or continental scale, mountain ranges (Figure 2.10) enhance or decrease amounts of precipitation in the surrounding regions, which in turn control the soil moisture regimes.

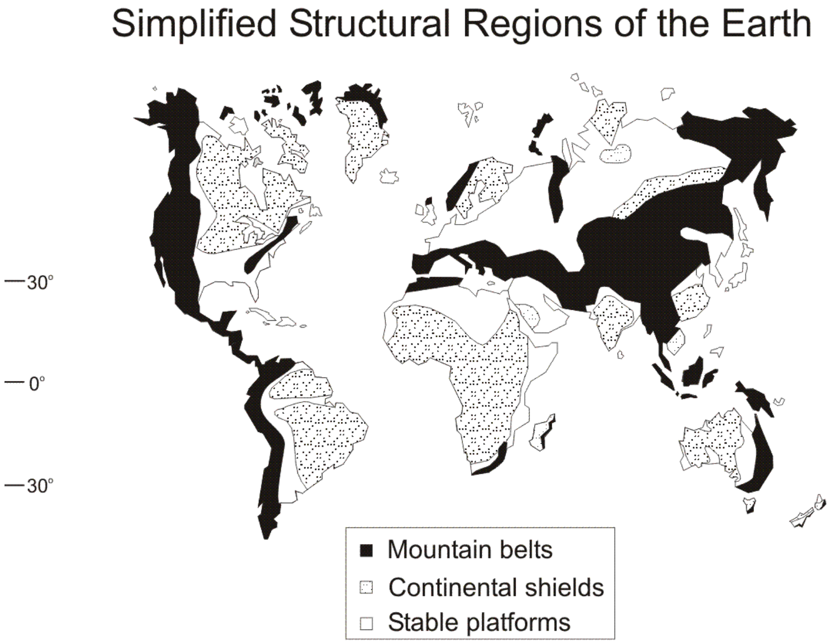


Figure 2.10. *Simplified structural regions of the earth.*

On a local scale, the distribution of mountains and hills can influence the soil moisture regime, which in turn will affect the soil types and soil fertility regimes. A good case study for this type of local variation is the area around Mount Kilimanjaro in Tanzania. The volcanic parent material around Mt. Kilimanjaro is relatively uniform but the climatic conditions vary. The southern and southeast slopes of the mountain receive high rainfall and agricultural production is consequently high, while the northwestern and western slopes are drier and less productive (but not less fertile). With irrigation this part of the mountain area also becomes productive. This example illustrates the influence of moisture regimes and relief on the formation of soils and soil productivity on a local scale is such that even in a small area with a uniform parent material a wide variety of soil types can form.

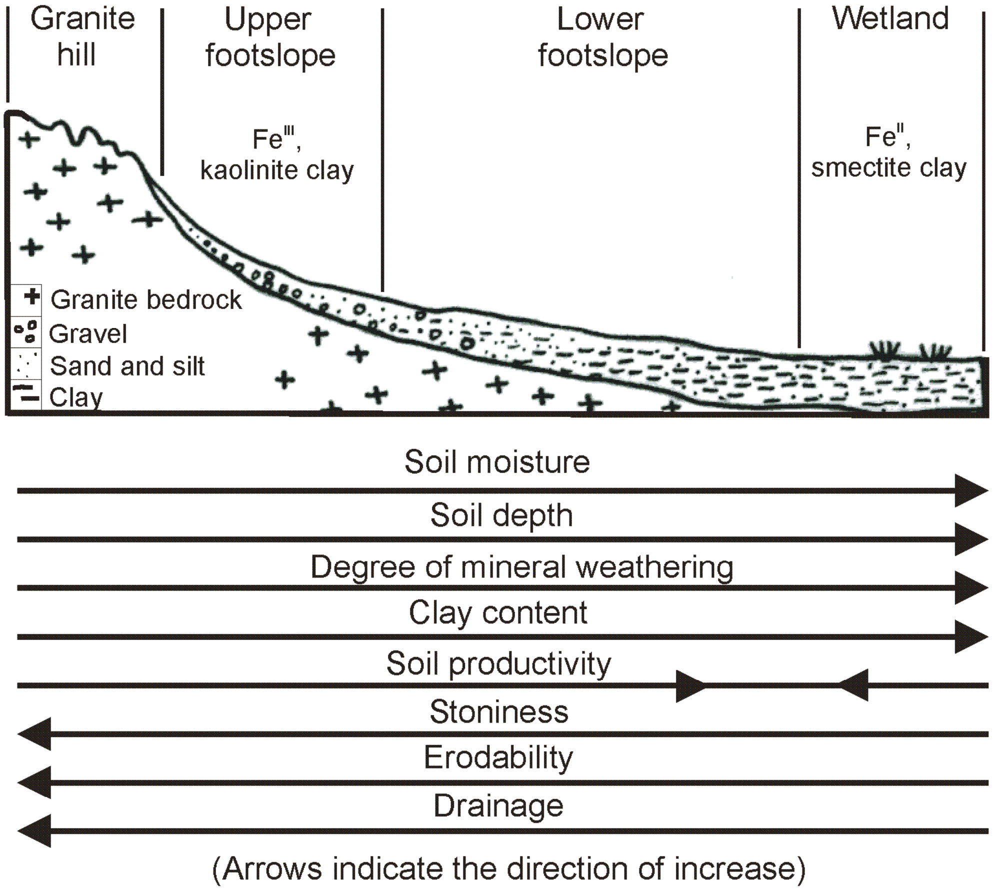


Figure 2.11. *Simplified catena showing variations in soil properties on a slope.*

Figure 2.11 illustrates generalized soil differences found along a topographical slope (a toposequence, or 'catena'), where the underlying geology is uniform, in this case granite. The physical, chemical and mineralogical properties of soils vary along the catena as a result of interaction of grain size of soils, drainage and chemical translocations of soluble weathering products. The exposed granite weathers preferentially along joints and disintegrated in rock and mineral fragments. On the upper slopes the weathered granite fragments and mineral particles are moved gravitationally down slope. The soils in the upper ‘footslope’ area are commonly shallow and stony. The lateral movement of water in this sloped position is generally fast. This means that the water stays in the soil for only a short period of time and there is relatively little chemical weathering. In mid-slope areas, water has a longer residence time in the soil and as a result more weathering takes place. Positions lower in the landscape receive some of the weathered rock material that was transported from higher elevations. The grain size of the transported materials decreases, as the larger grains cannot be carried as far. At the bottom of the topographic sequence, in valleys and depressions, the soils are clay rich and the drainage is impeded.

Materials transported downslope are not only transported physically, they are also translocated chemically. The soils formed along this topographic sequence are characterized by their differing clay minerals and in some cases iron mineralogy. Soluble weathering products leached in the upper reaches of the sequence can be translocated down-slope and re-arranged chemically and mineralogically. For example, highly leached soils in the upper slope area of the hypothetical example depicted in Figure 2.11 are dominantly kaolinites, while the clay minerals at the bottom of the sequence are mostly smectites.

During wet periods, iron is moved to lower positions along the slope. At the edge of the upper footslope, under good internal drainage conditions, the ferrous iron (Fe II) is oxidized and precipitated as ferric oxides (Fe III) and hydroxides. Here the soils are red and composed largely of kaolinite and Fe-oxihydroxides, eg. goethite (α-FeOOH). In the lowest topographic position, the valley flats, where internal drainage in the soils is very low, the soils are often black, with smectite being the main clay mineral. The smectite in this position was formed as a result of movement of soluble silica and cations down the slope. Here, iron occurs in the reduced state.

2.5.4 Living and Dead Organisms

Organisms play many important roles in the formation of soils. Plants and animals physically open up the soil with their roots and burrows, exposing fresh mineral surfaces for weathering. Plants, animals, and microorganisms add organic matter to the soil during their lives and after they die. This organic matter is generally rich in nutrients.

The cycling of nutrients from dead to living organisms is largely responsible for the existence of many tropical forests and jungles. These forests often thrive on old, highly weathered granitic soils, which are some of the least productive soils in the world. The organic matter on the forest floor is mainly composed of leaves, twigs and fallen tree trunks. This litter decomposes fast, releasing vital plant nutrients and organic compounds. Newly growing trees and other vegetation quickly take-up these nutrients. Examples from many parts of the world, including the Amazon rainforest as well as areas in tropical Africa and Southeast Asia, have shown the importance of the cycling organic matter and nutrients for forest regeneration. However, this process is interrupted by deforestation. Once the trees are removed, the soils quickly become infertile and unproductive. The nutrients contained in the organic matter are mainly gone, exported as timber, burnt or eroded.

Soils under grassland vegetation are often enriched in organic matter due to the prolific root development and decay of grasses (both shoots and roots). The influence of living and dead organisms on soil formation also includes animals. Organisms such as termites, earthworms, and gophers cycle and mix organic and inorganic matter in soils, and promote better aeration and drainage.

Soil organic matter (SOM) is important not only as a source of nutrients, e.g. N, K and trace elements. Organic matter also has a high buffering capacity (resistance to change of pH by adsorbing H^+ and Al^{3+}). Organic matter has a cation exchange capacity (CEC), commonly 20-70% of the total CEC in soils. It also often complexes with certain ions and thus influences their availability, e.g. Al^{3+}, Ca^{2+}, and Cu_2^+. Organic matter can also influence the aggregation of soil particles. It coats soil particles and bonds them together, forming better soil aggregates. This improves the soil structure for penetration of plant roots and also serves to stabilize the soil, reducing wind and water erosion, and increases water retention. Obviously, soil organic matter is vital in developing and maintaining productive soils.

2.5.5 Time

Weathering increases with increasing age. The formation of soils is in general very slow, but differs from area to area. For example, the time required to form a soil of 20 cm in a temperate climate like Canada requires approximately 10,000 years. In tropical countries the rate of soil formation is much faster, as can be seen from examples from Africa and New Caledonia (Table 2.2).

Soils require some time to develop their maximum fertility, but once this point has been reached, continued weathering, dissolution and removal of nutrients gradually cause the soil to become less fertile. Figure 2.12 illustrates the gradational stages of weathering, from the early to the late stages of the process.

Chesworth (1982) describes these three principal weathering stages and mineral formations over time: Stage 1 represents incipient weathering, disintegration of rocks and minerals. The primary minerals are dominant in the soil but the nutrients are not readily available. During stage 2, the weathering products of the primary minerals, specifically 2:1 clays (such as smectites) dominate the soils, and nutrients are readily available to the plants. In stage 3, the 2:1 clays of stage 2 weather into 1:1 clays. Kaolinite, iron-oxides and hydroxides as well as unweathered quartz dominate the soils. In these soils nutrients are only sparingly available to plants. These soils, at the end of the weathering cycle, are generally infertile.

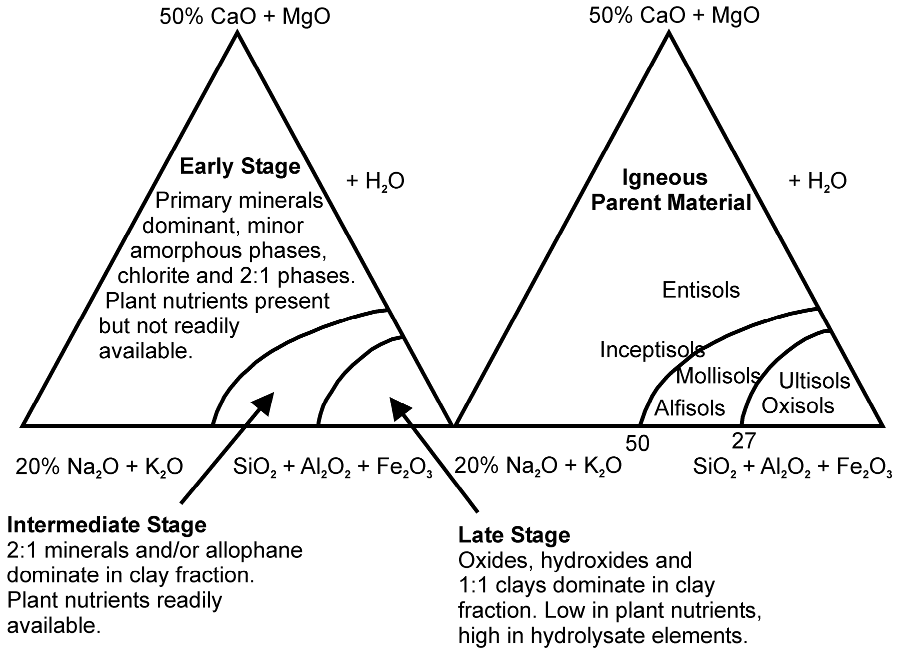


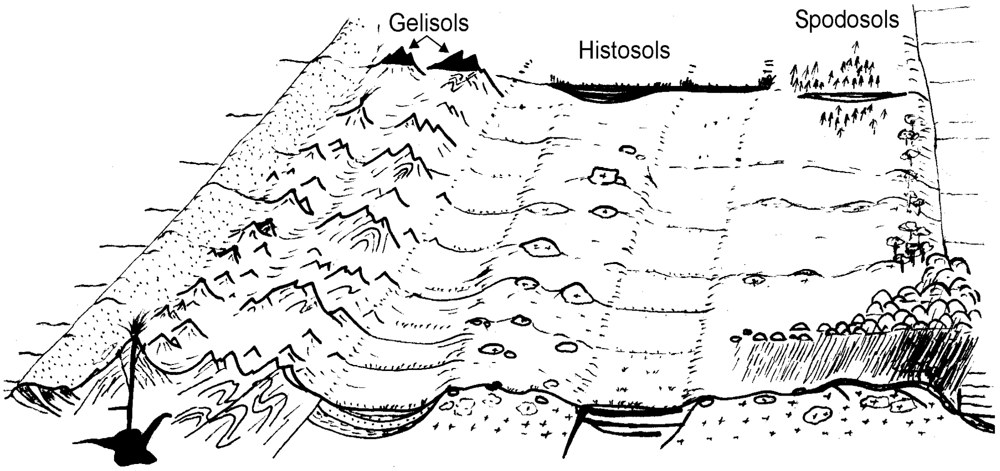
Figure 2.12. *Three gradational weathering stages for igneous rock in humid climates, based on Goldschmidt's division of the major components of the earth's surface into resistates, hydrolysates and oxidates (the* $SiO_2 + Al_2O_3 + Fe_2O_3$ *apex), carbonates (the CaO + MgO apex) and evaporates (the* $Na_2O + K_2O$ *apex) (Source: Chesworth 1982, with permission).*

The weathering of primary minerals via 2:1 clays to 1:1 clays illustrates the changes of minerals over time. Soil fertility is related to the release of elements from rocks and minerals as well as to the development of these mineral phases. The time that is necessary to transform primary minerals into 2:1 clays, and subsequently 1:1 clays, varies, of course, with environmental physico-chemical conditions and spans commonly in the range of 1,000 to 10,000 years, clearly too long to be called a renewable resource (Fyfe 1989, 1993, 2000).

2.6 Soils

Soils, made up of unconsolidated mineral and organic matter on the surface of the earth, have developed from various parent materials (rocks) through the interaction of various physico-chemical and biological processes. Soil classification systems have been developed to organize the knowledge on the properties and morphologies of soils. Primarily, soil classification systems have been developed for the purpose of scientific communication and for the implementation of soil inventories. These communication tools enable transfer and use of pedological data internationally and across disciplinary borders, not only by soil scientists, but also by other users.

Internationally, there are several soil classification schemes. Table 2.5 illustrates two of the main soil classifications, the US Soil Taxonomy (Soil Survey Staff 1998) and the FAO-UN based classification of soils, the World Reference Base (WRB) for soil resources (Deckers *et al.* 2002), endorsed by the International Union of Soil Sciences (IUSS). Other, more local soil classifications are widely used as well. These local soil classifications have the advantage of being more site specific. Detailed descriptions of soils, their classification and genesis are provided in Buol *et al.* (2003) and in Brady and Weil (1999).



Folded rocks	Volcanics	Folded rocks	Sediments	Granite & gneiss	Basalt	Granite & gneiss		Sediments
Aridisols	Andisols	Entisols	Mollisols	Inceptisols	Vertisols	Alfisols	Ultisols	Oxisols

Figure 2.13. *Distribution of soil orders (according to Soil Taxonomy 1998) in a hypothetical landscape across a hypothetical continent.*

Figure 2.13 illustrates the great variety and distribution of soils according to the Soil Taxonomy (1998) in a hypothecial landscape across a hypothetical continent, for example across South America. The distribution shows, in a very simplified way, the influence on soils of the two major soil forming factors, parent material and climate, and the influence of organic matter formation related to climate and parent material.

The cross section outlines differing geological substrates and structures, from folded sediments in the mountainous fold belt, to volcanics at continental margins, to granites and metamorphic rocks, like gneisses, as well as sedimentary rocks in a basinal structure. The differing bioclimatic conditions include arid environments, here depicted as coastal deserts, like at the west coast of parts of South America, to harsh cold conditions (like in Arctic zones, or high altitude environments with snow and ice), to wet humid environments in tropical to subtropical climate zones.

Andisols are generally found in geologically active structural zones of plate margins, either at collision zones (convergent plate margins) or at zones where plates start to separate (divergent plate margins), like in the Andes or in the Rift Valley of East Africa, respectively. Soils overlying pyroclastic volcanic materials are likely, but not exclusively, Andisols.

Vertisols can be found in low lying physiographic landscapes overlying basaltic rocks. However, Vertisols can also be found in similar landscapes over fine-grained Ca rich rocks, e.g. argillaceous limestones. Soils developed on these parent materials are of neutral to alkaline soil reaction, occur generally on nearly level or very gently sloping landscapes, and under climatic conditions with pronounced wetting and drying periods.

The influence of climate is strongest expressed under extreme dry and cold climatic conditions, for example in the form of Aridisols and Gelisols, respectively. The progression from Alfisols to Ultisols to Oxisols represents progressive losses of cations, like Na, K, Ca and Mg, as well as silica resulting from increased precipitation and subsequent leaching.

The distribution of Histosols represents a scenario where decomposition of organic matter relative to its accumulation is retarded due to excessive moisture or low temperatures.

Spodosols represent forested soils dominated by low-nutrient feeding trees. Mollisols represent grassland soils characterized by stabilization of organic matter due to Ca-rich parent materials. They can be found in plains covered by grass, prairies, savannas and transition zones to humid or arid environments. Mollisols are depicted in Figure 2.13 as overlying shallow sediments. Inceptisols and Entisols are soils characterized by their limited soil development.

The other major soil classification system, developed largely by soil scientists of the Food and Agriculture Organization of the United Nations (FAO) is the World Reference Base for soil resources (Deckers *et al.* 2002). A correlation of the two major classification systems, the Soil Taxonomy (1998) and the World Reference Base for soil resources (WRB 1998), is provided in Table 2.5.

Table 2.5. *Correlation between soil classifications based on the World Reference Base for soil resources (WRB) (1998) and Soil Taxonomy (1998). Source: Deckers* et al. *(2002).*

Soil Taxonomy (1998)	WRB (1998)	Description
Alfisols - Abruptic Albaqualf pp., Utisols - Aruptic Albaquulst pp.	Planosols	High base status, fertile soils with fine-grained subsoils in humid to subhumid climates.
Alfisols - Fraglossudalfs	Albeluvisols	
Alfisols - Paleustalfs, Ustalfs, Udalfs, Ustalfs pp.	Lixisols	
Alfisols pp.	Luvisols	
Andisols	Andosols	Soils formed on pyroclastic volcanics (ash, pumice, cinders) and other volcanic parent material.
Aridisols - Calcids pp.	Calcisols	Soils of dry regions.
Aridisols - Durids pp.	Durisols	
Aridisols - Gypsids pp.	Gypsisols	
Aridisols - Natrargids pp.	Solonetz	
Aridisols - Salorthids pp.	Solonchaks	
Entisols – Fluvents	Fluvisols	Recently formed soils with very shallow soil profile.
Entisols - Psamments pp.	Arenosols	
Entisols pp.	Regosols	
Entisols, Lithic subgroups pp.	Leptosols	
Gelisols pp.	Cryosols	Soils of very cold climates, e.g. in the Arctic.
Histosols pp.	Histosols	Organic matter-rich soils common in boreal zones, where organic matter production exceeds rate of organic matter decomposition, e.g. peat soils. *
Inceptisols - Aquepts pp., Entisols -Aquents pp.	Gleysols	Young soils with few diagnostic features; soil composition closely resembles parent material.
Inceptisols pp.	Umbrisols	
Inceptisols pp.	Cambisols	
Inceptisols pp., Plaggepts	Anthrosols	
Mollisols - Borolls pp.	Chernozems	Organic-rich, dark-coloured grassland soils of steppes, prairies, savannas; commonly over carbonate-rich parent material. *
Mollisols - Udolls pp.	Phaeozems	
Mollisols - Ustolls, Xerolls pp.	Kastanozems	
Oxisols - Kandiudox pp., Ultisols - Kandiudults pp.	Nitisols	Deeply weathered, low fertility acid soils, commonly red in colour, including soils previously classed as ‘lateritic soils’, commonly found in tropical and subtropical environments.
Oxisols - Plinthaquox pp.	Plinthosols	
Oxisols pp.	Ferralsols	
Spodosols	Podzols	Soils with subsoil accumulations of organic matter complexed with Al and /or iron under light coloured E horizon, found commonly in humid boreal climates over coarse textured parent materials; spodosols encompass ‘podsols’.
Ultisols - Udults pp.	Alisols	Low base status acid red soils with fine-grained subsoil horizons; commonly found in tropical environments on acidic parent material.
Ultisols - Udults, Ustults, Haplustalfs pp.	Acrisols	
Vertisols	Vertisols	Shrinking and swelling dark 2:1 clay-rich soils, commonly found over argillaceous limestones, weathered basaltic rocks and in fine-textured alluvial depressions.

* pp. = pro parte

2.6.1 Soil Fertility and Productivity

Soil fertility can be described as the chemical capacity of soils to support the growth of vegetation. The presence of major and minor plant nutrients is essential for this but the quantity and type of clay minerals and the organic matter in the soil also plays an important role. Generally speaking, fertile agricultural soils have the capacity to hold plant nutrients loosely on the surface of clay minerals and organic matter in such a way that they are not lost by leaching, but are available for plant use. For root uptake nutrient ions must be in soil solution, and there is equilibrium of nutrient ions in solution with nutrient ions adsorbed on clays and inorganic matter.

The ability of soil components to hold and release positive ions (cations) from soil constituents is expressed in centimoles of cations per kg of soil (cmol (+) kg^{-1}) and is known as cation exchange capacity (CEC). In addition, the proportion of cations like Ca^{2+}, Mg^{2+}, K^+ and Na^+ (bases) should be high relative to the proportion of cations like Al^{3+} and H^+ in order to have high soil fertility. Expressed as effective cation exchange capacity (ECEC) and 'base saturation' or percent base saturation (PBS) these soil chemical parameters are important for the assessment of soil fertility. As a general approximation: the higher the ECEC and PBS, the better the soil fertility. Clay minerals with a 2:1 structure, that is two Si-Al tetrahedral sheets and one Al octahedral sheet, have higher CECs than other soil minerals. Common 2:1 clay minerals are smectite, illite (clay mica) and vermiculite. The most common 1:1 clay mineral is kaolinite. Older soils and those formed under warm humid conditions on stable land surfaces contain mainly 1:1 clay minerals (e.g. kaolinite). Organic matter commonly has a high CEC.

Table 2.6. *The cation exchange capacities of some common soil constituents.*

Material	**CEC (cmol (+) kg^{-1})**
Organic matter	100-300
Vermiculite	80-150
Smectite	60-100
Illite	15-25
Kaolinite	2-8

The term soil health, largely synonymous with soil quality, has been mentioned in recent years (Sherwood and Uphoff 2000). Soil quality is defined by Dorran and Parkin (1996) as "the capacity of a soil to function within land use and ecosystem boundaries, to sustain biological productivity, maintain environmental quality and promote, plant, animal and human health".

For a soil to function biologically and to be ‘healthy’ it also has to be fertile. Fertile soils derive their nutrients largely from:

- Weathering of minerals and rocks,
- Decomposition of organic matter,
- Nutrient storage on organic matter and clays,
- Addition of manures or other fertilizing materials,
- Addition of new material via sedimentation, volcanism, dust, etc,.
- Biological fixation of N from the atmosphere.

Soil productivity is the total capacity of soils to support the growth of vegetation. Productive soils must be fertile, but in addition they must also be well aerated, have good texture and structure, have good water holding capacities and receive sufficient water. If the soil is fertile but other criteria are not met, problems such as water-logging, soil water loss, moisture stress and soil erosion may occur, and consequently the soil, despite being fertile, will be unproductive. Clay-rich soils are fine textured, “heavy”. They can have good structure, adequate water-holding capacity and excellent resistance to erosion, but still cause soil management problems due to poor drainage and water-logging, and they may be difficult to cultivate when too wet or too dry. In contrast, sandy, quartz-rich soils, which are coarse textured (light), generally have good drainage and are easy to cultivate, but are susceptible to erosion (by wind and water) as well as water loss.

Fertile soils may also exist in unfavourable climate conditions, such as extreme heat, dryness or cold, as found in desert or arctic, or high altitude environments. These severe circumstances may prevent otherwise fertile soils from being productive. Human intervention can also severely degrade soils, for example unsustainable soil management practices with subsequent soil erosion and soil nutrient depletion and exhaustion.

2.6.2 Soils and Land Use

Historically, farmers discovered that some soils are inherently more fertile than others. They settled first in areas with higher soil fertility. Consequently, the population densities in these areas are much higher than in areas with low inherent soil fertility. The very simplified map of the geology of Tanzania geology in relation to population densities (Figure 2.14) illustrates the close apparent correlation between fertile soils on Tertiary to Recent volcanic rocks as well as other volcanic areas with high population densities. Other areas with high population density are those areas that receive high rates of precipitation. These maps also show that granitic shield areas, known for their low soil fertility status, have relatively low population densities.

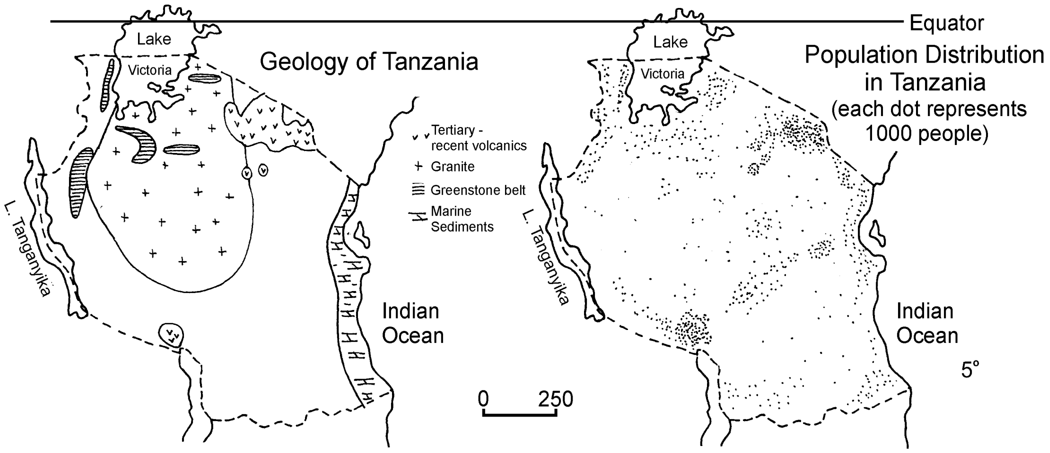


Figure 2.14. *Maps illustrating simplified geology, and population distribution in Tanzania. Note the spatial correlation between population concentrations and areas underlain by certain rock types, especially Tertiary to Recent volcanic rocks. Highest population densities are found in areas with soils overlying volcanic rocks, and in areas with high rainfall.*

The same phenomenon can be shown in Indonesia, comparing the geology and population densities of the island of Java and the Indonesian part of the island of Borneo (Kalimantan). Java is composed mainly of Tertiary to Recent volcanic rocks and supports a population of >900 people per km^2, while the large neighbouring island of Borneo is predominantly underlain by granitic and metamorphic rocks. The Indonesian part of Borneo (Kalimantan) supports only about 17 people per km^2 (Table 2.7). In China, the highest population densities are found in areas with alluvial soils, but also areas with high precipitation rates, for example in the southern parts of the country, in Guangdong and Fujian Provinces.

Table 2.7. *Population densities in selected areas of Indonesia.*

Area	Geological Composition	Size (km^2)	Population (millions)	Population Density (persons per km^2)
Java	Mostly volcanic	132 107	120	908
Kalimantan (Indonesian Borneo)	Mostly granitic	539 460	9	17
Sumatra	Partly sedimentary, partly volcanic	473 606	40	84

These examples illustrate that areas with favourable geological substrates in combination with favourable climatic conditions are fertile and attract farmers. The combination of inherently nutrient-rich, 'fertile', rocks with favourable climatic conditions provides for good soils, good yields and ultimately healthy farmers. Whether the healthy farmers are also wealthy farmers depends on the size the farm, and a myriad of other factors.

Figure 2.15 illustrates that volcanic and alkaline igneous rocks are source materials for very fertile soils in contrast to the surrounding sandy soils with low soil fertility, which are derived from granitic rocks. Population density and land use are strongly related to the geological base and the overlying soils.

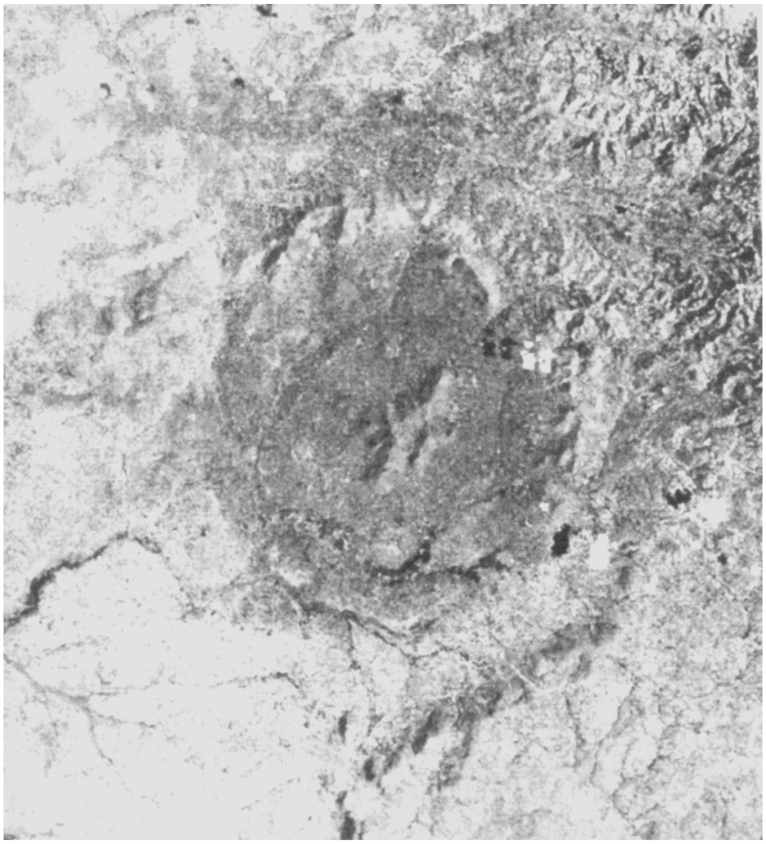


Figure 2.15. *Satellite image of the Bukusu alkaline igneous complex in eastern Uganda, illustrating the geological parent materials and structure and the differing land uses associated with different parent materials. Centre: volcanic cone and alkaline rocks: high soil fertility, mainly banana and maize/corn production, high population density. Outside of the ring complex: granite and gneisses: low soil fertility, low yield groundnut and cotton production, low population density. Scale: diameter of ring complex = 15 km.*

Another example of the relationship between land use, geological parent materials and overlying soils comes from Zimbabwe. Soils in Zimbabwe differ strongly in soil physical and chemical properties and consequently in soil fertility. They illustrate the result of a simplified weathering system. Assuming that all other soil forming factors remain constant, a comparison of soils formed from granite and soils formed from basalt (or greenstone) reveals large differences in fertility. Soils covering granitic rocks are generally sandy and kaolinite-rich, with a low ECEC. They are generally low in cations and P. In contrast, soils covering the greenstone belts (metamorphosed basaltic rocks) have a loamy texture and are rich in the 2:1 clay minerals, smectite and illite, with relatively high ECECs, a high 'base saturation'. Concentrations of Ca and Mg as well as micronutrients and P are often elevated in soils overlying greenstones. Typical mineral compositions and weathering products of granite and basalt in a tropical environment are shown in Table 2.7.

Table 2.7. *Typical mineral composition of granite and basalt and their chemical weathering products.*

Mineral	Granite	Basalt
Original rock composition:		
K-feldspar	30	
Plagioclase	30	44
Quartz	30	
Mica (muscovite, biotite)	10	
Pyroxene (augite)		50
Olivine		6
Weathering Products:		
Major elements	Si, Al, Fe	Ca, Na, Mg
Clay minerals	Kaolinite (1:1)	Smectite(2:1)→Kaolinite (1:1)
Oxide and hydroxide minerals	Quartz, Fe^+, Al oxides/ hydroxides	no free quartz, Fe^+, Al oxides/ hydroxides

On a purely mineralogical and physical base, the soils formed from granites are relatively rich in weathering resistant quartz grains, they are coarse grained and sandy with a low water-holding capacity and a low ECEC. In contrast, soils developed under the same environmental conditions from greenstones (basaltic composition) are more clay-rich, and thus have a higher water-holding capacity and a higher ECEC. A practical consequence: the soils on greenstone belts are agronomically more fertile and productive than the soils developed on granites.

2.7 Selected soil types

The distribution of soil types on the surface of the earth is determined by many factors, including parent material, present and past climatic conditions, topography, biological activity and age. The processes and pathways that change rocks into soils are complex. It involves the five soil forming factors that act simultaneously and interactively. The formation of soils commonly starts with the physical and chemical breakdown and transformation of minerals into secondary minerals, e.g. clays, and release and translocation of solutes which are in part plant nutrients. The transformation of rocks into soils also leads to physical differentiation into soil horizons with differing physico-chemical properties. In the following section some selected soils will be described showing specific properties and transformations, nutrient release and availability to plants along with some of the physical and nutrient management challenges of these soils.

2.7.1 Volcanic soils

The land use patterns of Tanzania, Indonesia, and Uganda (Figure 2.15) illustrate that the fertile soils that develop from volcanic ash and lavas attract farmers. Soil orders that have developed on volcanic parent materials are considered ‘young’ but have had a long and profound effect on human civilizations, food supplies and population growth (Buol *et al.* 2003). Ever since humans discovered agriculture, rich volcanic soils have been utilized because of the good growing conditions they provide. Examples of long lasting civilizations that were supported by prosperous agriculture on these fertile soils stretch from the area around Naples in Italy, to the volcanic areas in Central and South America, to volcanic areas in Indonesia and Japan.

Historic records and recent examples from volcanic areas in various geologically active volcanic areas show us that volcanic eruptions destroy large areas of land and habitats as well as killing many people, animals and above ground plants. The devastating volcanic eruptions not only release large amounts of energy and large volumes of very hot lavas and ashes that cover large portions of land, but also poisonous gases and potentially lethal hot and fine volcanic dust. Additionally, the energy released and the accumulation of lava and ash can trigger landslides and volcanic ‘avalanches’ destroying much of the terrestrial life in its way.

Despite all the negative effects of these devastating events, farmers like to farm in volcanic areas. The reason for this is the fertile nature of volcanic soils. Soil fertility in these areas does not immediately follow eruptions and the coverage of soils by ashes and lava. The speed of recovery from volcanic eruptions and the associated disruption of life depends on several climatic and geological factors.

Warm and wet climates speed up the process of weathering and release rock and mineral bound plant nutrients. Under humid tropical conditions the volcanic sites of massive eruptions can recover relatively fast, for example, the Krakatau volcano in Indonesia. Krakatau experienced an extremely large eruption in 1883, but by the 1930s large parts of the island had become naturally reforested. Today, the island is covered by an almost impenetrable jungle. The influence of climate on soil development is evident in the soil development in different areas of Hawaii. Although the composition of the volcanic flows in Hawaii are similar (mainly basaltic), the soils developed on the wet side of the islands weather within a hundred years while the basaltic lava flows located on the dry side show little signs of weathering altogether (Fisher *et al.* 1997).

The rate of weathering and recovery is considerably slower in dry and cold climates. For example, Mount. St. Helens, located in Washington State USA, erupted in 1980 but the surrounding area is still barely re-vegetated.

In addition to climate the compositions of lavas and ashes also has a profound effect on weathering rates and soil fertility. The rate of soil development is slower on lava flows than on volcanic ash. Furthermore, basaltic lavas and ashes weather to clay more easily than SiO_2-rich rhyolitic volcanics. The composition of lavas and ashes can also have a strong influence on the suitability of land use. For example, the soils developed on the silica rich pumice ashes on the North Island of New Zealand proved to be deficient in the micronutrients Cu, Co and Se and thus not suitable for sheep grazing. Only with corrective measures like introducing these micronutrients through fertilization have these areas attained their full potential (see Chapter 8, micronutrients)

The thickness of the covering ashes also determines whether land can be used shortly after eruptions. When the ash cover is more than 1.5 m thick, all plants die and recovery from such dramatic event may take several hundred years. When the soil is only covered by a few centimeters of volcanic ash with lots of fast weathering glass shards, these ashes can be incorporated into the soil easily and increase the soil fertility relatively fast as ‘slow-release fertilizers.’ The glassy material are weathered into poorly crystalline silicate minerals called allophone, which easily form complexes with Al (or P) and organic matter. The light, organic-rich Andisols can be easily tilled.

A cover of unconsolidated light-weight ash can also be a good insulator of plant roots protecting them from rapid temperature changes. Volcanic rocks can also help with water conservation. A volcanic eruption that sent a thin veneer of volcanic rock (dark-coloured scoria and light-coloured pumice) over volcanic soils in the Canary Islands triggered the soil water conservation technique of ‘rock mulching’, see Chapter 10. Porous light-weight ashes as well as volcanic cinders commonly have high water-holding capacities and serve as good growth media. In Japan and Indonesia, volcanic ash rich in volcanic pumice is used as a growth medium for root crops like radish, sweet potatoes and carrots, as well as good for upland rice due to the high water-holding capacity. In Ecuador and other Andean countries, the slightly acid, pumice-rich, light and well-drained soils found there are very suitable for the growth of potatoes.

Soils developed on volcanic ash, as well as volcanic tuff, pumice and scoria cinders are classified as Andisols in the Soil Taxonomy (Soil Survey Staff 1998) and Andosols in the WRB soil classification (after typical black soils overlying volcanic parent material in Japan, from Japanese ‘an’ meaning black and ‘do’ meaning soil). Andisols are generally very fertile.

A major negative effect of these soils is their tendency to ‘fix’ large amounts of phosphate ions making P-fertilizer application very expensive. To reduce the effects of P-fixation, which is caused by high Al activity, the application of lime, silica and organic matter as well as phosphate fertilizers or phosphate rocks is recommended. Buol *et al.* (2003) describe the application of large P superphosphate pellets or the soaking of potato tubers in P-rich solutions. The application of phosphate rock in Andisols has also been successful. Apart from their chemical limitations some Andisols are also prone to wind erosion. In Iceland, fine-grained Andisols, susceptible to wind erosion, have contributed to severe soil degradation in the centre of the island.

Andisols are among the most fertile and thus most populated areas on earth despite the fact that they cover less than 1% of the earth’s ice-free surface. Andisols are found in areas that have experienced active volcanism over the last few hundred thousand years, e.g. the Pacific Rim (‘Ring of Fire’) and the Rift Valley and various volcanic areas underlain by mantle plumes.

2.7.2 Deeply weathered soils of the tropics

At the other end of soil spectrum are soils that are extremely weathered and chemically depleted. These are the types of soils that predominantly occur in humid subtropical and tropical environments under tropical rain forest cover, such as in the lower Amazon Basin or parts of Africa, or South-East Asia. They are usually red in colour and deeply weathered. In the classification of the Soil Taxonomy (Soil Survey Staff 1998) these soils are called Oxisols and, less deeply weathered, Ultisols. In the classification of the World Reference Base for soil resources (WRB) they are termed Ferralsols. Together, these soils make up approximately a fifth of the world’s soil area.

Generally, these soils have good physical properties but are poor in soil fertility. They are characterized by their high proportion of clay sized Fe and Al hydrous oxides particles and 1:1 clays, mainly kaolinite. Overall, these soils have low cation exchange capacities (CEC). Due to the clay types that do not shrink and swell, and their good permeability and drainage characteristics as well as stable aggregate structure these soils are easily workable for farmers.

Many of these soils have been disturbed by termites, which tend to accumulate organic matter from the surface, hence the organic matter content of these soils is commonly good. In fact, the organic matter content in these soils under natural vegetation is generally similar to that of soils from temperate climates.

Chemically, these soils are characterized by low concentrations of N and P, as well as low exchangeable Ca^{2+}, Mg^{2+}, and K^{+}. Due to their high amounts of Fe and Al hydrous oxides, they exhibit strong phosphate retention (phosphate fixation). Usually these soils are acidic and thus prone to Al toxicities. Some of these soils exhibit Zn and Cu deficiencies, and Si deficiency might be a problem when silica demanding crops like sugar cane are grown.

Physically these soils have very good properties. They are soils with good drainage properties and deep profiles, enabling good rooting conditions for plants. Despite their low soil fertility these highly weathered soils support considerable numbers of people in tropical countries, largely living on subsistence agriculture. Traditionally, these soils were covered by forests and slash and burn cultivation practices were used. With increasing populations and pressure on land, as well as better knowledge of the growth limiting factors of these soils and better management, many areas underlain by these soils have been gradually transformed into farmland.

The transformation of originally unproductive soils into productive soils has been made possible with the inputs of lime, gypsum and phosphate rocks or superphosphates. Examples of these transformations with external fertilizer inputs include areas with large-scale soybean production and pasture such as the Brazilian Cerrado (Goedert 1983, Lilienfein *et al.* 2003), or, in the same area with crop rotations, organic inputs, phosphate rocks and rock fertilizers in organic farming systems and family farms (Theodoro and Leonardos 2006). Low input technologies have also been successfully applied to increase the nutrient status and productivity of these soils (Sanchez and Salinas 1981). Mimicking the original natural conditions, farming systems using improved fallows and agroforestry practices have shown that nutrients can be cycled in similar fashions as in the original rain forest system, making these systems more sustainable in the long term (Sanchez *et al.* 1997; Brady and Weil 1999).

Despite the predominance of Oxisols and Ultisols in subtropical and tropical regions, soils of these regions are not uniform. The notion that they are all universally acid, infertile and incapable of sustained agricultural production as a function of the climate is largely incorrect. Sanchez and Logan (1992) showed that the chemistry and fertility are very variable and that large parts of the tropical regions of the world are actually covered by fertile soils, including Alfisols, Mollisols and Andisols.

2.7.3 Poorly developed soils (Entisols and Inceptisols)

Poorly developed soils are found in areas where parent materials have not been exposed to intensive weathering due to their young age or where rocks have been exposed due to recent geological tectonical events. These soils have generally only very shallow soil profiles (Entisol in the Soil Taxonomy 1998) or soils with few incipient diagnostic features (Inceptisols). In both cases, the soil compositions closely resemble the parent materials. These soils are found on all continents. Depending on the parent material and other parameters, such as organic matter, they have very variable natural productivity.

Some of these soils are characterized by their low soil productivity. For example sandy soils developed from sandstones or other silica rich clastic sediments and metamorphosed sediments, e.g. quartzites, are commonly infertile due to their mineralogical composition (mainly quartz), their paucity of nutrients in the rocks they originate from. They commonly possess only low water and nutrient holding capacity. They are commonly deficient in K and S as well as low in organic matter. Because of their low nutrient holding capacity they are susceptible to leaching of N and K and several micronutrients. In addition, because of their poor structure, they are susceptible to wind and water erosion.

Some poorly developed soils, found in the foothills of mountain ranges are relatively infertile due to the short period and low intensity of weathering from the parent material, lack of soil moisture and high rates of erosion.

In contrast, other poorly developed soils, for example Entisols on recent alluvial plains and covering river valleys are very fertile due to the high nutrient contents replenished and transported from a large catchment area. Plain topography and frequent flooding make these types of soils very productive. Soils derived from alluvial parent materials on plains and river banks have produced some of the most productive soils in the world, for example in China.

2.7.4 Shrinking and swelling dark clay soils (Vertisols)

Dark coloured, clay rich soils that shrink and swell upon drying and wetting are called Vertisols. Most Vertisols developed on nearly horizontal plains and plateaus in sub-humid to semi-arid climates, in areas underlain by basaltic rock types, argillaceous limestones and other Ca-Mg rich parent material. Vertisols are commonly dark grey to black in colour and yet generally low in organic matter (0.5-3%). The dark colour is however largely due to the complexation of organic colloids to smectites, which darkens the clays.

Areas where these soils are common include the Deccan plateau of central India, large parts of Eastern Australia, Ethiopia, Sudan, the central plains of the United States, Canada and other parts of the world (Ahmad 1996).

The distinctive properties of these dark clay-rich soils is that they shrink and crack open when dry and swell and become sticky when wet. The main reason for the shrinking and swelling properties is the high content (> 30%) of 2:1 clays, mainly smectite. When these clays take up water they swell and when they dry they contract. These features make Vertisol difficult to manage.

The main problem for plant growth is the relative movement and shearing of the plastic soil material relative to each other, causing root shearing during the drying process (generated by hydration of clays exceed the shear strength) and root compression during the wetting cycle. During the dry season the soil shrink, cracks open (to a depth of > 50cm) and surface soil material falls into them.

Cultivation of these soils is extremely difficult during the dry season (too hard) and equally difficult when too wet as the soils stick to implements and forms large clods. Plants can suffer from extremes of drought, or from excess water, leading to water-logging. The time range when moisture range optimal for tillage, is extremely short. Much research has been conducted over the last few decades to address these hydraulic and practical tillage problems, and summarized by Probert *et al.* (1987), Coulombe *et al.* (1996), Mermut *et al.* (1996), and Tomar *et al.* (1996).

Since these soils are mainly found in sub-humid and semi-arid areas with low or irregular rainfall, it is important to intercept and keep as much of the rain as possible in the soil and make it available to plants. The key to improving the crop production on Vertisols is effective control of water. Consequently, management strategies in times and areas with high rainfall involve adequate surface drainage to avoid plant injury or slow growth from water-logging once the cracks have closed. Simple but practical solutions include the construction of ‘cambered beds’, and other man-made micro-relief patterns designed to improve surface drainage. In contrast, in very dry areas or during very dry periods, waterlogging is less likely a problem, and timing and tillage practices are important to get every drop of water in the soil, and minimize runoff and evaporative losses.

Soil fertility in Vertisol management is commonly regarded as less important than soil water management. Crop yields can be increased more easily by improved surface drainage or increased available water to plants than by the use of nutrient inputs.

2.7.5 Other soil types

To get an understanding of other types of soils, their genesis and potential or constraints for agricultural production the reader is advised to consult texts from Buol et al. (2003) and Brady and Weil (1999) and soil specific literature.

Table 2.8. *Essential nutrients, form of uptake and role in plant growth (from various sources).*

Element	Form of uptake	Role in Plant Growth
Macronutrients, mostly from air and water		
Oxygen (O), Hydrogen (H), Carbon (C)	H_2O, CO_2	Photosynthesis, water supply, constituents of most nutrient compounds
Macronutrients, mostly from soil solutions		
Nitrogen (N)	NO_3^-, NH_4^+	Constituent of all proteins, chlorophyll, and in co-enzymes and nucleic acids.
Phosphorus (P)	$H_2PO_4^-$, HPO_4^{2-}	Important in energy transfer as part of adenosine triphosphate. Constituent of many proteins, coenzymes, nucleic acids, and metabolic substrates.
Potassium (K)	K^+	Little, if any role as constituent of plant compounds. Functions in regulatory mechanisms, in photosynthesis, carbohydrate translocation, protein synthesis, etc.
Calcium (Ca)	Ca^{2+}	Cell wall component, Ca plays role in the structure and permeability of membranes.
Magnesium (Mg)	Mg^{2+}	Constituent of chlorophyll, enzyme activator.
Sulphur (S)	SO_4^{2-}	Important constituent of plant proteins.
Micronutrients, mostly from soil solutions		
Boron (B)	HBO_3	Important in sugar translocation and carbohydrate metabolism.
Chlorine (Cl)	Cl^-	Activates system for production of O_2 in photosynthesis.
Copper (Cu)	Cu^{2+}	Catalyst for respiration, enzyme constituent.
Iron (Fe)	Fe^{2+}	Chlorophyll synthesis and in enzymes for electron transfer.
Manganese (Mn)	Mn^{2+}	Controls several oxidation-reduction systems; formation of O_2 in photosynthesis.
Molybdenum (Mo)	MoO_4^{2-}	In the enzyme nitrogenase, needed for nitrogen fixation.
Zinc (Zn)	Zn^{2+}	In enzyme systems that regulate various metabolic activities.
Nickel (Ni)	Ni^{2+}	Essential for activating urease; needed for germination of seeds

2.8 From Soils to Plants

Soils are natural growth media for most plants. They provide anchorage, water, oxygen, as well as nutrients for growth. Plants require at least 17 nutrient elements to grow and complete a life cycle. These essential nutrients include the so-called macronutrients; nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg) and sulphur (S); the so-called micronutrients, iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), chlorine (Cl), boron (B), molybdenum (Mo) and nickel (Ni); as well as carbon (C), hydrogen (H) and oxygen (O). All but four of these elements (H, O, C and N) are derived exclusively from rocks and minerals. Plants require these nutrients in various amounts and concentrations but an insufficient supply of any one of these nutrient elements renders a plant unable to complete a life cycle.

The definition of essential mineral elements involves three criteria:

I. A plant cannot complete its life cycle without this element.
II. The function of the element is not replaceable by another element.
III. The element must be involved in plant metabolism.

Elements directly involved in plant metabolism or required for certain metabolic steps, as well as the form in which they are commonly taken up by plants and their role in plant growth are listed in Table 2.8.

Plants take up most of their nutrients from the soil solution. The mechanisms by which nutrients are taken up by the roots from soils are dynamic processes including root interception, mass flow and diffusion (Barber 1995).

Root interception is the process of nutrient uptake at the root-soil interface where nutrients are directly absorbed by the root. The nutrients at the root-soil interface do not have to move to be available for absorption (Barber 1995). Larger root surface leads to greater capacity for absorption so the rate of uptake through root interception is determined by the extent of exploration of roots into the soil.

Mass flow is the process by which dissolved nutrients are transported passively with water taken up by the roots. Mass flow is the most significant uptake mechanism of N, Ca and Mg uptake by plant roots (Barber 1995). The amount of nutrients provided by mass flow can be calculated by multiplying the concentration of a given nutrient in soil solution by the amount of water used by a crop. For example, the average water use of a crop like maize/corn is 2.5 to 3.0 million liters of water per hectare per year (Barber 1995).

Nutrient diffusion is the process where nutrients move from a zone of higher concentration to the zone of lower concentration. When plants take up nutrients they can lower the concentration of these nutrients at the root-soil interface, forming a gradient from low concentrations (at the root-soil interface) to the higher nutrient concentrations in soil solution. Nutrients move down this gradient towards the root-soil interface to equalize the concentration. Diffusion is the most significant mechanism of P and K uptake by plant roots (Barber 1995).

2.8.1 Nutrient replenishment

Land degradation includes loss of soil fertility, loss of soil nutrients and soil organic matter, as well as loss of biodiversity, and the general degradation of natural resources. Land degradation can be caused by soil water erosion, wind erosion, nutrient depletion, salinization, overgrazing, deforestation, over-exploitation of the vegetative cover, and soil fertility depletion.

Land degradation is a widespread problem in many countries. Scherr (1999) estimated that 74% and 65% of the land in Central Amercia and sub-Saharan Africa respectively are degraded. Dregne (1990) estimated that approximately 20% of the soil productivity of Africa has been lost since 1950 due to land degradation. Soil fertility depletion (‘soil nutrient mining’) is one of the fundamental root causes of the declining soil fertility in many parts of the tropics and sub-tropics (Sanchez *et al*. 1997).

Under natural climatic conditions, the physical break-up, chemical weathering and release rate of nutrients from minerals to soils and plants is not fast enough to provide nutrients for continuous annual crop production. In the past, soils were given rest periods during which they recovered and naturally replenished their nutrients through various processes, including the weathering of minerals. However, these fallow periods have been shortened in recent years, or even abandoned altogether due to increasing pressure on the land base. In many parts of the world, soil is not given any rest and is cultivated more or less continuously.

It has been widely recognized that the removal of nutrients from soils through repeated harvesting, leaching, gaseous losses, runoff and erosion, is too high to retain enough soil nutrients in the soil for sustained crop production. The result is that soils are ‘mined’. To correct the imbalance between soil nutrient exports and imports it is necessary to replenish nutrients that have been removed or lost. To sustain crop production, soils need replenishment of nutrients.

To provide crops plants with a constant flow of nutrients, the concentration of nutrients in soil solution must be sufficiently high over the entire period of growth. Some soils of the world are so well supplied with plant nutrients that they will support high crop yields over prolonged periods of time without additional nutrient inputs. These soils have high inherent soil fertilities. However, most soils require nutrient replenishment when the rate of nutrient removal, through harvesting or other outputs, exceeds the natural nutrient replenishment rate. To maintain and enhance soil fertility and support crop growth most soils need additional nutrient inputs such as fertilizers, manures or other amendments.

Among the strategies employed to overcome soil fertility problems is the use of artificial fertilizers, materials that have been processed chemically into highly soluble and concentrated forms from rocks and minerals or completely synthesized from various natural resources including the air, e.g. nitrogen fertilizers.

Fertilizer industries are largely concentrated in the hands of a few international and national companies or state-owned and parastatal enterprises. The geological resources that these companies and enterprises extract, process and market are usually of large size and high quality. The extraction and processing of these resources is commonly governed by economies of scale. The companies and enterprises usually follow strict quality guidelines (quality assurance and control). Distribution networks span the globe and fertilizers are commonly transported half way around the world to get from suppliers to end-users. It is the reality that one sees fertilizers produced by Norwegian, American or Japanese companies in farm supply shops in China, Southern Africa or South America. It is rare, however to find local fertilizers or soil amendments in farm supply shops or on farmer's fields, produced from small deposits nearby.

Although most farmers appreciate the value of water-soluble fertilizers, smallholder farmers can seldom afford them, especially in developing countries. Furthermore, when the smallholder farmer does purchase the processed, soluble fertilizers he or she rarely applies them at the recommended rate. Fertilizer imports have been hampered in many parts of the developing world by political problems, civil wars, transport problems, the scarcity of foreign exchange. In addition, farmers often get low prices for their agricultural products, leaving them with little or no incentive to increase crop production.

Instead of spending their savings on expensive, mainly imported water-soluble fertilizers, farmers often resort to alternative ways of accessing vital plant nutrient resources. They utilize organic materials such as manure and plant material. In parts of sub-Saharan Africa, replenishment strategies for N have been highly successful though improved fallow and crop-fallow rotation practices (Sanchez *et al*. 1997; Sanchez and Jama 2000). But these organic resources generally have low nutrient contents, especially low phosphorus levels, and they are bulky. To substantially increase the inflow of new nutrients, farmers could add locally available agrominerals.

Some agrominerals occur naturally in concentrations and forms that can be used as alternative fertilizers or soil amendments. 'Reactive' sedimentary phosphate rock (PR), potash, gypsum, dolomite, limestone, and various other minerals fall into this category. In other cases, mineral resources do not occur in a form in which the nutrients contained in the mineral are directly available to crops and must be modified physically, chemically and biologically to become valuable nutrient sources for soils and crops. For other agromineral resources, such as ground silicate rocks, large quantities of rock material are needed to be agronomically effective (Roschnik *et al.* 1967; Gillman 1980; Gillman *et al.* 2000; Harley and Gilkes 2000).

The term fertilizer is kept very general in this book, as ‘any organic or inorganic material of natural or synthetic origin added to the soil to supply certain elements essential to the growth of plants’ (Brady and Weil 1999). Natural as well as commercially processed inorganic, ‘synthetic’ fertilizers are used to supply plants with nutrients to increase plant growth. Natural organic and inorganic fertilizers are unprocessed or only slightly processed materials that are formed in nature, such as manure and phosphate rock respectively. Commercially produced inorganic, ‘artificial’ fertilizers include ‘chemical compounds, made in a factory, or obtained by mining, which supply plant nutrients and are not residues of plant and animal life’ (Cooke 1982). In many parts of the world, the term fertilizers refers to soluble nutrient compounds with guaranteed minimum percentages of nutrient elements, such as nitrogen, phosphate or potassium (NPK).

Soil amendments are materials, natural or synthetic, that make the soil more amenable to plant growth when they are worked into the soil (Brady and Weil 1999). Many soil amendments do not contain high concentration of nutrients but improve the soil physical properties and thus indirectly enhance plant nutrition and plant growth. Soil amendments include lime, gypsum and other naturally occurring materials that improve soil structure, soil aeration, water-holding capacities and other physical characteristics of soils. They include organic and inorganic materials. Organic soil amendments include materials like composts, manure, and biosolids, inorganic soil amendments include vermiculite, perlite and other inorganic materials that enhance soil physical properties, like water holding capacities or aeration. Soil amendments that measurably improve the soil’s physical characteristics are called soil conditioners.

Chapter 3

Nitrogen and other nutrients from air and water

Four elements oxygen (O), carbon (C), hydrogen (H) and nitrogen (N) make up the main components of water and air, H_2O, O_2, CO_2 and N_2. As shown in Table 3.1, these four elements are also the most abundant elements in plants. Because the focus of this book is on the rock-soil-plant pathway, the complete role of O, C, and H in crop production is beyond its scope. Selected details of these three elements are summarized at the end of this chapter. Because N is of major importance in managing soil fertility for crop production, the role of nitrogen is dealt with in detail in the following sections.

Table 3.1 *Average element concentrations in plants (source: Havlin et al. 1999)*

Plant nutrient	Average concentration (dry weight)
O	45%
C	45%
H	6%
N	1.5%
K	1.0%
Ca	0.5%
Mg	0.2%
P	0.2%
S	0.1%
Cl	100 mg kg^{-1} (ppm) = 0.01%
Fe	100 mg kg^{-1} (ppm)
Mn	50 mg kg^{-1} (ppm)
B	20 mg kg^{-1} (ppm)
Zn	20 mg kg^{-1} (ppm)
Cu	6 mg kg^{-1} (ppm)
Mo	1 mg kg^{-1} (ppm)
Ni	0.1-1 mg kg^{-1} (ppm)

Like O, C and H, N is widely distributed in the atmosphere, hydrosphere, biosphere, and lithosphere (Table 3.2). On the surface of the earth, N occurs in many different forms and in the different pools. The understanding of N transformations and translocations in these surface-near pools are important for geochemists, agriculturalists and environmental scientists alike as these processes are related to many soil fertility and pollution related problems.

Table 3.2. *Terrestrial distribution of nitrogen (source: Stevenson 1972)*

Sphere	N content x 10^{13} metric tones
Lithosphere	16,360
Atmosphere	386
Hydrosphere	2.3
Biosphere	0.028

Nitrogen gas (N_2), is the main component in air (up 78.03%). However, nitrogen gas is not directly accessible to plants. In order to be taken up and used by plants it first has to be converted to ammonium (NH_4^+) and nitrate (NO_3^-). Nitrogen is essential for several crucial biological functions. Plants require it for growth of roots, shoots, fruits and seeds. Nitrogen is an essential building block in the production of proteins.

Nitrogen occurs only in very low concentrations in rocks and minerals, 56 mg N kg^{-1} in the continental crust (Rudnick 2003), and 25 mg N kg^{-1} in the composition of bulk earth (McDonough 2003). Despite the low concentration of N in the earth as a whole, the lithosphere is the largest reservoir of N because of its great mass. The second largest reservoir is the atmosphere, which is made up of 78.03% nitrogen gas (N_2).

The concentrations of N in the pedosphere, (in soils), vary widely from place to place, as does the amount of N available to plants. Some of the factors that influence the availability of N to plants are biological in nature others are physico-chemical processes.

3.1 Nitrogen in plants

Although nitrogen plays a crucial role for the growth of all plants, the N-requirements of individual crops varies widely. Cereal crops like maize/corn and rice commonly have a relatively high demand for N to be supplied from soil solution. Maize/corn commonly requires 100 kg N ha^{-1}. Leguminous crops on the other hand cover most of their N needs through a symbiotic relationship with N-fixing bacteria.

Plants require N for growth of roots, shoots and fruits and seeds. The addition of N to soils promotes the formation of chlorophyll. Nitrogen is essential in the process of photosynthesis, the primary process that converts inorganic forms of C into organic forms. Nitrogen is also an essential building block in the production of proteins. It promotes vigorous vegetative growth in plants as well as plant sugars.

Mass flow of nutrients, the movement of nutrients to the roots caused by plant water absorption, is responsible for most of the N uptake by roots of plants, although diffusion can also be important (Barber 1995). Plant roots can take up N in two forms: NH_4^+ (ammonium cation) and NO_3^- (nitrate anion). The roots of most higher plants take up N preferentially in the form of nitrate. However, before the plant incorporates N from nitrates into nitrogenous compounds it has to be reduced to ammonium forms.

In general, young plant tissue contains more N than plant tissue approaching maturity. The greatest concentration of N is found in those parts of the plant where growth is taking place and in the seed or reproductive portion of plants. Nitrogen is translocated from older parts of the plants to the portions where growth is taking place. Consequently, N-deficiencies develop first in older parts of plants, often in the lower leaves.

Figure 3.1. *Leaf of maize/corn (Zea mays) with N deficiency (left); Section of plant roots of soybeans (Glycine max) with N-fixing nodules (right).*

Typical symptoms of N-deficiencies in plants are paling (plant leaves become pale yellowish-green) and the formation of spindly stalks. A clear sign of N-deficiencies in maize/corn, for example, is the yellowing of the tip and centre of the leaves following a V-shape towards the mid-rib of the leaf (Figure 3.1).

Nitrogen is taken up from soil solution in larger quantities by grain crops than any other essential plant nutrient. In contrast, forage and vegetable crops contain generally higher concentrations of K than N.

Biological N_2-fixation

The process of biological nitrogen fixation (BNF), or more accurately biological dinitrogen fixation, converts the relatively stable atmospheric dinitrogen (N_2) to N-containing organic compounds. Leguminous crops like peas, groundnuts and soybeans, and leguminous trees such as *Leucena* and *Acacia* cover most of their own N needs through this process. The process is facilitated by a group of symbiotic microorganisms, mainly *Rhizobium* and *Bradyrhizobium* bacteria, which infect the roots of leguminous plants, form nodules, and fix N_2 from the air, thereby providing available N sources to their host plants (Figure 3.1). This nitrogen-fixing relationship is a major source of N for agriculture. Tree fallows and leguminous cover crops can 'fix' from 30 to 300 kg N per hectare per year from the air, providing abundant N for the crop and leaving behind some of the N containing organic matter N for subsequent crops (Roger and Ladha 1992; Brady and Weil 1999).

Some important plants, shrubs and trees that participate in N-fixing relationships (N-fixing plants) include:

Alfalfa (*Medicago sativa*)
Bean (*Phaseolus vulgaris*)
Broad bean (*Vicia faba*)
Cowpea (*Vigna unguiculata*)
Erythrina (*Erythrina abissinica, and E. poeppigiana*)
Gliricidia (*Gliricidia sepium*)
Inga (*Inga edulis*)
Kudzu (*Pueraria lofata* and *P. phaseloides*)
Lablab (*Lablab purpureus*)
Lentils (*Lens culinaries*)
Mucuna (*Mucuna pruriens*)
Peanut/groundnut (*Arachis hypogea*)
Peas (*Pisum sativum*)
Pigeon pea (*Cajanus cajan*)
Red Clover (*Trifolium pretense*)
Senna (*Senna simea*)
Sesbania (*Sesbania sesban*)
Soybean (*Glycine max.*)
Sunhemp/Crotolaria (*Crotolaria juncea* and *C. grahamiana*)
Tephrosia (*Tephrosia vogelii*)
Wild tamarind (*Leucaena leucocephala*)
Winterthorn (*Faidherbia albida*)

Not all legumes nodulate and fix N. Some legumes, such as common beans (Phaseolus vulgaris), fix N only poorly. In addition, low availability of nutrients such of P and K, the micronutrients Fe, Co and Mo, as well as droughts and other environmental factors can seriously restrict N_2-fixation. For example, to convert atmospheric N_2 into the ammonium form used by plants small amounts of phosphorus (P) are required for the Rhizobium bacteria. Robson *et al.* (1981) concluded that increased P supplies increased N_2-fixation of subterranean clover by stimulating the host plant growth. Ssali and Keya (1986) showed that the application of P increased the nodulation, dry matter yield and P uptake of three bean cultivars. Cadish *et al*. (1993) describe similar results of an apparent interaction and positive effect of P-addition on N_2-fixation by *Centrosema acutifolium* and *C. macrocarpum* on a P-deficient acid tropical soil in Colombia. Sanginga *et a*l. (1996) showed that the addition of P increased the weight of nodules but did not increase the proportion of N derived from the atmosphere. Somado *et al*. (2006) showed that the addition of a reactive phosphate rock (in this case Tilemsi phosphate rock from Mali), enhanced the biomass and N-accumulation of N_2-fixing green manure legume species, such as *Crotolaria micans*. Their study suggests that growing N_2-fixing green manure legume fertilized with phosphate rock can fix sufficient N_2 to meet the demand of subsequent crops.

Clark (2000) provides some examples of how isotope research can provide unequivocal resolution of effects of elements involved in the process.

Leguminous cover crops are widely used to increase the N concentration of soils in both temperate and tropical climates. In parts of Africa, in Southeast Asia, Latin America and Australia, leguminous cover crops are widely used in farmers' fields and in plantations. In addition to providing N, leguminous tree fallows also provide other benefits such as fuel wood production on farms. Both leguminous trees and leguminous cover crops also recycle other nutrients such as P and K, control weeds, protect the soils from erosion, reduce leaching losses and increase the soil's water holding capacity (Brady and Weil 1999).

Certain N_2-fixing cyanobacteria (blue-green algae) also participate in symbiotic relationships with plants, for example the blue green algae *Anabaena azollae* lives in symbiotic association with the aquatic fern *Azolla piniata* (Watanabe *et al*. 1980). Still other bacteria and cyanobacteria fix N_2 non-symbiotically, for example *Azotobacter, Rhodospirillium* and *Beijerinckia*. The quantities of N_2 fixed by these so-called free-living N_2-fixing bacteria are generally lower than that of *Rhizobia* species. Some free-living bacteria rely on the availability of organic matter as substrate to fix nitrogen (Marschner 2002).

3.2 Nitrogen in soils

The N concentration of soils varies considerably. Most soils contain 0.2–0.3% N with a global average of 0.2% N kg^{-1} (Ure and Berrow 1982). The total N content in soils varies from approximately 2–20 t N ha^{-1}, and is primarily related to the quantities of organic compounds in the soil. While the N concentration is generally very low in desert soils it can reach 2% in highly organic soils.

Only a fraction of the relatively small amount of total N in the soil is available to plants. The soil is a dynamic system and nitrogen substances are transformed from one form to another mainly through the activities of soil bacteria. In schematic diagrams, Figure 3.2 illustrates translocations and transformations of N in the soil environment.

Starting with the atmosphere the first transformation in this cycle is N_2-fixation. This can occur through biological N_2-fixation, industrial N_2-fixation, and lightning induced N_2-fixation. Nitrogen can also be recycled in the soil from organic sources such as plants and animals. For organic forms of N the next step in the N-cycle is the process of mineralization.

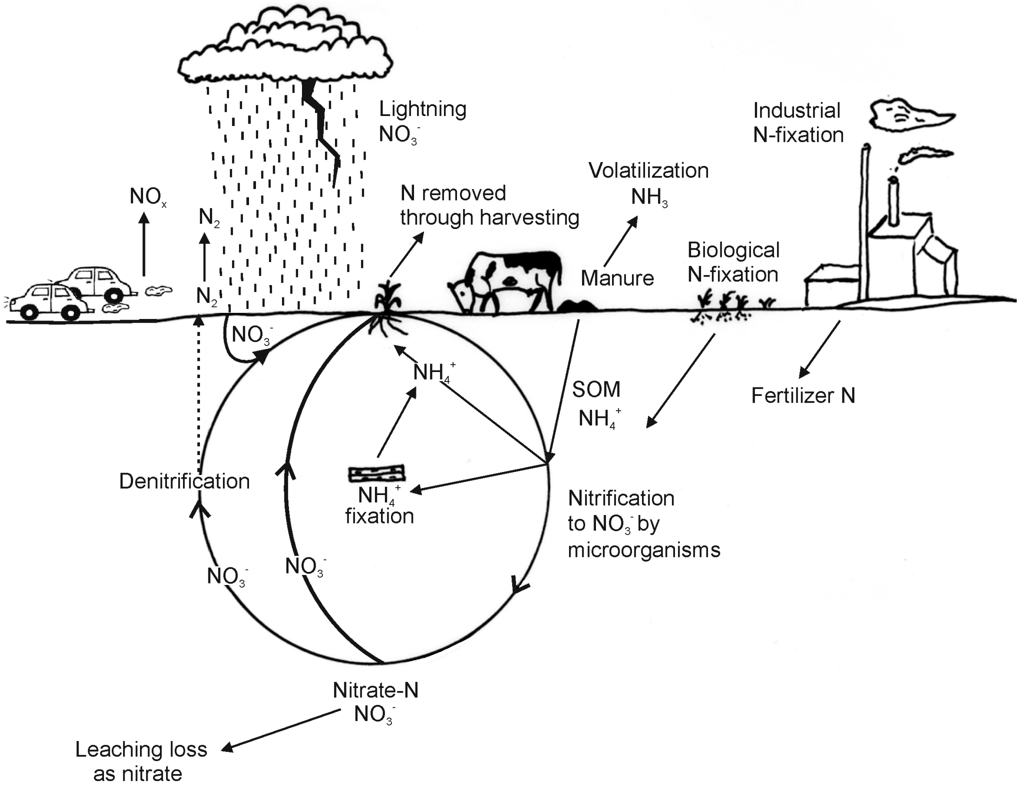


Figure 3.2. *Illustration of the natural N cycle.*

Mineralization means something different for biologists and geologists. The geologists speak of mineralization as inorganic mineral formation and mineral accumulation in mineral ore deposits. In contrast, biologists refer to mineralization as the conversion of nutrients such as N from organic forms into plant-available inorganic forms, mainly into ionic forms in soil solution such as NH_4^+ and NO_3^-. The following processes are steps in the process of mineralization of organic N:

Ammonification is the term that describes the reduction of organic compounds (chiefly amino acids) by microorganisms to ammonium (NH_4^+).

Nitrification is a term commonly used to describe the oxidation steps of NH_4^+ to nitrite (NO_2^-), and nitrite to nitrate (NO_3^-). This biological nitrification is a two step sequential process:

Nitrification pathway step 1: *Ammonium (NH_4^+) to nitrite (NO_2^-):*

$NH_4^+ + {}^3/_2\, O_2 \rightarrow \textit{Nitrosomonas} \rightarrow NO_2^- + H_2O + 2H^+ + 275\text{ kJ}$ (equation 3.1)

Nitrosomonas is the bacterium most responsible for this reaction. It is an aerobic bacterium, requiring oxygen to live. It has the highest productivity under dark, damp conditions with a pH of 7.6 or greater. The nitrite (NO_2^-) produced as a first step in this two-step process can be toxic if concentrations are elevated. However, the NO_2^- is normally converted to NO_3^- very rapidly. The liberated hydrogen ions, as shown in step 1 (equation 3.1) increase the acidity of the system. Soil acidification under legume crops has become a concern in Australia (Loss *et al.* 1993). Williams (1980) measured acidification in soils under clover pasture over time and found that the soil pH dropped by one unit over a 50-year period.

Nitrification pathway step 2: *Nitrite to nitrate:*

$NO_2^- + 1/2\, O_2 \rightarrow \textit{Nitrobacter} \rightarrow NO_3^- + 76\text{ kJ Energy}$ (equation 3.2)

Nitrobacter is the predominant bacterium in the second reaction.

In general, the rate of nitrification depends on a few environmental parameters:

- Oxygen supply, which is in turn related to the aeration and structure of the soil. Thus a well-drained sandy soil is expected to have a higher rate of nitrification than a poorly drained clay-rich soil,
- The population of nitrifying bacteria,
- The pH of the soil: neutral or near neutral pH is optimal,
- Soil temperature: the colder the soil the slower is the rate of chemical and biological activity.

Although nitrification is vital in supplying N to plants, highly mobile nitrate is often leached from the soil before a plant can take it up. As a result, efforts have been made to reduce the speed of the nitrification process. Impeding methods include chemical nitrification inhibitors, which block the microbial transformation of NH_4^+ to nitrite (NO_2^-) and then nitrate (Slangen and Kerkhoff 1984) and the use of slow-release N-fertilizers such as sulphur-coated urea or polymer-coated N-fertilizer (Oertli 1980). The successful application of slow-release fertilizers is often a function of optimal climatic and soil conditions as well as crop type (Oertli 1980). Slow-release fertilizers are more expensive than regular fertilizers and are applied mainly in greenhouse operations and on specialty crops.

Denitrification results in a net loss of plant-available N. It occurs when bacteria reduce NO_3^- to the gaseous forms N_2O or N_2, which are subsequently lost to the atmosphere. Nitrogen losses through denitrification are a problem under anaerobic and warm soil conditions. Microbial denitrification occurs preferentially when soils are waterlogged and warm (20-30°C). Waterlogged conditions mean that the soil is low in oxygen, which in turn allows reducing bacteria to flourish. This phenomenon can be seen in low-lying ‘wet’ areas in fields that often show poor nitrogen response (e.g., stunted corn/maize plants, yellowing of older leaves). Soils that are well-supplied with easily decomposable organic matter also tend to enhance denitrification.

Typical N-losses due to denitrification are 10-40%, although the amount can double if temperatures increase by 10°C. In flooded soils the loss of fertilizer N through denitrification can be as high as 50% (Aulakh *et al.* 1992).

Nitrite is a transitional product of both denitrification and nitrification, and is toxic to plants. Fortunately, these processes occur rapidly enough that accumulation of nitrite is not normally a problem.

Denitrification pathway

NO_3^-	$\rightarrow$	NO_2^-	$\rightarrow$	(NO)	$\rightarrow$	N_2O	$\rightarrow$	N_2	*(equation 3.3)*
Nitrate		Nitrite		Nitric oxide		Nitrous oxide		Nitrogen gas	

3.3 Sources of Nitrogen

Nitrogen used by plants is mainly obtained indirectly from the atmosphere and is transformed into plant-available complexes by various processes (see below). Although a large percentage of N is stored in the lithosphere, nitrate- and ammonium-bearing rocks are relatively rare. The only known naturally occurring nitrate-bearing rocks that serve as an economically viable source of plant-available nitrogen are found in the Atacama Desert in Chile.

3.3.1 Nitrogen additions to soils

There are four principle ways of fixing N_2 gas from the atmosphere into plant available N. The first of these, biological nitrogen fixation (BNF) is described in section 3.1. The second method of N_2 fixation, the Haber-Bosch process, is responsible for most N-fertilizer production and is described in section 3.5.1. Two further methods include N-fixation through lightning and N-addition from the atmosphere resulting from air pollution.

N-fixation through lightning

Lightning can cause significant atmospheric N_2-fixation. The oxidation process occurs as N_2 in the troposphere is converted photochemically to NO_2, HNO_2, HNO_3 and other by-products, which are then deposited onto the earth’s surface, mainly through precipitation (Yung and McElroy 1979). Global estimates for lightning induced N_2-fixation range from about 1 to over 200 million tonnes per year (Liaw *et al.* 1990; Galloway *et al.* 1995). In another survey, Lee *et al.* (1997)

reviewed published data and estimated that 2 to 20 million tonnes of NO_x-N is synthesized annually by lightning.

N-compounds from air pollution

Additional N, in the form of NO_3^-, NO_2^-, N_2O, NH_4^+ and organic N, can be provided from industrial and agricultural sites through precipitation and air pollution. Table 3.3 illustrates an example of nitrate-N and ammonium-N additions to soils from precipitation. The amount of N provided unintentionally by air pollution is generally very low in the Prairies of North America, but the situation is very different in industrialized parts of North America (Brady and Weil 1999).

Table 3.3. *Nitrogen supplied by precipitation in kg ha^{-1} yr^{-1} (Brady and Weil 1999).*

Area	**NO_3 – N**	**NH_4 – N**
Rural area, Ohio, USA	6.6 -10.6	6.2 - 8.2
Industrialized, NE USA	4.3 - 7.4	8.6 -14.8
Open areas of the Prairies, USA	0.4 - 0.6	0.8 - 1.2

3.3.2 N-containing rocks and minerals

Nitrogen ranks as the 31st most abundant element in magmatic rocks in the earth's crust, at a mean concentration of 20 mg kg^{-1} (Baur 1972; Baur and Wlotzka 1972) and 60 mg kg-1 for the continental crust (Wedepohl 1995). Estimates of total N in the earth vary due to uncertainties of the concentrations of N in the crust, mantle and core. Baur and Wlotzka (1972) estimated that the earth's mantle alone contains 5,600,000 x 1010 tons of N.

Highest concentrations of N, mainly in the form of NH_4^+, are reported from sedimentary rocks, especially clay and mica rich rocks, and rocks rich in organic matter (Table 3.4). Mica and clay-rich sediments, e.g. shales contain about 600 mg N kg^{-1} (Baur and Wlotzka 1972). Carbon-rich bituminous sediments commonly contain high N concentrations and can reach, in rare cases, up to 6,000 mg total combined N per kg (Baur and Wlotzka 1972).

Some metamorphosed pelite-rich sedimentary rocks also contain high N concentrations. For example, the ammonium concentrations in micas from 1.9 – 2.09 billion year-old metasediments range from 176 to 1,549 mg kg^{-1}, suggesting a biological origin of the nitrogen (Papineau *et al*. 2005).

Nitrogen concentrations are markedly lower in magmatic rocks than in sediments or metamorphosed sediments (metasediments). The N-concentration in granitic rocks varies from 0-200 mg N kg^{-1} and is probably related to specific local geotectonic conditions (Hall 1999). Most of the N in granites is accumulated in micas where NH_4^+ replaces K^+ and in some feldspars. The origin of the nitrogen is unclear but possibly related to partial melting of sedimentary precursors, interaction with surrounding clay and mica-rich sediments, as well as hydrothermal alteration (Hall 1999; Boyd 2001).

Volcanic rocks generally contain more N than other igneous rocks. The average N concentration of volcanic rocks is 37 mg kg^{-1}, more than twice the 16 mg kg^{-1} average of intrusive rocks (Baur and Wlotzka 1972).

Table 3.4. *Nitrogen concentration in various rocks (compilation by Baur and Wlotzka 1972; Boyd 2001).*

Rock type	N (ppm) mg kg^{-1}
Granites	21
Basalts	30
Ultramafic rocks	14
Shales	600
Sandstones and greywackes	150
Limestones	70
Coal	2,000 – 30,000

Volcanic rocks release large amounts of N in a gaseous form into the atmosphere. Part of the release of N to the atmosphere is probably related to 'degassing' of the mantle of the earth which has a different isotopic N signature than most igneous rocks in the continental crust, and in sediments and the atmosphere and hydrosphere (Marty and Zimmerman 1999). Baur and Wlotzka (1972) estimated that volcanoes release approximately 105 tonnes of N per year, thus contributing only a very small portion to the atmospheric N_2 pool of 3.86 x 10^{15} tonnes of N.

Large amounts of N are also probably released or recycled at major geotectonic zones, at divergent plate margins, like mid-ocean ridges or rifts, or at convergent plate margins where altered oceanic volcanic crust and sediments are subducted under other plates. Hall (1989) speculated that when NH_4^+-enriched ocean floor basalts are subducted under continental or other oceanic plates they could return atmospheric N to the mantle or recycle the N to the atmosphere through subduction-related magmatism. How much of the hydrothermally incorporated ammonium is recycled and finally released into the atmosphere via volcanism or added to the mantle is not clear.

Sano *et al*. (2001) shed some light on the fluxes of N from the earth's mantle to the atmosphere, with focus on fluxes in mid-ocean ridge environments, hot spots and subduction zones. However, more nitrogen isotope studies are needed to determine the global N flux from the earth's interior and the cycling of N in the lithosphere, atmosphere, hydrosphere and biosphere.

There are a few silicate minerals that contain high NH_4^+-levels in their crystal structure. Buddingtonite, a rare NH_4^+-bearing silicate (Erd *et al.* 1964; Voncken *et al.* 1993), is an anhydrous NH_4^+-feldspar, and can contain up to 5% N. It is found in andesitic rocks that have been altered by ammonia-bearing hot springs, as well as in some oil shale deposits (Loughnan *et al.* 1983). Other NH_4^+ silicates associated with sedimentary exhalative ore deposits contain 0.2-0.25% (2,000 -2,500 mg kg-1) NH_4^+-N (Williams *et al.* 1987).

Highly soluble nitrate salts are the most concentrated forms of N in minerals, in this case in the form of nitrates. Nitrate salts are found at very few near-surface environments on earth. There rarity at the near surface is largely due to the fact that nitrate salts in contact with moving water are easily dissolved and washed away. However, small deposits of nitrate minerals are found in extremely arid, vegetation-free conditions and in cave deposits. The main minerals in cave deposits are soda-niter ($NaNO_3$) and niter, also called saltpeter (KNO_3) (Heaton 1987). Locally, these resources offer potentially valuable fertilizer resources but they are often used instead in the manufacture of local gunpowder.

The only economically viable nitrate deposits on earth are found in northern Chile.

Chilean Nitrate Deposits

The most significant deposit of nitrates found at or near the surface in extremely arid, vegetation-free conditions occurs in the Atacama Desert in Northern Chile. The nitrate ore consists of layers of ‘caliche’, a 1-3 m in thick crust in porous sediments found under 2-3m’s of overburden. The nitrate content of the caliche varies but average caliche ore contains 7-25% $NaNO_3$, 2-3% KNO_3, 4-10% NaCl and 10-30% $NaSO_4$, together with various mineral salts containing Mg, Ca, K, B and I (Ericksen 1981). The genesis of these deposits is discussed in detail by Ericksen (1981). Smaller accumulations of nitrates are also found in soils of the Death Valley, California (Ericksen *et al.* 1988), in northern Kenya (Owen and Renault 1988), and surprisingly, in the Antarctic desert (Claridge and Campbell 1968; Wada *et al.* 1981). Long periods of aridity are a key factor in the formation of nitrates as these forms of the mineral accumulate very slowly. Lack of vegetation is also important, since plants would consume the near-surface nitrates.

The Atacama nitrate accumulations are found in closed basins, in a belt about 30 km wide and 700 km long, between the western coastal range and the Andes (Figure 3.3). This area has an average annual rainfall of approximately 1 mm and a mean interval of 20 years between rainfalls. The cold Humboldt Current runs parallel to the South American coast with nutrient-rich upwelling zones. During the nights of the winter months (June to August) a dense fog or low cloud cover (‘camanchaca’) passes over the Coastal Range with the condensate of the fog clouds moistening the soil, in some cases down to a depth of 2mm (Ericksen 1981). Groundwater resources occur near the surface and are largely regarded as being recharged by faults and the Andes Mountains.

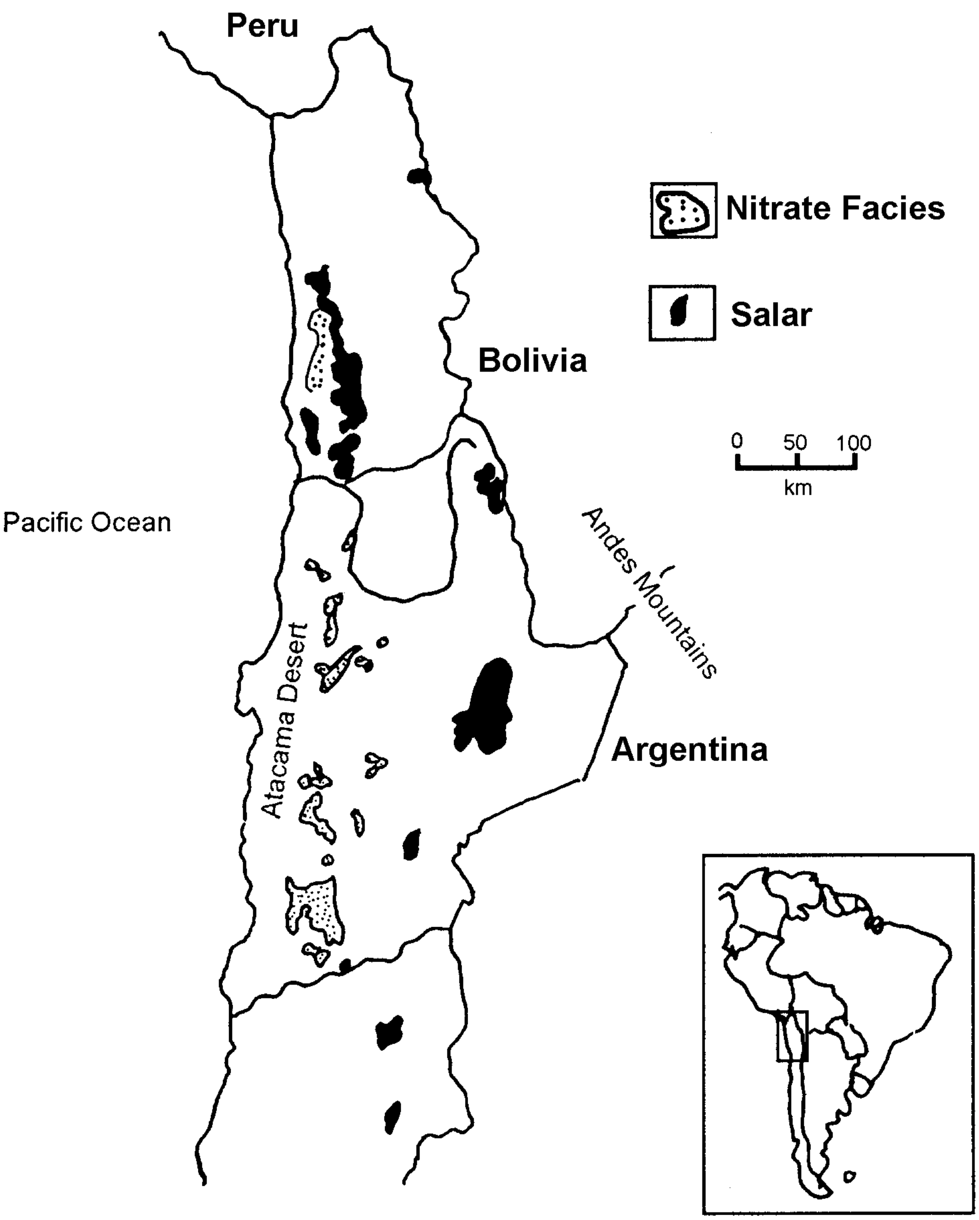


Figure 3.3. Nitrate deposits and salars (saline lake deposits) of the Atacama Desert, Northern Chile (adapted from Ericksen 1981).

This climate regime has existed since mid-Miocene times (since about 15 million years) and has promoted the gradual accumulation of nitrate salts as nitrate-rich soils and surface crusts (Ericksen 1981). These nitrate-rich soils and crusts occur over a variety of rock types and show no correlation with underlying rocks. For example, N-containing minerals are found on N-free rocks, implying an outside source for these deposits (Searl and Rankin 1993). In addition, nitrate accumulations are not only found in basins, but also on slopes of the large valleys and on topographic highs along the eastern side of the coastal range (Figure 3.4) (Ericksen 1981).

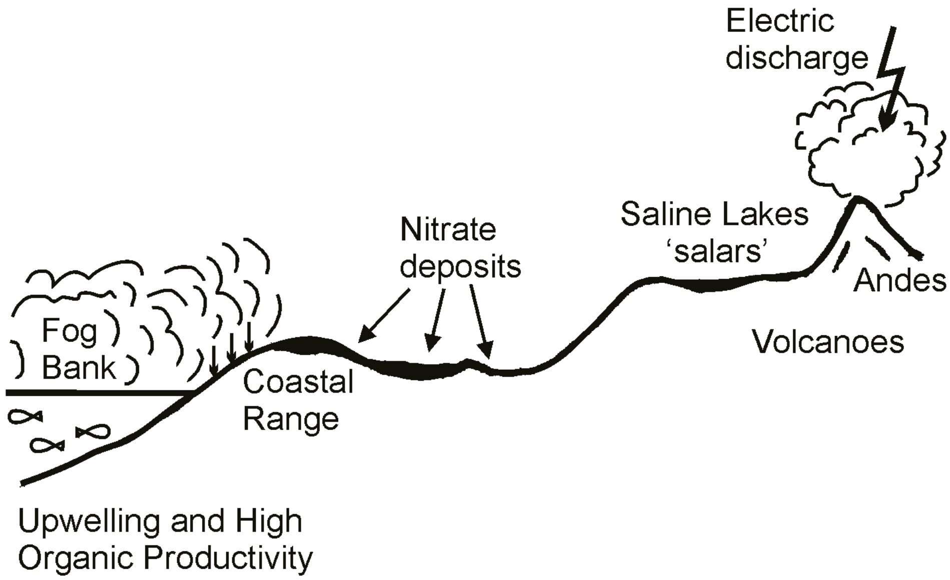


Figure 3.4. *Schematic cross-section of northern Chile and location of nitrate deposits.*

The chemistry of the Chilean nitrate deposits is unique. The main minerals are shown in Table 3.5. Not only are there high concentrations of nitrate, there are also high concentrations of iodate, high iodine to bromine (I/Br) ratios and the only known natural occurrence of perchlorates (ClO_4^-) (Ericksen 1981). While perchlorates were most likely formed in the atmosphere by photochemical reactions, the iodates might have originated from seawater of the nearby Humboldt Currrent. The high I/Br ratio is however still difficult to explain (Ericksen 1981).

The formation of large economic nitrate deposits in the Atacama Desert of Northern Chile is still poorly understood. For over more than 140 years various hypotheses on their genesis have been forwarded (Forbes 1861; Müntz 1887; de Kalb 1916; Singewald and Miller 1916; Wetzel 1932; Brüggen 1938; Mueller 1968; Claridge and Campbell 1968; Ericksen 1981; Garrett 1983; Searl and Rankin 1993; Böhlke *et al.* 1997). Older hypotheses are summarized in Ericksen (1981).

Possibly several factors play a role in the formation and accumulation of these nitrate deposits. Box 3.1 details some of the arguments for and against the proposed hypotheses. Likely mechanisms include biological N_2-fixation by micro-organisms, catalytic photo-chemical oxidation, or simply long-term accumulation of atmospheric deposition in the absence of biological activity or soil leaching. Smaller nitrate deposits have been found in other arid regions, such as Antarctica, the western USA and Northern Kenya, but the conditions in these environments vary dramatically from those in the Atacama Desert. The common factor shared by all these deposits is very low rainfall, high aridity.

Hypotheses for the formation of Chilean nitrate deposits

Decay of seaweed in cutoff bays

The seaweed decay hypothesis postulates that seaweed remnants from a former inland sea formed the nitrate deposits (Forbes 1861, Müntz 1887). If this were true, then the nitrate deposits would occur only in the valleys of the Atacama Desert. However, the nitrates also occur in higher altitudes as well as in the valleys. Also, the hypothesis does account for the presence of iodine in the nitrate deposit, and the iodine to bromine ratio (I/Br) in the deposits is inconclusive. Seawater and oceanic plants contain bromine, but the Chilean deposits contain only minute amounts (Ericksen 1981).

Leaching of guano on the margins of saline lakes (salars)

This hypothesis states that the nitrates are accumulations of bird guano, accumulated over millennia (Brüggen 1938). The guano would not leach because of the extremely dry climatic conditions, and the N from the guano would accumulate because of the lack of plants to absorb the nitrogen. Once again, there is the topographic argument against this theory. But more importantly, the Chilean Nitrate deposits do not contain any phosphate compounds, and guano commonly contains high phosphorus concentrations. The guano should also reflect the diet of the birds that produced it, and a marine diet would contain bromine. However, the Chilean nitrates contain only traces of bromine (Ericksen 1981).

Photochemical reactions in the atmosphere

Electrical discharges from thunderstorm activities that accompany volcanic activities are common in the high Andes. The Andes rise to heights of several thousand metres to the east of the Atacama Desert. It is theoretically possible that thunderstorm activities could provide a lightning-induced source of nitrates. However, the nitrate deposits occur on the eastern side of the central valley, far away from the Andes and the western Atacama Desert.

Catalytic photochemical oxidation of atmospheric N on TiO_2 and Fe_2O_3 surfaces

This hypothesis was brought forward by Garret in 1983. He suggested that some rock surfaces which contain Fe-Ti coatings could ‘fix’ N through photocatalytic processes. There are very limited data available on this photocatalytic process. However, experiments with Fe-Ti surfaces show that N can be fixed on these surfaces to the range of 2-25 kg NH_3 $year^{-1}$ ha^{-1} (Garret 1983).

Nitrogen from volcanic gases

De Kalb (1916) suggested that the accumulations of N compounds were of volcanic origin from the Andes volcanoes. Indeed, volcanic gases discharged from the volcanoes of the Andes contain low concentrations of N, but the areas with volcanic activity are simply not close enough to nitrate deposits. Furthermore, one would expect nitrate accumulations in salars near the Andes to contain elevated concentrations of nitrates, but no saline crusts or brines in these areas contain unusual concentrations of nitrates (Ericksen 1981).

Nitrogen from ocean spray and fog

The hypothesis of N complexes and saline materials being transported by sea spray from the Pacific Ocean was considered one of the most plausible explanations for the deposition of nitrates and salts (Ericksen 1981). The cold Humboldt Current passes along the west coast of South America, bringing with it nutrient-rich waters. However, the I/Br ratio is much lower in seawater than in the nitrate ores, which indicates that they do not have an oceanic origin (Böhlke *et al*. 1997).

Biological nitrogen fixation by cyano-bacteria and subsequent nitrification.

The capture of nitrogen from the atmosphere by cyano-bacteria (blue-green algae) has also been suggested as a possible source of N (Brüggen 1938; Ericksen *et al*. 1988). It was originally thought that micro-organisms would not be able to proliferate in such a harsh, and arid environment, but studies of the soils in playas (central parts of shallow desert plains) at nuclear bomb testing sites in Nevada’s desert, USA, have shown that cyano-bacteria can indeed exist in arid conditions if the substrate and pH conditions are favourable (Leatham *et al*. 1983). However, this hypothesis has been put in doubt by oxygen isotope investigations carried out by Böhlke *et al*. (1997).

Accumulations from atmospheric deposition in the absence of biological cycling

Precipitation and dry deposition of nitrogen compounds (reactive N-compounds of N and S in rain, fog, dew and dry deposition of particulates and other aerosols) in the absence of biological degradation and cycling was suggested by several authors, including Claridge and Campbell (1968), West (1978), Ericksen (1981), and Böhlke *et al*. (1997). Nitrogen and oxygen isotope investigations by Böhlke *et al*. (1997) indicate that atmospheric deposition is very similar to isotopic compositions of atmospherically derived N. Atmospheric deposition is a very probable source of N-compounds in the nitrate deposits of northern Chile.

Table 3.5. *Main minerals of the Chilean Atacama Desert nitrate deposit (after Ericksen 1981, Searl and Rankin 1993).*

Minerals	Mineral Forms
Chlorides	Halite (NaCl)
Nitrates	Soda-niter ($NaNO_3$) Niter (KNO_3)
Borates	Ulexite ($NaCaB_5O_9 \cdot 8H_2O$)
Sulphates	Thenardite Glauberite Kieserite Epsomite Gypsum, Anhydrite
Iodates and chromates	Lautarite, Lopezite

3.3.3 N-storing minerals

Although there are few geological N-resources worldwide, there are minerals that can store N and release it slowly. Zeolites have been used successfully for this purpose. Zeolites are naturally occurring alumino-silicate minerals with an open framework structure, a high internal surface area and a high cation exchange capacity (Mumpton 1984) (see Chapter 10).

3.4 Agricultural inputs of N

As soils are often deficient in this critical nutrient, N-sources have to be added to the soil to ensure steady supplies of N for the growing plants. A variety of methods to supply N to crops are commonly used including biological N-fixation, manure and other organic matter as well as industrially produced ammonium fertilizers. Less common methods to supply N to crops include nitrate-based fertilizers and the use of N-storing minerals.

3.4.1 Agricultural use of biological N fixation

The process of biological N_2 fixation (BNF) is described in section 3.1. This process is widely used to increase the N concentration of soils in both temperate and tropical climates. In parts of Africa, in Southeast Asia, Latin America and Australia, leguminous cover crops are widely used in farmers' fields and in plantations. Both, leguminous trees and leguminous cover crops recycle other nutrients such as P and K, control weeds, protect the soils from erosion, reduce leaching losses and increase the soil's water holding capacity (Brady and Weil 1999). However, the continuous cultivation of legumes may increase soil acidity over time (Williams 1980, Loss *et al*. 1993).

The efficiency of BNF has been increased by artificial infection of the roots of legumes with selected species of *Rhizobium*. To increase the BNF capacity of legumes through inoculation it is not only important to select the right *Rhizobium* strain for the host legume crop or pasture plant, it is also important to screen the most adapted strains for tolerance to environmental factors such as acidity. Soil acidity and Al toxicity can affect the production of many legumes and their N_2 fixation. In addition, the nutrient requirements of *Rhizobia* bacteria have to be considered, especially their need for sufficient amounts of Ca, P and the micronutrients Fe, Co and Mo. Ways to increase the infection rate of these bacteria in acid soil environments and to meet many of their nutrient requirements is to add inoculants to the seed and mix the inoculants with finely ground limestone or phosphate rock (Sanchez and Salinas 1981).

Nitrogen-fixing cyanobacteria can also be used to increase agricultural production, for example the blue green algae *Anabaena azollae*, which live in symbiotic association with the aquatic fern *Azolla piniata* (Watanabe *et al.* 1980) can be used to fix N in rice paddies. In parts of South Asia, for example China, blue green algae or the '*Azolla*' association is cultivated in tanks, dried, and sold to farmers who use it to inoculate their paddies. The *Azolla* or the blue green algae are dug into the soil as green manure where they become N sources for the following crop, usually rice. Under optimal conditions *Azolla* can fix as much as 465 kg N ha^{-1} in one year (Watanabe *et al.* 1980). Limiting factors of this century-old practice are mineral nutrition, especially P and some trace elements, as well as environmental factors such as temperature (optimal 25-30ºC), pH, water and pest infestations by insects, fungi and competing free-living algae (Watanabe *et al.* 1980; Lumpkin 1987).

3.4.2 Agricultural use of manure and other organic matter

Manure is one of the most important natural N-resources. Farmers throughout the world collect and use solid (and liquid) animal manures to improve soil fertility. The nutrient concentrations in manure varies considerably, from high quality manures such as chicken and dairy cattle manure that increase subsequent crop yields, to low quality manures that actually depress crop yields because of N-immobilization (Mugwira and Mukurumbira 1986). In general, N-concentrations in animal manures are below 5% N, in the case of cattle manure, usually only 1 -2% N.

Nitrogen in manure occurs in the solid portion and the liquid portion, the urine. In the solid portion the N is mainly concentrated in digested and decomposing organic matter. The liquid manure can potentially and effectively be used for fertigation (a combination of irrigation and fertilizer application). The under-use of this valuable resource is due to the relative difficulty of collecting, storing and distributing the liquid manure as compared to solid manure. Large amounts of N in the form of NH_3 gases (more than 50%) can be lost from manure piles and surface-applied cattle slurries due to volatilization and poor manure management (Lockyer *et al.* 1989; Sommer and Olesen 1991).

Techniques of green manuring, improved fallows and biomass transfer, have been successfully introduced into farming systems of some parts of sub-Saharan Africa and Latin America (Giller and Wilson 1991; Buresh and Niang 1997; Boddey *et al*. 1997; Sanchez 1999; Buckles and Triomphe 1999; Kwesiga *et al*. 1999); Pali *et al*. 2004). Green manuring and biomass transfer from fast mineralizing N-rich plants, leguminous or non-leguminous, can provide N to soils. For example, the non-leguminous 'Mexican sunflower' *Tithonia diversifolia* (N=3.6-4.2%, P=0.27 -0.35%, and K=4.0-4.3%), which is found in many tropical and subtropical environments, can provide substantial amounts of N along with P and K when applied as green manure (Palm *et al*. 1997). However, the composition and nutrient release patterns of the added organic matter are crucial, if the added organic matter is to be released in a way that meets the nutrient requirements of crops. Palm (1995) and Palm *et al*. (1997) outlined the critical values for net N-release from organic matter and the importance of analyzing the lignin and polyphenol concentrations that largely determine the N-release from organic matter.

Comparatively large amounts of organic matter (commonly in the tonne range) are needed to provide sufficient N to crops. This can confer further benefits to he soil. The addition of organic manures contributes to the organic matter stocks in soils, important for biological activities and the physical properties of soils.

Table 3.6. *Alternative N resources (from various sources).*

Commonly Used Organic Inputs	**% N**	**% P**	**% K**
Alfalfa Meal	5	1	1
Bat Guano (fresh)	10	3	1
Bat Guano (old)	2	8	0
Blood (dried)	13	0	0
Castor Pomace	6	1.5	0.5
Cattle Manure (dried)	2	2.3	2.4
Cotton Seed Meal	6.6	2.5	1.5
Crab Meal	4	3	0.5
Feather Meal	11	0	0
Fish Meal	5	3	3
Guano (Peruvian)	13	12.5	2.5
Peanut Meal	7.2	1.5	1.2
Poultry Manure (dried)	4	4	2
Soybean Meal	7	1.2	1.5

Table 3.7. *Composition of N fertilizers.*

Common Names (Formulas)	% N	% P	% K
Sodium Nitrate [$NaNO_3$]	16	0	0
Ammonium Sulphate [$(NH_4)_2SO_4$]	21	0	0
Ammonium Nitrate [NH_4NO_3]	34	0	0
Calcium Nitrate [$Ca(NO_3)_2$]	15	0	0
Calcium Ammonium Nitrate [$NH_4NO_3 + CaCO_3$]	21	0	0
Urea [$CO(NH_2)_2$]	45	0	0
Calcium Cyanamide [$CaCN_2$]	18-22	0	0
Ammonium Chloride [NH_4Cl]	24	0	0
Ammonium Sulphate - Nitrate [$(NH_4)_2SO_4 + NH_4NO_3$]	26	0	0
Anhydrous Ammonia [NH_3]	82	0	0

3.4.3 Nitrogen fertilizer products

Most commercial N fertilizers are linked to the production of ammonia from the Haber-Bosch process described in section 3.5.1. The main N-based commercial fertilizer products are listed in Table 3.7.

Anhydrous Ammonia (NH_3)

Anhydrous ammonia makes up more than 50% of the N-fertilizer applied to fields in the USA. Ammonia (NH_3) is a gas and must be pressurized and liquefied before use. It must also be applied 15 to 25 cm below the ground surface to avoid volatilization losses. One limitation of using anhydrous ammonia is the need for special safety precautions such as gloves and breathing apparatus because the gas is highly irritating.

Urea $CO(NH_2)_2$

Urea is produced through combining ammonia produced through the Haber-Bosch process with CO_2. The process has to be well adjusted in order to avoid production of the toxic material ‘biuret’ with the fertilizer. The simplified process of urea production is shown in equation 3.4.

Urea production

$$2NH_3 + CO_2 \rightarrow H_2N\text{-}C\text{-}NH_2 + H_2O \qquad \text{(equation 3.4)}$$

The advantages of urea are twofold; it has a high nitrogen concentrations (in its pure form urea contains 46.47% N) and the cost is relatively cheap. The price of granular urea fluctuates widely, ranging from about US$100 to $200 depending on various factors including the price of natural gas. In May 2005, the price of urea hit a high of US$ 276 per tonne (Fertilizer Works, Aug. 26th, 2005).

A disadvantage of urea is its potential to 'cake', or glue together in storage. As a countermeasure to caking, the urea pellets are often coated with diatomaceous earth or special clay minerals. Urea also has a high rate of volatilization in certain soils and may be toxic to plants if placed too close to seeds and roots. Moreover, urea has an acidifying effect on soils. In areas where soils have low buffering capacity, liming must be carried out in conjunction with urea application. Approximately 2 kg of $CaCO_3$ (limestone) must be added for each kilogram of urea to avoid the acidification of soils.

Considerable efforts have been made by the N-fertilizer producers to develop products that increase the fertilizer use efficiency of urea by releasing the N at concentrations and rates that match the plants' needs and that reduce the rate of nitrification and losses to the environment. Among these so-called 'slow release' N-fertilizers are sulphur coated urea pellets and polymer coated N-fertilizers that are used for specialty crops, mainly in horticulture and floriculture and for high value crops (Oertli 1980). However, these 'slow release' and 'controlled release' N-fertilizers are considerably more expensive than common N-fertilizers.

Ammonium sulphate ($(NH_4)_2SO_4$)

Ammonium sulphate $(NH_4)_2SO_4$ is another ammonium-based N-fertilizers which is produced through reacting sulphuric acid with ammonia. The resulting slurry is sprayed onto a seed bed of small granular particles to form product size granules. The simplified process is shown in equation 3.5.

Ammonium sulphate production

$$2NH_4 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \qquad \text{(equation 3.5)}$$

Ammonium sulphate, $(NH_4)_2SO_4$ contains 21% N and 24% sulphur (S). The advantage of using ammonium sulphate as N fertilizer is that it is a good source of both N and S, and therefore it may be useful for crops that have both high N and high S requirements. The disadvantages are that it has a low N-concentration, and that it is highly acidifying. About 5 kg of $CaCO_3$ are required per kilogram of $(NH_4)_2SO_4$ to offset the acidifying effect in the soil. Although the price is lower (US$38 to US$45 per tonne in 2003) than other N fertilizers, ammonium sulphate is not a popular fertilizer in most countries.

Ammonium nitrate NH_4NO_3

Ammonium-nitrate is a product from the reaction of NH_3 with nitric acid. To increase the handling properties of ammonium nitrate fertilizers, they are often 'prilled'. Prilling is the process whereby the material is condensed into small beads during the fall and solidification in the prilling tower. Agricultural grade ammonium nitrate is often mixed with calcium carbonate to produce calcium ammonium nitrate (CAN), which has an N content of 20.5% and a much lower volatility. The price of ammonium nitrate in 2003 fluctuated around US$ 100 per tonne.

The N-fertilizer ammonium-nitrate (NH_4NO_3), consists of the cation NH_4^+ and the anion NO_3^-, and contains 35% N. To increase the handling properties of ammonium nitrate fertilizers, they are often condensed into small beads, 'prilled.' Ammonium nitrate is often coated with diatomaceous earth or the clay mineral attapulgite to prevent water from entering. This is required because NH_4NO_3 is highly hygroscopic.

A major problem with pure NH_4NO_3 is that it has a strong oxidizing tendency and a low ignition temperature (200°C). This makes it potentially explosive, and dangerous to handle and store in an agricultural setting. Ammonium-nitrate mixed with diesel fuel is the favoured explosive for most mining operations, but it has also been used by criminals for other ends, for example during the Oklahoma bombings in 1995, and the Bali bombings in 2002. There are regulations and technical efforts under way to restrict the use of ammonium nitrate and to reduce the explosive nature of ammonium nitrate. Some ammonium nitrate is manufactured in such a way that it prevents the absorption of fuel oil through the addition of polymer coatings. Agricultural grade ammonium nitrate is often mixed with calcium carbonate to produce calcium ammonium nitrate (CAN), which has an N-content of 20.5% and a much lower volatility. The price of ammonium nitrate in 2003 fluctuated around US$ 100 per tonne.

3.4.4 Nitrate-based fertilizers

Many nitrate-based fertilizers are derived from the Chile nitrate deposits (predominantly as Na-nitrates and in the processed form, K-nitrates). In the Chilean nitrate deposits, the 'caliche' (the nitrate ore) is excavated in large-scale operations, crushed, and then leached in large open vats for about 80 hours. The leachate is then concentrated in a cooling circuit, and the nitrate 'melt' (at 325°C) is sprayed from a prilling tower, where during its fall it solidifies into spherical pellets (prills). The finished product contains 98.5% $NaNO_3$.

The current market for nitrates from Chile is mainly in the speciality crops and tobacco industry. The export markets for Chilean nitrates include vegetable (40%), tobacco (30%), fruit crops (15%), flowers (10%) and others (5%). An important market for Cl-free K-nitrates is the tobacco industry, where even moderate chloride concentrations can result in inferior leaf quality and smoking characteristics. The application of natural nitrates for vegetable crops and fruit crops increases early maturity, increased storage life and fruit firmness.

3.4.5 N-storing minerals

Zeolites have high affinities for NH_4^+ (ionic radius 1.61 Å) and K^+ ions (ionic radius 1.46 Å), which make them very good as plant growth materials especially as potting 'soils' (Hershey *et al.* 1980). Zeolites as N-storing mineral matter and as odour reducing minerals have been used in various animal confinements. When zeolites are mixed with fresh manure, they adsorb some NH_4^+ and when incorporated into soils, release it slowly into the soil. Natural zeolites can only store < 5% N, and so are only valuable as a soil amendment and manure improvement material if their source is very close to the site of application. Nitrogen treated zeolites (treatment of zeolites in molten N-salts at elevated temperatures) have good potentials as slowly releasing NH_4^+–fertilizers (Park and Komarneni 1998). Other potential NH_4^+-storing minerals are vermiculites and smectites, which have high cation exchange capacities (> 100 cmol (+) kg-1).

Baur and Wlotzka (1972), Itihara and Suwa (1985), Boyd and Phillippot (1998), Boyd (2001), Papineau *et al.* (2005) report of naturally NH_4^+–rich micas, especially biotite where K^+ has been replaced by NH_4^+, in metasediments of various ages. Reported values range from 150 to 1600 mg NH_4^+ kg^{-1}) (Boyd 2001) with isotopic signatures that indicate biological precursors.

3.5 Industrial N-fixation

3.5.1 Haber-Bosch process

The principal process of industrial nitrogen fixation, the so-called Haber-Bosch process was invented and developed by the German chemists and engineers Fritz Haber and Carl Bosch in the first decades of the 20th century and is still the principal process for N-fertilizer manufacture. In the Haber-Bosch process, atmospheric N_2 is industrially 'fixed' from the air and combined with hydrogen to produce ammonia, according to the very simplified equation (equation 3.6).

Simplified Haber-Bosch process

$N_2 + 3H_2 \rightarrow 2NH_3$ (equation 3.6)

Smil (1999) called the discovery and development of this process the most important invention of the 20th century. At present, 97-99% of all N-fertilizers used in agriculture are produced by this process. Nitrogen fertilizer products that are created by use of this process include anhydrous ammonia and downstream products like urea, ammonium nitrate, ammonium sulphate, and other N-fertilizers, as well as NP-fertilizers like mono-ammonium and di-ammonium phosphates.

The main manufacturing option for N_2 is the 'steam reforming process' (equation 3.7), combining CH_4 (methane) from natural gas with steam, as well as oxygen and nitrogen gas (in approximately the same concentrations as are found in air).

Steam reforming process

$7CH_4+10H_2O + 8N_2 + 2O_2 \rightarrow 16NH_3 + 7CO_2$ (equation 3.7)

Nitrogen for this large-scale industrial process is derived directly from the air and the hydrogen is supplied by means of fossil fuels (hydrocarbons), or through the electrolysis of water. Most of the methane used in this process is from natural gas. Because of the amount of hydrocarbons involved, it is closely associated with the production of oil and gas. Details of this process are shown in Figure 3.5.

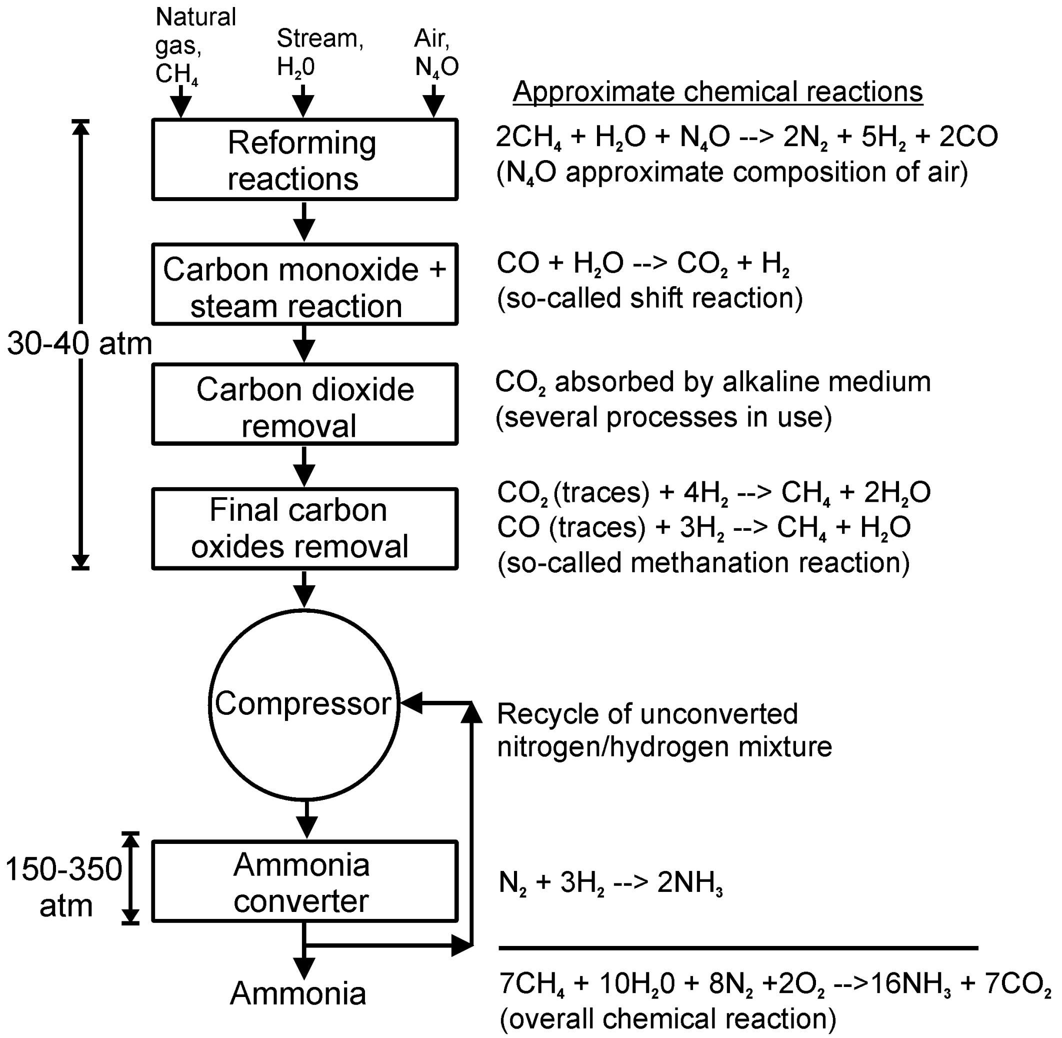


Figure 3.5. *Flow chart of the Haber-Bosch process of ammonia synthesis (steam reforming of natural gas) (International Fertilizer Development Research Center 1979).*

In the first part of the twentieth century nitrogen fertilizers were mainly produced in North America, Western Europe and Japan. In the 1970's, the construction of N-fertilizer plants shifted to large N-fertilizer consuming countries like China and India, and natural gas-rich countries, specifically countries of the Caribbean and the Middle East. In 2002, developing countries accounted for over 50% of the world's total ammonia production, approximately 107 million tonnes (US Geological Survey, 2003).

Nitrogen resources are extremely extensive as the gas N_2 forms more than $^3/_4$ of the atmosphere. However, the industrial production of N-based fertilizers requires other finite non-renewable resources, in particular natural gas. Approximately 4% of the total natural gas consumption in North America and Europe is used to produce ammonia. Natural gas and other hydrocarbon resources are not distributed evenly over the surface of the earth. They are concentrated in specific regions of the world, mainly in the Middle East, regions of the former Soviet Union, North Africa (Figure 3.6).

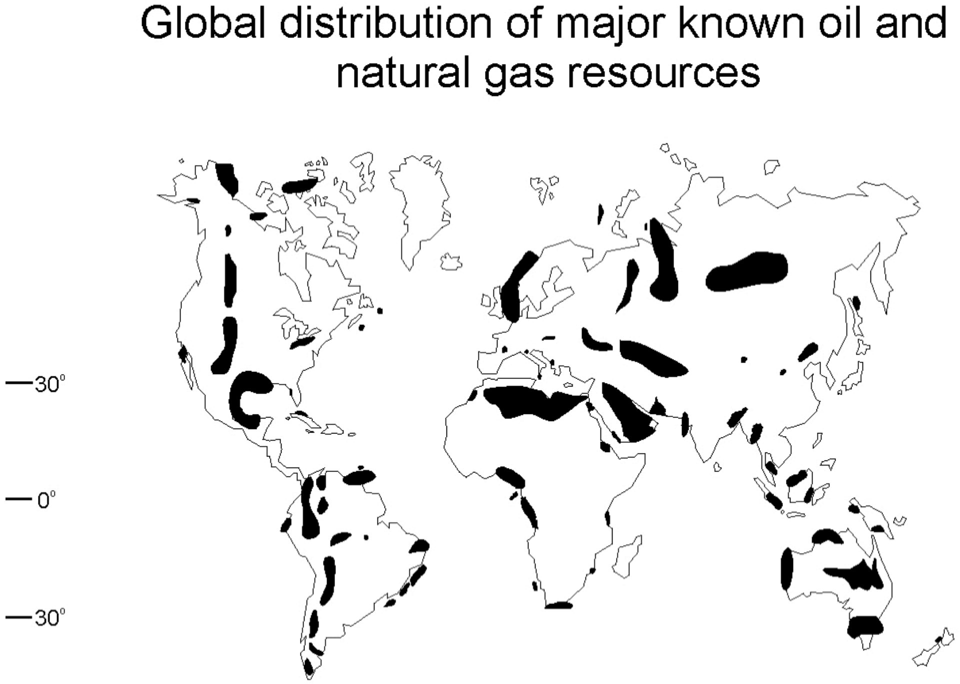


Figure 3.6. Generalized map of the global distribution of oil and natural gas resources.

Natural gas is a critical feedstock for the production of N-fertilizers, accounting for 70-90% of the cash production costs. There is thus a strong linkage between prices for natural gas and N-fertilizers (see Figure 3.8).

Another potential resource that can be used as feedstock for the synthesis of ammonia is coal bed methane. It is expected that coal bed methane, which is found in many major coal basins of the world, will become a significant supply source of methane in the near future. It is estimated that more than 146 Trillion cubic feet (Tcf) of methane can be recovered from coal beds in the United States alone (American Gas Association 2004).

Still another potential source for the production of synthetic N-fertilizers is methane from gas hydrates, located in ocean sediments and on land in sediments underlying the Arctic permafrost zone. It is estimated that these deposits constitute the largest source of methane on earth, with more than 850 million trillion litres of gas, several thousand times the conventional natural gas resources. However, major challenges lie ahead to characterize these resources in terms of volume and practical extractability. As methane is a greenhouse gas, considerable environmental and engineering hurdles need to be overcome in order to extract the gas hydrate methane in environmentally safe ways.

Small-scale fertilizer generator

A little known, small-scale method to produce N-fertilizers was developed in the 1970s by scientists and engineers from the Batelle-Kettering Research Laboratory in Columbus, Ohio, USA (Treharne *et al.* 1979; Sheldon and Treharne 1978). The fertilizer generator produced at the Batelle-Kettering Research Laboratory uses modified technologies that were used and developed between 1902 and 1904, adapted for small scale farm use. The process is based on the high temperature oxidation of N to NO_2 in an electric arc reacted with water to produce weak nitric acid, which in turn is reacted with limestone to produce Ca-nitrate (Figure 3.7).

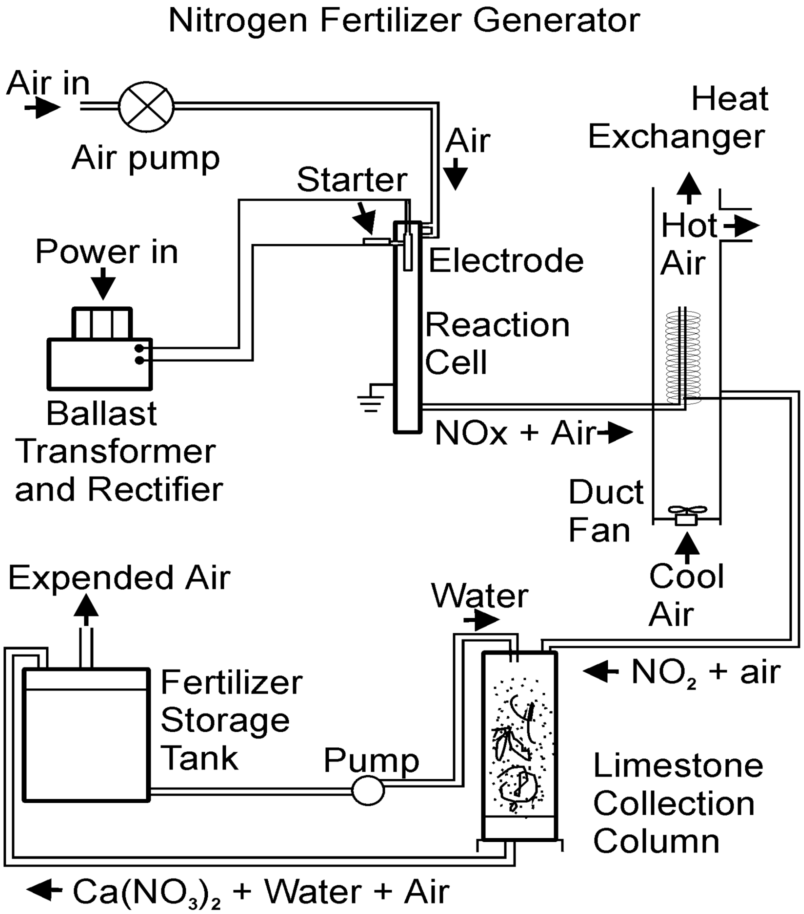


Figure 3.7. Flow diagram of the electric arc system developed to produce Ca-nitrate fertilizers on a farm sized scale (after Treharne et al. 1979).

The first on-farm, appropriate-technology N-fertilizer unit using the modified electric arc system was developed in Columbus, Ohio (Treharne *et al*. 1979) and tested during 1979 and 1980 on its operational performance and economic viability at the University of Nebraska (Rein *et al*. 1980). The preliminary tests showed that it would take 60,000 kWh to produce one tonne of N, much higher than energy required for commercial N-fertilizer production. Rein *et al*. (1980) demonstrated that unless the waste heat could be utilized (for example for space heating), this technology would not be economic under current US conditions. They mention however that with further refinement this N-generator could be used in remote locations where commercial fertilizers are often not available. Further tests using solar, wind and hydro-electric energy have been undertaken with modified appropriate technology type of N-generators using renewable energy resources in India, Nepal and in the USA (Slakter 1985).

Global reserves of natural gas

The world's natural gas reserves were estimated at 5,504.91 trillion cubic feet at the end of 2002 (Oil and Gas Journal 2002, quoted in Energy Information Administration of the US Dept. of Energy 2002). About 71 percent of these non-renewable natural gas reserves are located in the Middle East and countries of the former Soviet Union. Proven reserves are those that could be economically produced with the current technology. The former Middle East accounts for 40% of the world's natural gas reserves followed by the Russian Federation (27% of the world's total). Together they account for 67% of world natural gas reserves (United Nations Conference on Trade and Development 2004).

The principal natural gas reserves of the world, according to ranking by country (MacGregor 1998) occur in:

1. Russia
2. Iran
3. Oman
4. United Arab Emirates
5. USA
6. Venezuela
7. Algeria
8. Nigeria
9. Iraq
10. Indonesia
11. Lybia
12. Egypt

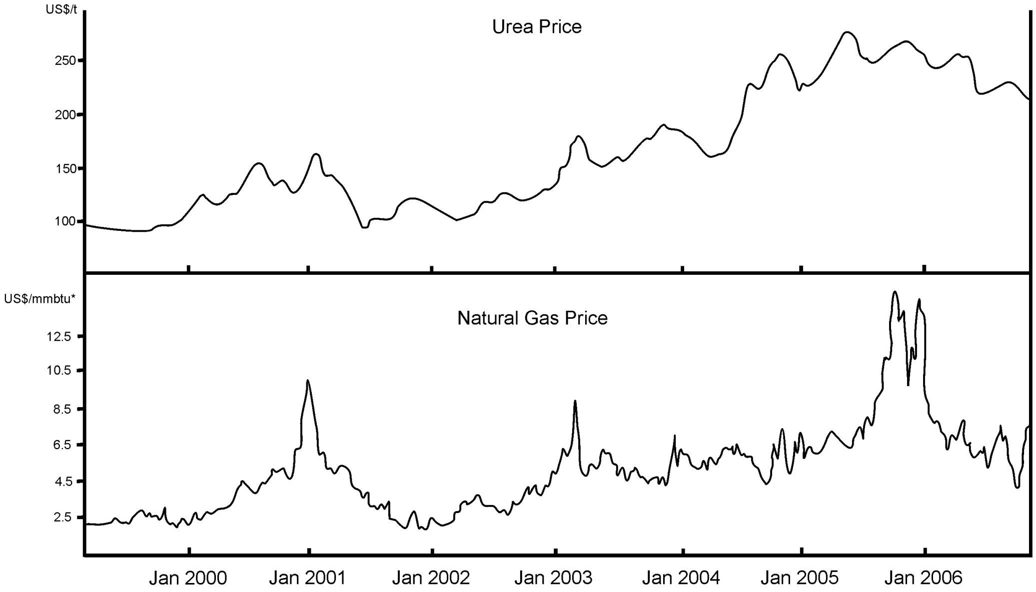
Global reserves of natural gas have more than doubled in the last twenty years. And yet, the world's ratio of proven natural gas reserves to production at current levels is between 60 and 70 years, meaning the time that remaining reserves would last if the present levels of production were to be maintained (United Nations Conference on Trade and Development 2004).

3.6 Environmental and Health Concerns

There are two main sets of concerns related to N fertilizers: those related to production, transport and storage of N-fertilizers, and those related to the actual application of the N fertilizers to soils.

Water and Energy use of N-fertilizer production

Fertilizer production requires approximately 1.2% of the world's fossil fuel consumption (Kongshaug 1998). Most of the energy required is for the production of ammonia. While the production of one tonne of K- fertilizer requires 7.1 GJ of energy, and the energy required to produce one tonne of P-fertilizer is 4.4-7.3 GJ, the energy consumed per tonne of N-fertilizer is 44.5-54 GJ (Kongshaug 1998). In general, industrial production of fertilizers and specifically N-fertilizers consumes large amounts of the world's non-renewable natural resources.



*mmbtu= 10 000 million British Thermal Units

Figure: 3.8. *Fluctuations of the price of urea in North America as function of price of natural gas. Source www.fertilizerworks.com/html/market/BasketPrice.pdf*

In North America, the price of N-based fertilizers, such as urea, has been greatly influenced by the price of natural gas. North American natural gas prices almost doubled between mid-2002 and mid-2003 (from US$ 3.65/mbtu to more than US$ 6/mbtu) and above US$ 10 in 2005. This sharp increase in natural gas prices resulted in a steep rise in N-fertilizer prices (Figure 3.8). The price of Ammonia (US Gulf) rose from US$ 140 to US$ 250 per tonne, and urea rose from US$ 120 to $US 270 , between 2002 and 2005. The increase in N fertilizer prices failed to cover the increased costs of at least one company in the United States, Mississippi Chemical, forcing it to file for bankruptcy protection in May 2003 (Harben 2003). When in 2003 and 2004 and parts of 2005 the price of natural gas spiked, the price of urea spiked almost simultaneously.

The production of N-fertilizers is not only very energy-intensive it also requires large amounts of water. To produce one tonne of NH_3, it requires between 70,000 and 650,000 litres of water. To help put this in perspective; a fertilizer facility that produces 600 tonnes of NH_3 per day could use water at a rate of 270,000 litres per minute. Fortunately, most of this water can be recycled, resulting in the consumption of only 500-5,000 litres of water per tonne of the final product.

Atmospheric losses and leaching

Concerns associated with the application of N-fertilizers are related to losses of NH_3, N_2O and NO_x to the atmosphere and to leaching into surface and ground water. Losses of N-fertilizers are not only incurred during application, but also during production, transport and storage. A concern is also the safe storage of highly concentrated and potentially explosive N-fertilizer materials.

The application of N-fertilizers to soils and crops has been studied for many years to improve on the uptake of N to plants and to enhance the relative low N-fertilizer use efficiency (commonly approximately 50% in the year of application) (Baligar *et al*. 2001). In many industrialized countries with intensive agriculture, considerable amounts of N, both from manure sources and from N-fertilizers, are lost to surface water and groundwater, as well as to the air through volatilization.

Bouwman *et al*. (1997) estimated that ammonia emissions on a global scale reach 41 million tonnes per year (Table 3.8). During and after application of N fertilizers there may be substantial losses of the greenhouse gases NH_3, N_2O and NO_x to the atmosphere. The NO_3^- that is leached from the soil can enter surface waters, leading to eutrophication, or it can enter groundwater and affect drinking water supplies. There is also the problem of soil acidification when using ammonium-based fertilizers.

Considerable research is thus directed to slow down the release of N from fertilizers and synchronize with the needs and uptake by crops. ‘Slow release’ and ‘controlled release’ N-fertilizers have been manufactured to optimize N release to plants, and to reduce losses to the environment.

Table 3.8. *Worldwide ammonia emissions (Bouwman et al. 1997)*

Anthropogenic source	Ammonia (million t N year^{-1})
Domestic animals and their manure	22
Fertilizer (urea and others)	9
Vegetation burning	6

Ammonia volatilization

Ammonia volatilization is dependent on the pH of the soil. Alkaline soils have an excess of OH^- ions over H^+ ions and this tends to drive the reaction (above) to the left and cause production and release of the gaseous NH_3. In dry soils there is less water and again the reaction is driven to the left with the same result. Ammonium volatilization is thus also a function of moisture content of the soils.

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad \text{(equation 3.8)}$$

Acidification

The application of ammonium sulphate to soils with low buffering capacities can lead to an increase in H^+ production and hence acidity (Figure 3.9). The application of liming materials is needed to correct the acidification.

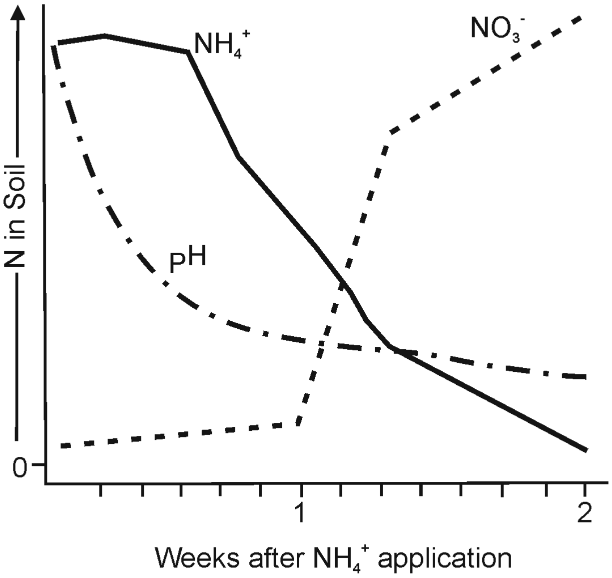


Figure 3.9. *Relative abundances of nitrogen compounds in the soil after application of NH_4^-. Note the decrease in pH (acidification) upon application of NH_4^+ (Mengel and Kirkby 2001, modified from Duisberg and Buehrer 1954).*

Nitrification

Ultimately, nitrification of ammonium fertilizers results in the production of nitrate and acidification. If the release of nitrate does not coincide with uptake by the crop then there may be substantial losses of nitrates to surface and groundwater because nitrate is very mobile in soils. The losses of N (and P) to surface waters is responsible for nutrient enrichment in lake and river waters, which can stimulate the rapid growth of organisms (e.g. algae) and causes subsequent deficiencies of oxygen needed for fish and other aquatic species.

This process, called eutrophication, upsets the natural nutrient balance in the water body and can lead to the death of fish and other aquatic species.

Eutrophication is mainly found in regions where fertilizers are used in excess of plant needs and with poor soil management. In large parts of sub-Saharan Africa this is not a problem, as fertilizer applications are very low. Biological N fixing processes associated with the continuous cultivation legume pastures can also lead to soil acidification as observed in Australia (Williams 1980; Loss *et al.* 1993).

Human health concerns

Imprudent use or overuse of N-fertilizers and high rates of manure application can negatively impact human health. Most foods (and drinking water), naturally contain nitrates (Table 3.9). However, these concentrations can easily be elevated beyond a safe point through unsound agricultural practices.

Table 3.9. *Nitrate concentrations of various foods and drinks (from various sources).*

Food or Drink	**Nitrate concentration (in mg kg^{-1})**
Meat	100
Milk	30
Cheese	45
Vegetables	200
Potatoes	60

Although much concern related to nitrates is focused on its concentration in drinking water in developed countries, most nitrates and nitrites come from food. The problem of nitrates in food is especially noticeable in leafy vegetables and some of the leafy greens grown hydroponically in greenhouses. Other foods with elevated nitrate concentrations are related to food preservatives (e.g. in hotdogs).

The behaviour of nitrates in the human body is complex. Approximately 82% of ingested nitrate is excreted in urine and the remainder is exhaled or converted to nitrite. Bacterial reduction of nitrate to nitrite can take place in the mouth or in the stomach and approximately 6% of nitrate is converted to nitrite within 24 hours (Tannenbaum 1979). Studies in China suggest that long-term ingestion of nitrate-contaminated water may increase the rates of gastric cancer through the formation of nitrosamines (Xu *et al.* 1992). In contrast, recent reports have found no compelling evidence that nitrate ingestion is a likely factor for gastric cancer (Forman *et al.* 1995; Addiscot and Benjamin 2000).

Nitrites, which are produced through reduction of nitrates, are able to oxidize the haemoglobin (Fe_2^+) in blood to methaemoglobin (Fe_3^+). Methaemoglobin, unlike haemoglobin, is inefficient in binding O_2 disabling the delivery of oxygen to the body. If more than 5% of the haemoglobin is converted to methaemoglobin (Fe_3^+), the first symptoms of the ‘blue baby syndrome (cyanosis = blue skin colour) appear. Concentrations of greater than 50% are generally fatal.

The acceptable daily intake (ADI) of nitrate is 3.65 mg per kilogram of body weight and the ADI for nitrite is 0.4 mg kg^{-1}. For a person weighing 60 kg, this means 219 mg of nitrate and 8 mg of nitrite is the maximum daily allowance (European Commission 1998).

As with most toxicities, infants are the most vulnerable, and concerns have been raised to the potential occurrence of the ‘blue baby syndrome’. About 2,000 cases of blue baby syndrome have been reported worldwide, mostly in the period 1950 -1970 (WHO 1985). In general, however, the incidence of nitrate-nitrite induced infant methaemoglobinemia is very rare and mainly restricted to babies who ingest baby formula prepared with contaminated water. Water with elevated concentrations of nitrate originates predominantly from unsafe private water supplies (Knobeloch *et al*. 2000).

Recent research and reviews of historical cases discuss the complexities of causes of infantile methaemoglobinemia (Avery 1999). Epidemiological studies on the role of nitrate exposure through drinking water as a risk factor for specific cancers and chronic health outcomes are detailed in Ward *et al*. (2005).

Oxygen

Oxygen occurs in various forms in the atmosphere, hydrosphere, lithosphere, biosphere and pedosphere. In the atmosphere it occurs mainly in the form of a gas (making up 20.99% of the atmosphere by volume). In the hydrosphere, it occurs mainly in the form of water. In the biosphere, oxygen is a major component of organic matter. In the lithosphere it is found primarily in the form of oxides and silicates, carbonates, sulphates, and other substances. Oxygen is the most abundant element in the earth’s crust, making up approximately 46.6 percent of its mass. In the pedosphere, oxygen occurs in different forms. Approximately one half of the total volume of soil on the earth is made up of rock fragments and minerals, most of which are clay size to sand size silicates or carbonates, which usually contain sizeable amounts of oxygen. The other half of the soil volume is made up of air (25%), and water (25%), both containing oxygen. A small portion of soils, commonly 1-5% is made up of organic matter, which also contains oxygen. As such, oxygen is one of the most common and most important elements in every sphere.

In the atmosphere, oxygen has not always been a major component. About 4 billion years ago, when the earth started to cool and the first consolidated rock masses formed, the atmosphere was probably dominated by volcanic gases: carbon dioxide (CO_2), methane (CH_4) and ammonia (NH_3). Geoscientists estimate that the oxygen concentration at that time was about 0.000000001%. During the early Proterozoic, some 2.5 billion years ago, the atmosphere became gradually more oxygen-rich (0.01-1%). The first iron oxides, cherts, and SiO_2-rich sediments precipitated out in oceans at this time.

Oxygen continued

About 1.8 billion years ago a proliferation of blue-green algae (*Cyanophyceae*, *Cyanobacteria*) produced a sharp increase in the percent of oxygen in the atmosphere through photosynthesis, converting gases like CO_2 to oxygen. This newly created oxygen-rich atmosphere enabled a great diversification of living organisms. From about 570 million years onwards, oxygen content of the atmosphere increased even more to reach present day levels of 20.99%.

Living organisms evolved and took advantage of this change in the atmosphere. Plants and animals, including many microorganisms need oxygen for growth, and uptake of other nutrients. Root growth as well as water and nutrient uptake are severely reduced and finally stop when the roots are not supplied with oxygen gas. Oxygen is needed for the process of aerobic respiration, the process of oxidizing sugars to yield energy for growth, reproduction and other metabolic functions. It is the process in which the chemical bonds of energy-rich molecules are converted into energy usable for plant growth. In the process of oxidation of glucose large amounts of energy are released along with CO_2 and water, according to equation 3.9.

$$C_6H_{12}O_6 \text{ (glucose)} + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy } (2830 \text{ kJ mol}^{-1}) \qquad \text{(equation 3.9)}$$

Plants take up oxygen through small openings in plant leaves, the stomata, and in larger amounts through roots. Most plant roots get their oxygen from the soil through the process of diffusion although some plants that grow in water, for example rice, have special mechanisms that move oxygen from the water's surface to their roots. The rate at which air and thus oxygen moves to the roots in soils depends on the size and distribution of soil pores. Large pores provide better access to oxygen than fine pores. Oxygen diffuses through the air much faster than through water. Consequently, when pores in the soil are filled with water, the movement of oxygen is extremely slow. Clay soils have low oxygen diffusion rates and are thus more susceptible to low respiration. Furthermore, when soils are too wet, respiration is reduced, leading to reduced plant growth. Prolonged lack of oxygen results in blackening of root tips and necrosis of older leaves. Maintaining good soil structure is thus important for aeration and plant growth. The aeration status of soils can be a controlling factor for crop selection. Several deep-rooted plants and legumes, e.g. alfalfa and fruit trees require deep, well-aerated soils, while shallow-rooted plants like grasses can do well on shallow, poorly aerated soils.

Oxygen is also required for oxidation processes, for example the oxidation of nitrogen in the form of ammonium to nitrate and sulphur and H_2S to sulphate (SO_4^{2-}). Both sulphates and nitrates are more readily available to plants than the reduced forms. Also, the oxidized forms of elements like Fe and Mn are more easily utilized by plants than the reduced forms. In moist, acid-soils the reduced forms of Fe and Mn can become toxic to plant growth.

Carbon

Carbon occurs in all five major natural reservoirs: the atmosphere, the hydrosphere, the biosphere, the lithosphere and the pedosphere. In the biosphere and the lithosphere, C is cycled as biological and residual organic matter as well as a gas, predominantly CO_2. Carbon dioxide, the most abundant source of C in air and water, is essential for the process of photosynthesis (Equation 3.10), in which light energy converts CO_2 and water into organic compounds, then into sugars (Figure 3.10). Green plants use sugars produced via photosynthesis as structural and energy sources to build stems, roots, leaves and seeds.

$$6CO_2 + 6H_2O \xrightarrow{\text{solar energy + enzyme}} C_6H_{12}O_6 + 6O_2 \qquad \text{(equation 3.10)}$$

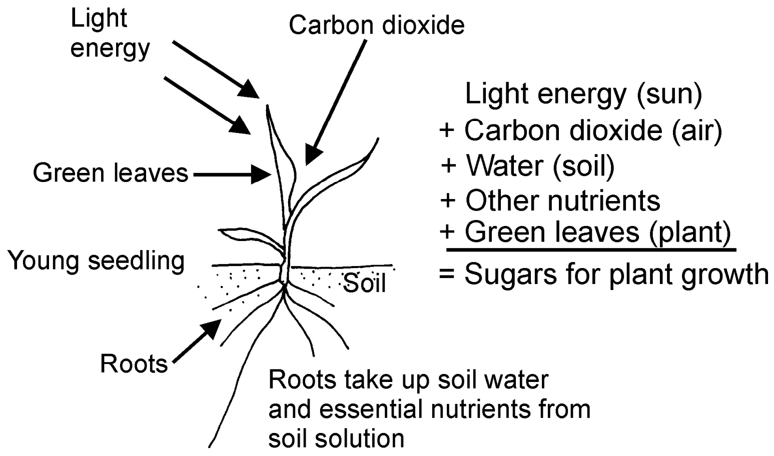


***Figure 3.10**. Generalized inputs for plant growth, including carbon dioxide (CO_2).*

Carbon is not only cycled through the organic phases in living and dead plants and animals, carbon is also involved in geochemical cycling involving processes in the hydrosphere, pedosphere, lithosphere and atmosphere. In geological processes, C is released as CO_2 from volcanoes and released through weathering processes of rocks. C is also captured and immobilized into mineral phases, for example in carbonate minerals. Carbon is fixed in large amounts into limestones and dolostones, made up largely of $CaCO_3$ and $CaMg(CO_3)_2$, as well as in peat bogs and carbon-rich environments that finally turn into coal, graphite and hydrocarbon reservoirs of oil and gas.

In pre-industrial times an equilibrium condition existed in the cycling of C between the C reservoirs. In the last hundred years however, this equilibrium has been altered through human activities. The lithological reservoir of C has been continuously reduced by the burning of fossil fuels such as oil and gas, and the calcining of carbonates for the production of cement.

Carbon continued

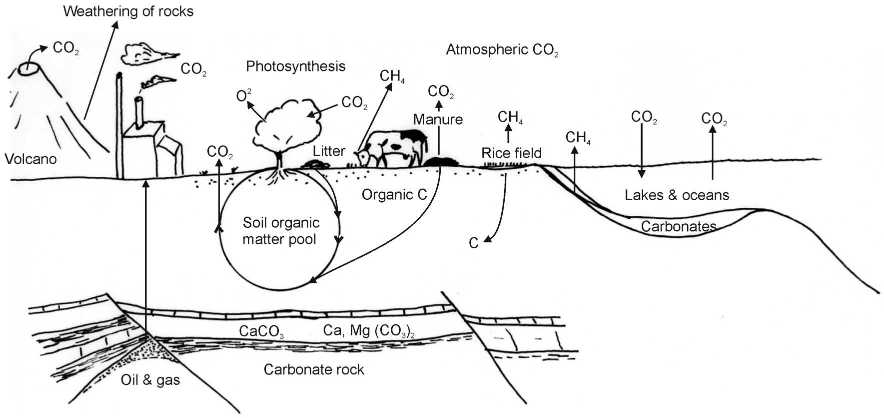


__Figure 3.11.__ Illustration of the carbon cycle.

The biosphere reservoir of C has also been increasingly converted into the greenhouse gas CO_2 through increased transformation of forests to agricultural land and through the burning of living C sources such as biomass of forests (e.g. deforestation of tropical forests) and through the annual burning of grasses in the savannas. These conversions result in an increase in CO_2 concentrations in the atmosphere. There is now a general consensus that increased levels of CO_2 (Figure 3.12) will lead to global warming and mitigation measures are needed to reduce greenhouse gases.

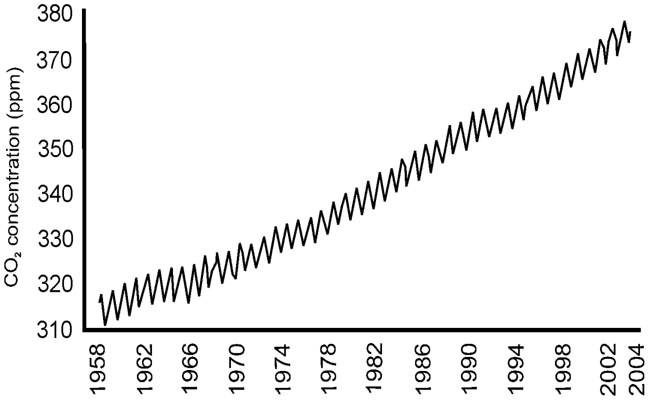


***Figure 3.12**. The steady rise of atmospheric CO_2 concentration (1958–2004), measured at Maona Loa Observatory, Hawaii.*

In recent years, the role of soils in global carbon cycling and its influence on greenhouse effects has been examined (Lal *et al.* 1995). Soils are not only sources of carbon but also carbon sinks and buffers. The amount of C held in soils is estimated at 1.5 x 10^{18}g of C, approximately twice as much as the carbon contained in the atmosphere and three times as much as in terrestrial vegetation (Post *et al.* 1990).

The historic and current loss of C from agricultural activities has been caused by agricultural expansion, conversion of forests to cultivated land (e.g. slash and burn), and loss of organic carbon due to burning or other poor organic matter management techniques such as increased soil aeration that enhances mineralization and physical SOM losses through erosion.

Soil organic matter (SOM) is largely made up of carbon-based complexes. Carbon is sequestered in soils when the rate of organic matter addition by vegetation or other organic matter exceeds the rate at which organic matter is lost from soils due to oxidation or physical loss through erosion. Efforts in recent years focus on the sequestration of carbon to soils, making them sinks of carbon rather than sources. Soil conservation techniques and management strategies such as minimum tillage, crop rotation, improved fallowing and advanced residue management, aim at economically viable and sustainable crop production as well as improved carbon sequestration. Experiences of various soil management practices and their potential for carbon sequestration in soils from diverse parts of the world are described in Lal *et al.* (1997).

Hydrogen

Hydrogen, the lightest of all known chemical elements, is the most abundant element in the solar system. In its elemental form it makes up 74% by mass of the sun. Prior to the consolidation of planet earth, the earth's atmosphere contained large quantities of hydrogen in the form of H_2, methane (CH_4), and ammonia (NH_3). Today, elemental hydrogen occurs in the terrestrial system only in relatively small amounts, mainly as a gas associated with volcanic eruptions. However, hydrogen occurs in the lithosphere in substantial quantities in the form of hydroxides and as part of water molecules in minerals and rocks.

Hydrogen occurs in the biosphere in a large variety of hydrogen compounds, including carbohydrates, proteins and fats. Water, a simple compound containing one large oxygen atom and two much smaller hydrogen atoms, is arguably the most important of these compounds. Water is absolutely crucial for plant growth and water-stress results in low plant growth or no growth at all. In growing plants, water is the most abundant substance. It makes up 75% or more of the plant's weight. Water is a critical component of photosynthesis. It is responsible for the turgor pressure in cells, vital for cell growth and maintaining cell shape. It is the medium in which most biochemical reactions take place. It is the principal transport medium of nutrients along with carbohydrates and other substances through the plant.

Hydrogen continued

Water is the key substance for vital functions and biochemical reactions in plants, for example for the opening and closing of stomata, small leaf cells that control transpiration and the crucial life process of photosynthesis.

For biochemical functions plants use only about 5% of the total water absorbed. Most of the water is released from the leaf stomata through transpiration. A plant has different water needs at different stages of growth. While the water requirements at the beginning of plant growth are relatively small, they are essential. At the vegetative and reproductive stage the plant needs more water. At the maturity stage the need for water is reduced.

The need for water differs with plant species. Some plants require large amounts of water for growth while others have developed mechanisms and structures that reduce water loss, for example of a cactus with leaves reduced to spines. Plants that require large amounts of water include rice and sugar cane and many other crops found in tropical environments.

Plants take up water mainly through their roots from soil. Nutrient uptake by the roots is through root interception, mass flow and diffusion (Barber 1995). Water is the key ‘transporting agent’ of nutrients to the roots.

Water conservation is largely related to soil management. Increased water infiltration, decreased evaporation of water from the soil surfaces and reduced runoff and erosion contribute to better water use efficiencies from soils. Principals and methods to enhance water use efficiencies of plants are described in Bacon (2004).

It is necessary not only for the plants themselves but also the micronutrients in soils. Water is also needed to ‘soften’ the soil for root penetration. Roots are the entry points of water from soils. Shallow-rooted plants require more frequent watering than deep-rooted plants. Water is extracted to a large extent from the upper quarter of the root zone and more slowly from lower portions of the soil. Water uptake by the roots is dependent on the availability and flow rate of water from the soil.

The availability of water from soil particles and pores is a function of soil texture and composition. Soils hold water in two ways, as a thin film around soil particles and as water contained in pores by capillary forces. Water is retained around soil particles by surface tension. When plant roots take up water for various biochemical and biophysical processes, the layer around the soil particles becomes thinner, the surface tension increases making it more difficult for the root to extract water. When roots cannot extract water from these layers and pores any more the plants start to wilt and if not watered die.

Chapter 4

Phosphorus

Figure 4.1. *(left) Maize/corn (Zea mays) with P-supplement showing increased growth compared to maize/corn without P-supplement (Photo: Anthony Njenga); (right) Sedimentary–biogenic phosphate beds at the Minjingu phosphate deposit, North Tanzania.*

Phosphorus (P) plays a central role in life processes, especially for energy storage and transfer. It is a crucial building block in ribonucleic acid (RNA) and deoxyribonucleic acid (DNA), in plants. Phosphorus is also essential for adequate root growth and the development of fruits and seeds and many biochemical processes (Table 4.1).

Phosphorus is naturally available only in very small quantities in soil solutions. Not surprisingly, the amount of P available to plants is often the predominant limiting factor for agricultural production in large parts of the world. In many tropical regions, low P-reserves in soils have been caused by long periods intensive leaching and weathering and low P status of the underlying rocks. In addition, P in the soil has been widely depleted through continuous removal of nutrients through agricultural practices such as residue removal, as well as harvesting. This human induced P-depletion through farming is one of the key biophysical causes of declining food security in many developing countries (Sanchez *et al*. 1997). In order to replenish the removed P, farmers are forced to use P fertilizers or manures or other P- bearing materials.

Table 4.1. *Phosphorus as a nutrient, its forms in plants and in common minerals.*

Nutrient	P in plants	Uptake form	Common mineral forms
Phosphorus (P)	Needed for energy metabolism, constituent of RNA and DNA, phospholipids. Essential for cell division and protein, root, seed and fruit development.	HPO_4^{2-}, $H_2PO_4^-$	Minerals of the apatite group (primary Ca-phosphate mineral) Ca-Al-Fe phosphates of the secondary environment e.g. crandallite, wavellite, millisite.

Crops with P-deficiency symptoms are encountered frequently on inherently P deficient soils and in agricultural systems where nutrient are removed and not sufficiently replenished. Visual signs of P-deficiencies are stunted growth, restricted root development, delayed maturity and poor seed and fruit development. In acute cases of P-deficiency, plants (e.g. maize/corn) show purpling of leaves and stems (Figure 4.2).

Figure 4.2. *P-deficiencies as shown by purpling of leaf edges in maize/corn (Zea mays).*

Phosphorus occurs in soils in the form of relative insoluble rocks and minerals and in organic (P_o) and inorganic (P_i) forms. Phosphorus is taken up by plants primarily from soil solution as inorganic anions, in the form of orthophosphates. In the 'normal' soil pH range between 4 and 9 only the two orthophosphate species HPO_4^{2-}, $H_2PO_4^-$ will occur in soil solution. Most of the P-ions are supplied to roots via the mechanism of diffusion, the movement of nutrients from the zone of higher concentrations to the zone of lower concentration (Barber 1995).

From a plant nutrition point of view, the 'total' P in soil is less important than the 'plant available' P; the portion of P in soil that can be taken up by plants. Forms of P in soils are shown in Table 4.2.

Table 4.2. *Predominant forms of P in soils*

Name	Symbol	Formula	Found
P-bearing rock and mineral fragments	PR	Mostly apatite, $Ca_{10}(PO_4)_6F_2$ and secondary phosphates	In soils as apatite and other P-minerals of the secondary environment
Organic P	P_o	Complex organic forms	In organic complexes in soils, such as inositol phosphates, phosphate esters
Inorganic P ions	P_i	$H_2PO_4^-$, HPO_4^{2-}	In soil solution; plants can use this form

The total P content in soils varies considerably. This is largely related to the influence of the underlying parent material and climatic factors. Phosphorus in soils and plants is ultimately obtained from rocks and minerals, released to the soil through the process of weathering as discussed in Chapter 2. Concentrations of P in the soil are sometimes used as an index of weathering (Sanchez 1976). They can also be indicative of the parent material, as there are substantial differences in P concentration in soils over different parent materials.

There are substantial differences in P concentration in rocks and minerals. The main groups of common rocks, and the minerals they are composed of, were introduced in Chapter 2. The P_2O_5 concentration of the upper continental crust is 0.15% (Rudick 2003). Igneous rocks commonly have low phosphorus concentrations: granitic rocks containing generally 0.1-0.2% P_2O_5 and mafic rocks, like basalts contain 0.3-0.5% P_2O_5. Sedimentary rocks, making up only 5 -8% of the earth's crust, but covering about 75% of the land surface of the world (Pettijohn 1975) also generally contain low concentrations of phosphorus (sandstones 0.07% P_2O_5; limestones 0.17% P_2O_5). However, some sedimentary rocks such as phosphorites can be extremely rich with regards to phosphorus (20 -34% P_2O_5) depending on the amount of phosphate mineral grains in the phosphorite. Some marine clays and glauconitic marls are often enriched in P.

Phosphorus or phosphate concentrations in rocks and minerals are commonly expressed in terms of P or P_2O_5 although both P and P_2O_5 do not occur in minerals and rocks as such. Because of its high affinity to oxygen, P is not found in rocks and minerals in its elementary form but mainly in the form of Ca-phosphates (primarily minerals of the apatite group), and Ca-Al-phosphates and Fe-phosphates (secondary phosphate minerals in the weathering environment).

The input of P to soils is critically important for agricultural production. While N can be captured from the air, very little P is supplied naturally to soils from external sources. Commonly, the amount of P released from mineral phases during one growing season is not enough to support growth and development of crops. When plant growth is limited due to P deficiencies, P is commonly added to the soil in the form of fertilizers that contain phosphate, or phosphate rock, bone meal, or P recycled from plant and animal residues, for example animal manures.

Except for bonemeal, all P-fertilizers are derived from phosphate rock deposits. Worldwide, the mining, concentration and processing of phosphate rocks to soluble P fertilizers is a large resource based industry. In the past, the main P fertilizers produced were superphosphates, such as single superphosphate (SSP) and triple superphosphate (TSP). In recent years there is a shift towards P fertilizers that also contain nitrogen, for example mono- and di-ammonium phosphates (MAP and DAP). These P fertilizers are very soluble and when poorly or inefficiently applied on the land can release P into the environment and cause eutrophication. Other concerns are related to trace element concentrations (such as Cd) in both, natural and processed P-fertilizers.

Table 4.3. *P-sources with differing concentrations (various sources). Conversion factors shown on page vi.*

Source	Concentration	Specifics
Fluorapatite	42% P_2O_5	Predominant form of apatite in igneous P deposits
Francolite	34-38% P_2O_5	Predominant form of phosphate mineral from the apatite group in sedimentary P deposits
Human bone	28.6% P_2O_5	85% of P in humans concentrated in bones and teeth
Cattle Manure	0.1-1.1% P	Mainly in the form of organic P
Plants*	0.1 – 0.5% P	Varies with plant species
Soil	0.08% P	In various forms, commonly organic P (P_o) exceeds inorganic P (P_i)
P in soil solution	0.2 – 1 mg P kg^{-1}	P in plant available form as orthophosphates, specifically HPO_4^{2-} and $H_2PO_4^-$

* dry weight

Environmental concerns and economic considerations have raised interest in slow release alternatives to highly reactive, soluble P-fertilizers. Research on the direct application of phosphate rock, on slow release phosphate fertilizers and modified phosphate rocks focuses on the processing of phosphate rocks with low energy inputs and alternative available solubilizing materials and processes. Examples of phosphate modification processes will be provided in this chapter. Various sources and concentration ranges of P-bearing matter is compiled in Table 4.3.

In this chapter the forms of P in soils will be discussed followed by an account of the geological resource base of phosphates. The nature of primary geological P resources will then be described, as well as a review of the environmental conditions under which phosphates were formed in rocks and minerals. Finally, we will discuss the ways in which geologists explore and discover phosphate rock (PR) resources, and subsequently find out how phosphates are mined and processed from geological phosphate deposits into plant available phosphorus forms.

4.0 Phosphorus in plants

The main functions of P in plants are related to energy transfer and storage. Phosphorus is a key component in the molecule adenosine triphosphate (ATP) and adenosine diphosphate (ADP), which are integral to most energy requiring processes in living organisms. P is also a vital constituent of chromosomes. Phosphorus is essential for the formation of proteins and enzymes and is a fundamental component of the cell membrane, as well as dioxyribonucleic acid (DNA) and ribonucleic acid (RNA). Phospholipids play a vital role in the formation of cell membranes. P is needed by plants for crucial physiological processes, like photosynthesis and nitrogen fixation. P stimulates the development of roots and specifically the development of fibrous roots. Roots will proliferate extensively in areas with higher P concentrations.

Phosphorus is needed in the final growth stages of a plant for seed and fruit development. It is concentrated in grain, seeds and fruits. The P reserve in seed is concentrated in the form of phytin, the inositol hexaphosphate. In cotton seeds the P concentration often exceeds 0.7% P. In addition, sufficient P will strengthen the straw in cereals.

Phosphorus is relatively mobile in plants and will translocate from older to younger plant tissue. Higher percentage of available P is contained in young plant tissue than in older, more mature plants. Plants which are unable to take up enough P experience stunted growth, dark blue-green colouration of mature leaves, and restricted root development, as well as delayed maturity and early senescence as well as poor seed and fruit development. If the deficiency is acute, the leave edges and stems may take on purple colour. Visual P-deficiency symptoms can be readily observed on maize/corn (*Zea mays*) as it is a plant that requires considerable amounts of available P at the early stages of growth (Figure 4.2).

4.1 Phosphorus in soils

The total P content in soils varies considerably. The global average is 0.08% P (800 mg P kg^{-1}) (Ure and Berrow 1982). While the average total P concentrations in the plough layer of soils of the United States are 0.062% (620 mg P kg^{-1}), concentrations of less than 150 mg P kg^{-1} are common in strongly weathered soils of the tropics (Jones and Wild 1975; Sanchez 1976).

***Table 4.4**. Conventional P-testing calibrations for soil (in mg kg^{-1}), source: Havlin et al. (1999).*

P sufficiency level	Bray-1 method	Mehlich-III method	Olsen (bicarbonate) method
Very low	< 5	< 7	< 3
Low	6-12	8-14	4-7
Medium	13-25	15-28	8-11
High	> 25	> 28	> 12

Concentration of P in soil solution necessary for optimum growth of plants vary, but are commonly in the range of 0.2 mg P kg^{-1} to 1 mg P kg^{-1}. Of this amount, only a small fraction is available to plants. This means that only 0.1% or less of the total P in soils is available to plants. Available P is measured by various extracting agents and methods. The conventional soil testing methods designed to rapidly provide a quantitative measure of plant availability of a certain nutrient element in a soil sample include the P test methods of Bray 1 and Mehlich III in acid soils and the Olsen (bicarbonate) method in neutral to alkaline soils (Table 4.4). The soil testing methods involve the mixing of a fixed quantity of soil and with some chemical extractants, shaking for a standard time, filtration and analysis of the extract. In recent years iron impregnated paper strips were used to estimate the quantity of available P in the soil that is adsorbed to the FeO strips (Menon *et al.* 1997).

Limitations to these extraction methods are largely related to the complexities of the soils with many inorganic and organic species being in a dynamic system. These methods are useful for prediction of nutrient requirement of soils but cannot be used to predict bioavailability in all types of soils.

The five main forms of P in soils are:

- P in solution,
- Inorganic P mineral grains (mainly apatite),
- P adsorbed on Fe-Al hydrous oxides and clay edges,
- precipitated P, (mainly Fe-, Al-, and Ca-phosphates),
- organic P.

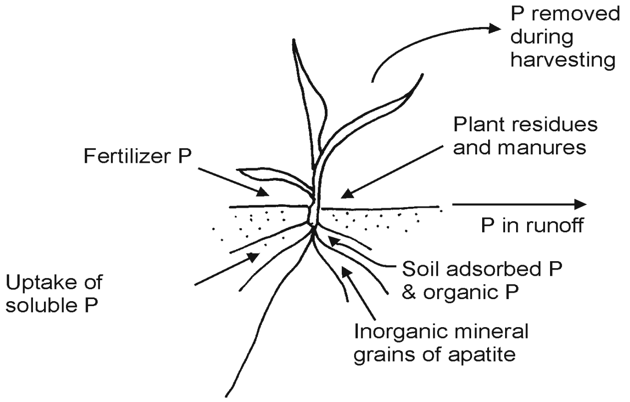


Figure 4.3. *Generalized phosphorus gains and losses in the rock-soil-plant system.*

Figure 4.3 shows the general inputs (gains) and outputs (losses) in a rock-soil-plant continuum. There are several organic and inorganic phases of P in soils as well as substances that bind and release phosphorus forms. The soil is a dynamic system and phosphate substances are transformed from one form to another, they are adsorbed, desorbed, incorporated into microorganisms, released and finally taken up by plant roots. A simplified model diagram, portraying the different forms of P-species, their transformation and pathways in the root zone (rhizosphere) and their final uptake by roots is shown in Figure 4.4.

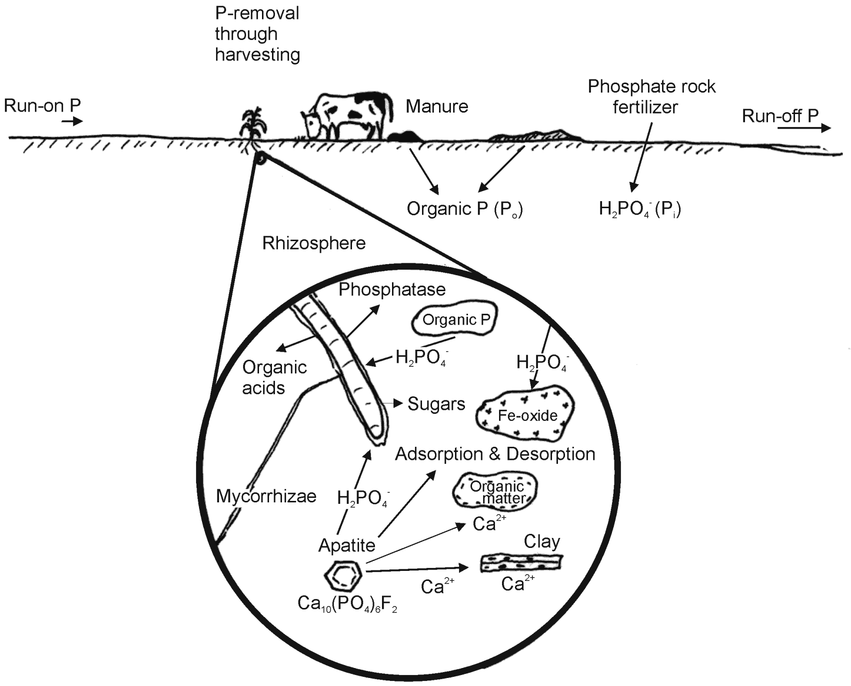


Figure 4.4. *Forms and transformations of P in the near root environment.*

In agricultural systems the P added to the soils comes either from fertilizers, phosphate rocks or organic matter. Fertilizer P occurs mainly in the form of rapidly available orthophosphates, for example monocalcium phosphate. Phosphate rock additions require commonly some solubilization to become into the orthophosphate form. Organic matter in the form of plant residues, green manure or animal manure also needs to be 'mineralized' to become plant available. Cows and other animals feeding on grain crops excrete more P than those feeding on roughage because more P is concentrated in the seeds and grains than in stalks and straw. Virtually all P excreted by animals is contained in the solid feces and the P contained herein is transformed only very slowly into plant available orthophosphate forms.

The process of transformation from one P species to another and the competition for the various P-species is interactive and very complex. A hypothetical pathway of P from the solid mineral phase (e.g. apatite), to P species in solution, to root uptake is presented in Figure 4.4 to illustrate the various forms of P in the soil and rhizosphere and the interactive processes of this mineralogical-chemical-biological system.

To start with, we hypothetically assume that we have inorganic phosphate minerals in the soil, for example P-rich rock underlying the soil or P rich mineral grains from the weathering environment, such as crandallite. There are many pathways possible to transform these mineral, inorganic P (P_i) sources into plant available forms of P.

In our soil scenario the pH is low, due to prolonged leaching processes, or perhaps because of the formation of organic acids from the breakdown of organic matter or from root exudates. Under the influence of organic or inorganic acids, the solid phosphate mineral phase (mainly apatite) is slowly broken down. Apatite dissolution increases with decreasing pH. Under low pH conditions, the breakdown of apatite is predominantly congruent, meaning that the dissolving species (Ca, P and F) are released from the apatite in stochiometric amounts. Microorganisms in the soil can increase apatite dissolution by producing their own organic acids (Welch *et al.* 2002).

If apatite grains are added to the acid soil (for example, through direct application of phosphate rocks with apatite being the principal mineral), it is likely that the apatite grains will initially release Ca species in stochiometric excess relative to P and F (Welch *et al.* 2002; Guidry and MacKenzie 2003). However, after a few days the release of Ca, P and F species will begin to occur in stochiometric amounts. The likely inorganic P (P_i) species that will be released into the soil solution is the anion $H_2PO_4^-$. This P species is the form that roots take up, mainly through the process of diffusion.

Before the P-ion reaches the root surface there is considerable competition for this anion in the soil. The competing sites for $H_2PO_4^-$ are positively charged surfaces of iron and aluminum hydroxides, and/or amorphous alumino-silicates (allophane), and/or positively charged clay edges, for example edges of kaolinite. Adsorbed P can be desorbed again, by organic acids or other competing anions.

Some of the soil solution P_i may also be taken up by micro-organisms or transformed into organic forms of P (P_o). Organic P compounds such as phytin and other inositol phosphates have to be mineralized, usually by phosphatase enzymes, to become available to plant roots. Through the action of these enzymes released by micro-organisms and/or plant roots, the P_o fraction can be broken down into inorganic soluble P (P_i).

Models have been developed that calculate the changes and the dynamics in this system (Jones *et al.* 1991; Boghal *et al.* 1996; Lewis and McGechan 2002; Karpinets *et al.* 2004) and aim at predicting P dynamics and status in the various P pools as response to applications of P over time.

The reactions of soluble P-fertilizers in soils are complex. The principal processes and factors that influence the reactions of P-fertilizers in soils are discussed extensively in Hedley and McLaughlin (2005).

Cows and other animals feeding on grain crops excrete more P than those feeding on roughage. Virtually all P excreted by animals is contained in the solid feces. The P contained in the solid part of manure is released relatively slowly.

4.1.1 Phosphorus in soil solution

Plant roots take up P from the soil solution as inorganic P (P_i), mainly in the forms of the anions $H_2PO_4^-$ and HPO_4^{2-}. The relative concentration of these two ions is pH related, with HPO_4^{2-} being available mainly in a pH range >7.2 and $H_2PO_4^-$ being available between pH 4.0 and 7.2 (Figure 4.5). The measured concentration of P_i in a typical soil solution is very low ranging from <0.001 mg P kg^{-1} in very infertile soils to 1 mg P kg^{-1} in well fertilized soils. Optimum P concentration in soil solution is > 0.2 mg kg^{-1} (Norrish and Rosser 1983; Wild 1988). From this pool, a very small portion of P is taken up directly through root interception (<1%), a small percentage is taken up passively during water movement to the roots (mass flow), but most is taken up through diffusion because of a concentration gradient near the root (Barber 1995). This small inorganic fraction has to be replenished in synchrony with plant uptake to be most effective for plants. In general, the mobility of P in soil solution is very low.

The dynamics of P in soil are complex and can be affected by management practices, such as crop rotation, organic matter addition (Kabengi *et al.* 2003), and physical disturbance of soils. Long-term drying periods usually have negative effects on P availability (Kabengi *et al.* 2003).

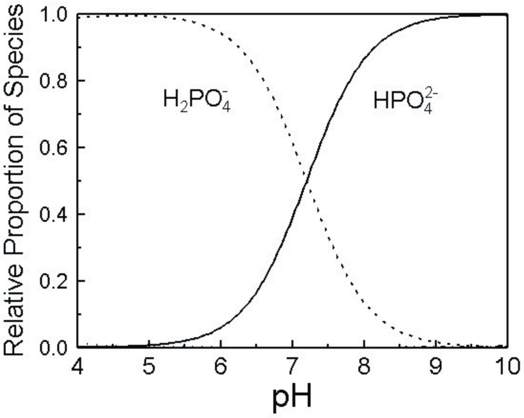


Figure 4.5. *Plant available forms of phosphorus as a function of the soil solution pH.*

4.1.2. Inorganic phosphate minerals

There are more than 200 known phosphate minerals. The main mineral group of phosphates in soils is the group of calcium phosphates of the apatite group, specifically fluorapatites, francolites, hydroxyapatites, chlorapatites and carbonate-hydroxy-apatites. Francolites are also called carbonate-fluorapatites. Other phosphate minerals in soils, pedogenic phosphates, include crandallite group minerals, $CaAl_3(PO_4)_2(OH)_5H_2O$, as well as phosphates from the plumbogummite, gorceixite group of minerals. Norrish and Rosser (1983) analyzed more than 150 soils for phosphate minerals in weathering environments in Australia and noted that the commonly postulated phosphate minerals variscite ($AlPO_4{\cdot}2H_2O$) and strengite ($FePO_4{\cdot}2H_2O$) do not seem to be as common in secondary weathering environments as phosphate minerals of the crandallite group.

Apatite is generally characterized by a chemical formula involving $Ca_{10}(PO_4)_6F_2$. The main phosphate minerals of the apatite group are shown in Table 4.5:

Table 4.5. *Common mineral species of apatites.*

Name	**Formula**	**Found**
Fluor-apatites	$Ca_{10}(PO_4)_6F_2$	Common form, mainly associated with igneous rocks such as carbonatites, and mica-pyroxenites.
Francolites	$Ca_{10\text{-}x\text{-}y}Na_xMg_y(PO_4)_{6\text{-}z}(CO_3)_zF_{0.4z}F_2$	Common form, predominantly found in marine environments. In the francolite formula x ranges from 0-0.35, y ranges from 0-0.14 and z ranges to about 1.26 (McClellan and Lehr 1969).
Hydroxy-apatites	$Ca_{10}(PO_4)_6(OH)_2$	Found mainly in biogenic bone deposits, but also in igneous and metamorphic environments.
Carbonate-hydroxy-apatites	$Ca_{10}(PO_4,CO_3)_6(OH)_2$	Commonly found on islands and in caves, as part of bird and bat guano.

To make the P in apatite available to plant growth, it must first be dissolved. Environmental conditions that increase the dissolution of apatite minerals in soils are:

- ○ Low pH,
- ○ High Cation Exchange Capacity (CEC),
- ○ Low Ca concentration,
- ○ Low P concentration,
- ○ High P sorption capacity,
- ○ High organic matter content.

These conditions drive the dissolution of apatites into plant available P_i (mainly as $H_2PO_4^-$ and HPO_4^{2-}) and various ions. The principal reaction of fluorapatite dissolution is:

$$Ca_{10}(PO_4)_6F_2 + 12\,H^+ \Leftrightarrow 10\,Ca^{++} + 6\,H_2PO_4^- + 2F^- \quad \text{(equation 4.1)}$$

The Law of Mass Action dictates that either increasing the activity of H^+ or decreasing the activity of Ca^{2+} or the P-species will enhance apatite dissolution. The reaction is 'pushed' from left to right by increasing the H^+ ion concentrations through protonation/acidulation. Alternatively, by decreasing the Ca^{2+} and/or P concentrations, the reaction will be 'pulled' from left to right. The principal 'push and pull' factors of apatite dissolution are shown below (Table 4.6)

Table 4.6. *'Push and pull' factors of apatite dissolution.*

Push (H^+ source)	**Pull (Ca^{2+} sink)**
○ Industrially produced acids	○ Ion exchangers, e.g. zeolites
○ Acids produced from oxidation of sulphides	○ Organic matter as Ca^{2+} sink
○ Root exudates	○ Plant uptake of Ca^{2+}
○ Organic acids produced by micro-organisms or decomposing organic matter	○ Ca-chelating materials

In acid soils with excess H^+ ions, the reaction is 'pushed' from left to right. The lower the pH of the soil solution, the more available P_i becomes, unless P_i is sorbed or taken up by other soil constituents. Soils with high P-sorption capacities such as Oxisols and Ultisols or Andisols 'pull' the dissolution reaction from left to right by reducing the P concentration in the area immediately surrounding the PR (Smyth and Sanchez 1982; Cabala-Rosand and Wild 1982a; Syers and MacKay 1986). The conditions of low pH, low exchangeable Ca and low P concentrations are common in many tropical, strongly weathered soils. Consequently, the dissolution of apatite is enhanced in these acid soils, but reduced in Ca^{2+} rich, alkaline soils.

Sources to augment H^+ concentrations and ‘push’ the dissolution reaction include industrially produced acids, natural organic acids such as those found in peat bogs, or low molecular weight acids produced by bacteria and fungi or organic acids exuded from roots. Providing soils with NH_4^+ based fertilizers can also have measurable effects on the pH in the soil solution, as H^+ is released by the roots when NH_4^+ is taken up by plants.

A practical way to ‘pull’ the dissolution reaction of apatite from left to right is to reduce Ca^{2+} ion concentrations in the soil solution. There are many methods for decreasing Ca^{2+} activity in the soil, for example adding ion exchangers like zeolites, adding biologically produced Ca-chelating compounds, or by using plants with high Ca requirements and uptake. The addition of organic matter to the soil also acts to pull the dissolution reaction of the apatite because of the strong binding potential of Ca^{2+} with organic matter.

4.1.3 Sorbed and precipitated phosphates

When phosphorus compounds are applied to soils, reaction occur among the soluble P sources and the soil constituents as well as non-phosphatic components which remove P from the solution and render the soluble P-compounds less soluble than before. This phenomenon of removing P from the soluble forms into a less soluble form is widely called ‘fixation’or ’retention’ (Sample *et al.* 1980). Phosphorus provided to soils has a very low mobility, largely because P is easily adsorbed as phosphate ions to the solid surfaces of various Fe and Al oxides and hydrous oxides. Adsorption of inorganic phosphates is a phenomenon in which orthophosphates from solution is adsorbed to the surface of a solid phase. It is a combination of orthophosphates with cations, e.g. Fe and Al, to form two-dimensional solid phases. Negatively charged phosphate ions are also adsorbed to positively charged clay edges, particularly 1:1 clays like kaolinite, and to amorphous alumino-silicates, such as allophane and imogolite (Wada 1985). The site on which the P-anion is adsorbed depends largely on the amount and the sorption capacity of the adsorbing species, which in turn can be largely pH dependent. For example, the adsorption of phosphate ions on a solid Fe and Al hydrous oxide phase is pH dependent due to the variable charge characteristics of these phases. In acid soils adsorbed phosphate complexes are formed by ligand exchange reactions in which orthophosphate complexes are formed resulting from the release of OH^- ions from hydroxylated surfaces (Goldberg and Sposito 1985). Some soils (e.g. volcanic soils) can ‘fix’ large amounts of soluble P compounds and make them unavailable to plant roots.

Amorphous Fe hydrous oxides are known to adsorb 10 to 100 times more P in comparison to crystalline oxides and hydrous oxides, for example hematite (Fe_2O_3) or goethite (α-FeOOH). Norrish and Rosser (1983) noted that iron oxyhydroxides such as goethite can retain several times more phosphate ions than Al hydroxides, for example gibbsite ($Al(OH)_3$. Amorphous mineral phases like imogolite and allophane, which are clay-sized, non-crystalline short-range ordered aluminosilicates commonly associated with the weathering of volcanic ashes and glasses (Wada 1985) have very high P sorption capacities.

Soil P-sorption capacities affect the dissolution of phosphate rock (PR) resources by reducing the P concentration of the PR (Smyth and Sanchez 1982). While these soils can 'fix' a great amount of soluble P in the short term, in the long term the slow-release P-desorption process from these soils can and 'turn a liability into an asset' (Sanchez *et al.* 1997).

Precipitation of phosphates is caused by the combination of orthophosphates with cations in a three-dimensional solid form that is either still amorphous or which has turned into a crystalline phase from an adsorbed phosphate form. The distinction between adsorption and precipitation is very complex and has attracted much research (reviewed in Sample *et al.* 1980). Generally speaking, it seems that adsorbed phosphates proceed into a P-rich solid 'precipitated' phase over time.

The main determining factors for the adsorption and subsequent precipitation of P are pH and the availability of soluble Fe, Al, Mn, or Ca ions. Phosphates also precipitate out of saturated solutions when the solubility product constants are exceeded. Under these acid conditions, $H_2PO_4^-$ will react with soluble Al, Fe, Mn, and under alkaline conditions, with Ca, to form insoluble P-forms rendering the P ions insoluble and unavailable for plant growth. Under alkaline pH conditions, soluble Ca will react with the P ions resulting in the precipitation of insoluble Ca-phosphates such as $CaHPO_4 \cdot 2H_2O$ (Dicalciumphosphate dihydrate - DCPD) and $CaHPO_4$ (Dicalciumphosphate anhydrate (DCPA). Minerals found in nature with these chemical formulae are brushite (DCPD) and monetite (DCPA). The reaction of P compounds with the prevalent Ca and Mg carbonates $CaCO_3$ (calcite) or $CaMg(CO_3)_2$ (dolomite) found in calcareous soils respectively continues over time and after about a month $CaHPO_4 \cdot 2H_2O$ hydrolyzed into $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ octocalciumphosphate) (Lindsay *et al.* 1962).

4.1.4 Organic phosphorus

Phosphorus that is taken up by plants and micro-organisms is quickly transformed to organic molecules. Organic P (P_o) occurs predominantly in the form of inositol phosphates, phosphate esters and high molecular weight organic substances. Large proportions of P_o are constituents of microorganisms. To make the organic forms of P available for uptake by the roots, plant roots release the enzyme phosphatase which transforms the P_o into plant available inorganic P (P_i) in the forms of $H_2PO_4^-$ and HPO_4^{2-}. Phosphatase enzymes have been identified in the immediate surroundings of roots, in the rhizosphere. Microorganisms also seem to play a significant role in making P more available, through increased phytate activity, stimulation of root hair and release of organic acids (Richardson 2001).

The organic P fraction (P_o) can account for as much as 50% of the total soil P, and even up to 80% of the total P in some pasture soils (McLaughlin *et al*. 1990; Richardson 2001). This fraction is of great practical importance to maintain organic P in low input agriculture on highly weathered Oxisols, Ultisols and Alfisols of sub-Saharan Africa (Sanchez 1976).

4.2 Geology of phosphates

Phosphorus in the soil is derived almost totally from geological sources, phosphate rocks (Figure 4.6). Phosphate rocks (PR) have been defined as naturally-occurring materials containing one or more phosphate minerals as well as possessing chemical and processing characteristics that make it acceptable for commercial use as a source of phosphorus (Notholt 1980). It is an imprecise term as it not only describes the naturally occurring P-bearing mineral assemblages (phosphate rocks) but also beneficiated (physically concentrated) products.

There are five major types of PR resources in the world:

- ○ Sedimentary phosphate deposits,
- ○ Igneous phosphate deposits,
- ○ Metamorphic deposits,
- ○ Guano deposits,
- ○ Phosphate deposits as a result of weathering.

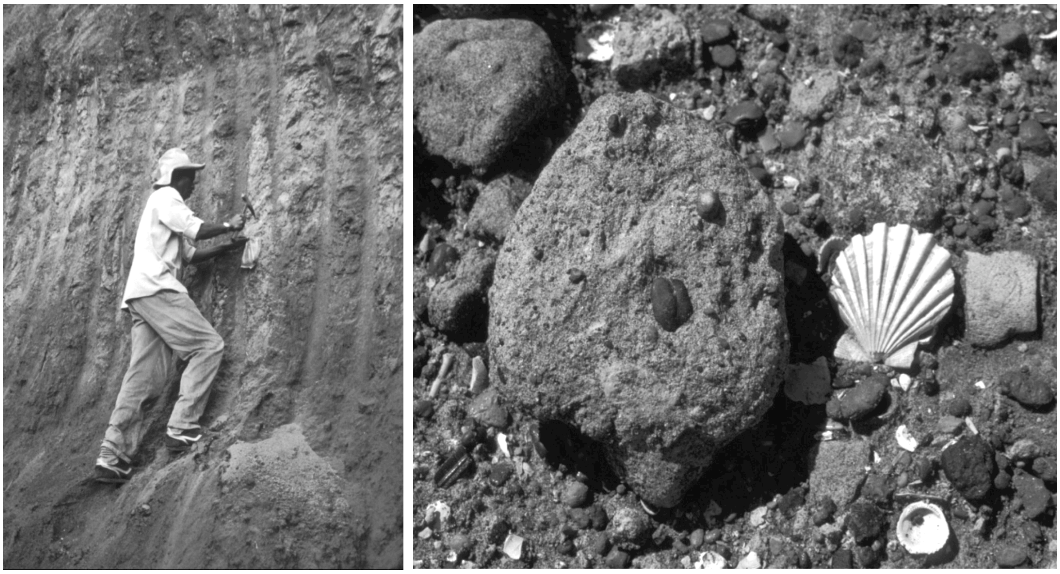


***Figure 4.6**. A: Residual phosphate rock over Busumbu carbonatite, Eastern Uganda (left): Sedimentary, reworked phosphate rock resources, Florida, USA (right).*

Each of these PR resources is finite and non-renewable. Reserve and resource estimates of phosphate rock are highly variable. Deposits that can be extracted profitably under current economic and technical conditions are considered to be global reserves. These are estimated by the US Geological Survey (2005) to be 18 billion tonnes phosphate rock. Known reserves plus all other geological mineral resources that may eventually become available are considered global resources. These are estimated to be in the range of 50 billion tonnes (US Geological Survey 2005). In 2004, the global phosphate rock production was 138 million metric tons (US Geological Survey 2005).

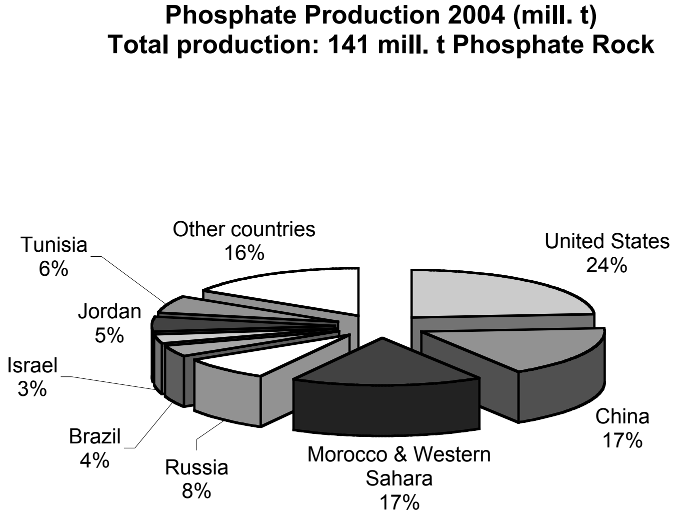


Figure 4.7. *Global 2004 phosphate rock production (source: US Geol. Survey 2005).*

Individual percentages produced by the main producing countries are shown in Figure 4.7. Under current technical and economic conditions and with the current rate of PR production, it would take more than 130 years to deplete global resources. However, as PR reserves become diminished the price will inevitably rise and increased profitability will shift some resources into the reserve category. Obviously, it is difficult to forecast the rate of depletion of PR resources due to uncertainties of future markets, economics, alternative resources, environmental concerns, government programs and politics. As such, PR production is expected to last considerably longer than 130 years. Steward *et al.* (2005) estimated the depletion rate of PR resources to be more than 680 years.

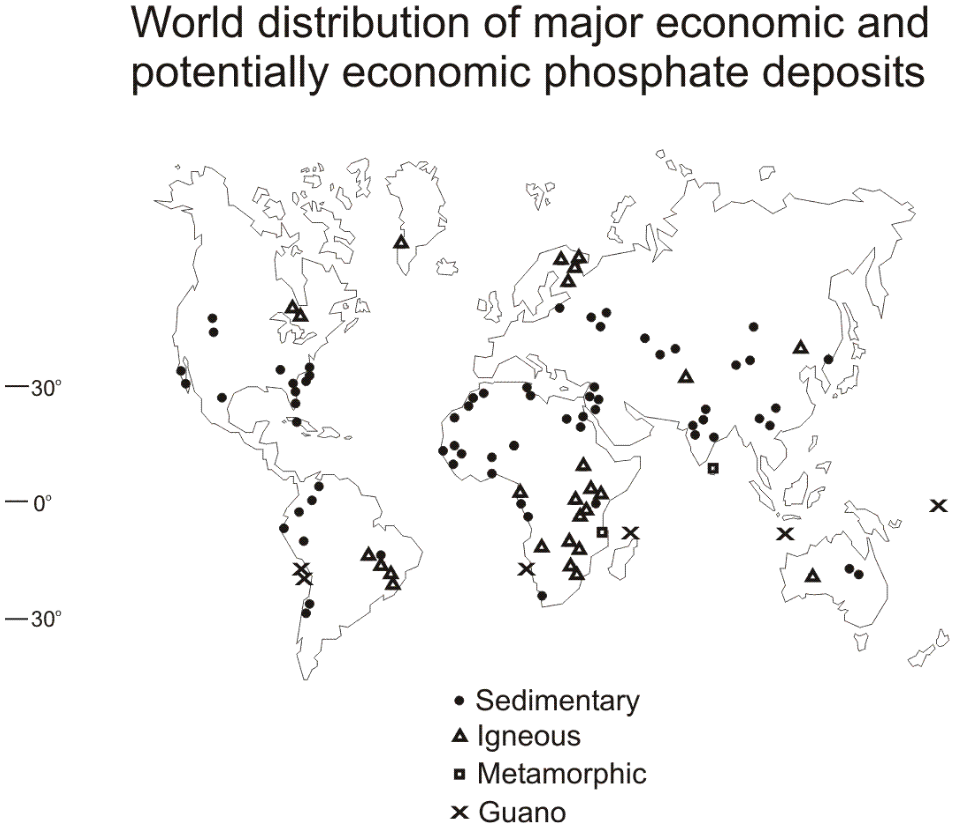


Figure 4.8. *Distribution of major economic and potentially economic phosphate deposits in the world.*

Phosphate rock resources are distributed around the globe such that all continents, with the possible exception of Antarctica, have an abundant PR resource base (Sheldon 1987). However, distribution of producing mines within the continents shows only a few countries with large production; for example, Russia has almost all the reserves of Europe, Morocco and South Africa dominate the PR production in Africa, and the USA holds more than 80% of the North American production. The world distribution of major economic and potentially economic phosphate deposits is depicted in Figure 4.8. Many additional small PR deposits exist. Some of them known (but not marked on the worldwide map of major PR deposits) and other PR resources have yet to be discovered.

Approximately 88% of the world's phosphate production comes from sedimentary, marine phosphate rock deposits, 12% from igneous and weathered deposits, and only a small fraction from guano-related resources, specifically bird and bat guano accumulations (Cook 1984; Van Kauwenbergh 2001, 2003). The sedimentary phosphate sources were mainly formed in biologically productive zones. Some of the biogenic phosphates are composed of phosphate rich bones and teeth.

4.2.1 Sedimentary Phosphate Deposits (Phosphorites)

Marine sedimentary phosphate rocks, also called phosphorites, constitute the majority of global phosphate resources (Howard 1979). They are widespread and have been found on all continents (Cook 1984) (Figure 4.10). Only very few lacustrine sedimentary phosphate deposits have been reported worldwide.

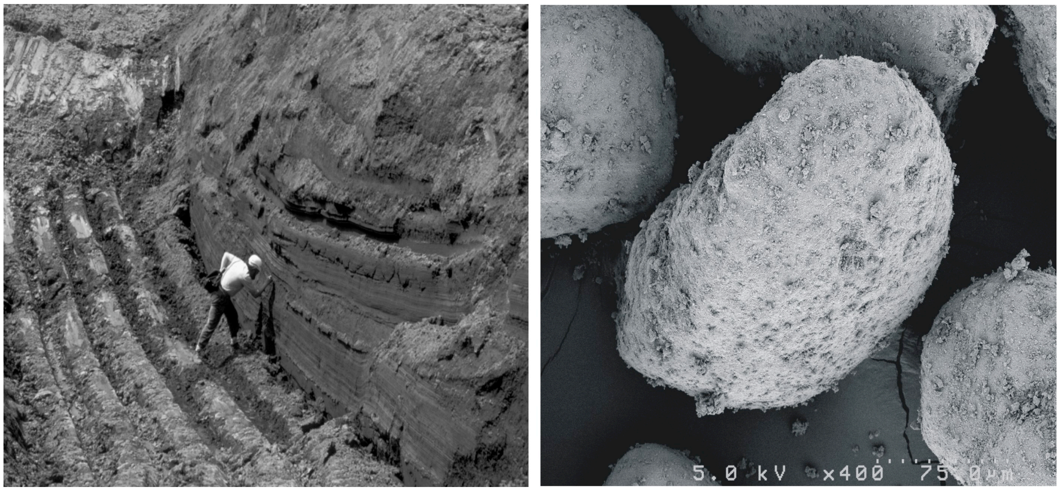


Figure 4.9. *A: Phosphorite deposit, North Carolina, USA. (left): scanning electron micrograph of phosphorite pellet from PR deposit in North Carolina, USA (magnification 400 times) (right).*

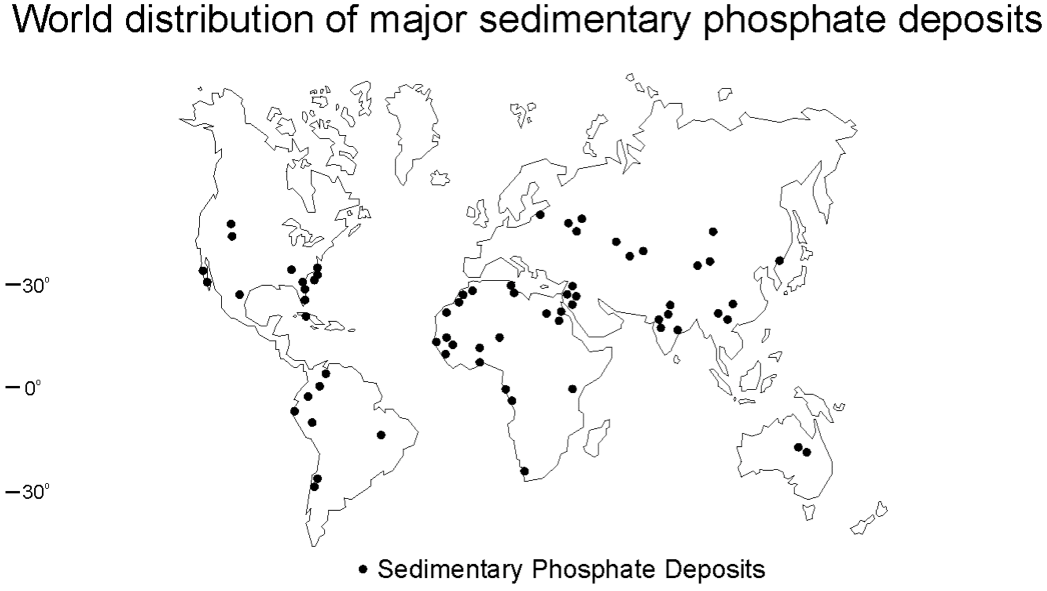


Figure 4.10. *Global distribution of major phosphorite (sedimentary PR) deposits.*

Phosphorites are layered, near surface sedimentary phosphate deposits of large volume and extent. Slansky (1986) defines phosphorites as marine sedimentary phosphate rocks that contain at least 50% apatite (18% P_2O_5). However, not all authors agree with this definition (Bentor 1980; Baturin 1982; Jarvis *et al.* 1994). In fact, the definition of a phosphorite varies from a sedimentary phosphate rock containing >10% apatite grains to >50% apatite (18% P_2O_5). A simplified section of a phosphorite deposit is shown in Figure 4.11.

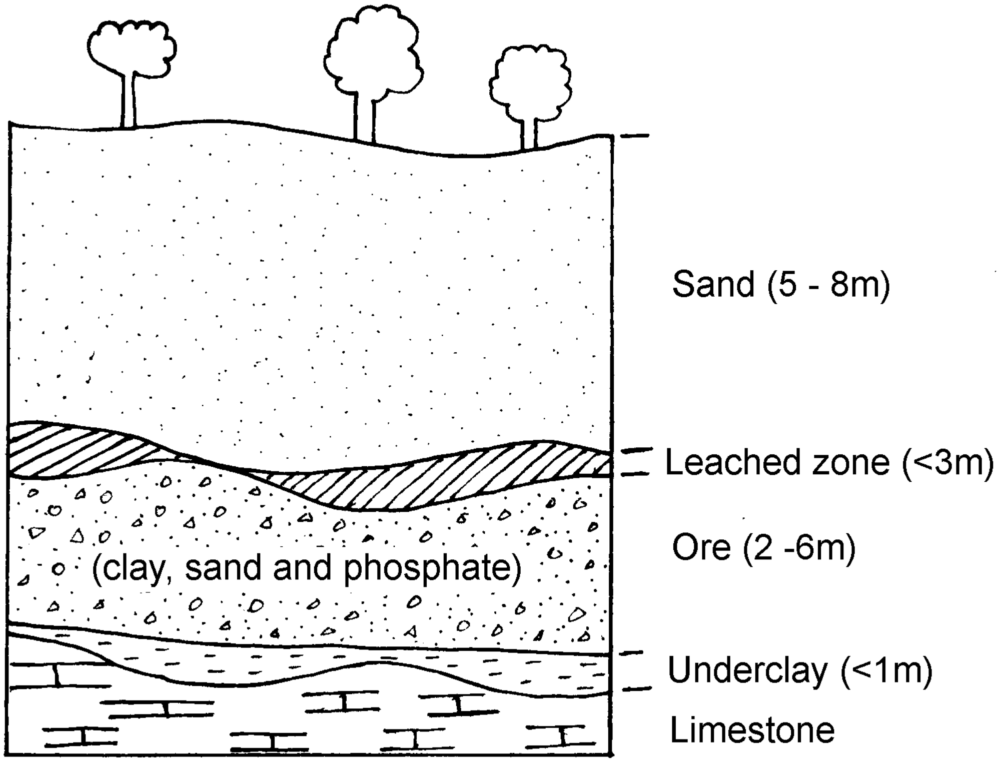


***Figure 4.11**. Simplified section of a sedimentary phosphate (phosphorite) deposit from Florida, USA.*

The apatite mineral francolite is the most common phosphate mineral in phosphorites, but other apatite minerals such as fluorapatite and hydroxyapatite may also be present, albeit in smaller amounts (McClellan 1980; McClellan and Van Kauwenbergh 1990). Francolites constitute a continuous series of carbonate substituted fluorapatites with end members with no carbonate substitution to end members with 6-7% carbonate ions substituting for phosphate ions. Francolites are known to contain many 'impurities', mainly trace elements that substitute either cations or anions in the apatite lattice. The main substitutions in phosphorites are shown in Table 4.7.

Table 4.7. *Possible ion substitutions in francolites (Jarvis et al. 1994).*

Constituent ion	**Substituting ion**
Ca^{2+}	Na^{+}, K^{+}, Ag^{+}, Mg^{2+}, Sr^{2+}, Cd^{2+}, Mn^{2+}, Zn^{2+}, Bi^{3+}, Sc^{3+}, Y^{3+}, REE^{3+}+, U^{4+}
PO_4^{3-}	CO_3^{2-}, $SO_4\ ^{2-}$, CrO_4^{2-}, F^{3-}, CO_3^{--}, OH^{-}, AsO_4^{3-}, VO_4^{3-}, SiO_4^{4-}
F^{-}	OH^{-}, Cl^{-}, Br^{-}, O^{2-}

One of the most common trace elements found in phosphorites is uranium (Altschuler 1980). In seawater, dissolved uranium (U) occurs in the hexavalent U^{6+} state, but is present in phosphate minerals also in the form of U^{4+} (Altschuler 1980), either incorporated into the apatite lattice, adsorbed to apatite surfaces, or associated with organic matter (Burnett 1977; Bentor 1980; Jarvis *et al.* 1994). Common concentrations of U in phosphorites range from 50 to 150 mg U kg^{-1}, with exceptionally high concentrations reaching 5600 mg U kg^{-1} (Bentor 1980; Slansky 1986).

Formation of Phosphorites

Modern accumulations of P-rich sediments are found in locations characterized by cold upwelling ocean currents and high biological productivity (e.g. major fishing regions, and areas with diatom blooms), for example off the coast of southwestern Africa and the west coast of South America.

In the oceans, P accumulates from dying plants, animals and microorganisms that sink into deeper parts of the oceans. These organisms are broken down by oxidation and/or microbial activity and release phosphate ions back into the water. Consequently, the bottom layer of water in oceans becomes enriched in P and other nutrients. These nutrient rich waters are transported to shallow continental shelf areas through upwelling currents.

Some upwelling currents are caused by trade wind induced ocean circulation-gyres that extend from the equator to about 50 degrees. In the northern hemisphere these gyres move clockwise, and in the southern hemisphere they move counterclockwise as a result of the force of the rotation of the earth (Coriolis Force) (Figure 4.12). This means that surface waters on the west coast of the continents are blown towards the equator while those on the east coast are blown away from the equator. When surface water is driven away by the wind, it is replaced by cold, nutrient-rich water from the bottom of the oceans. In coastal areas, this nutrient-rich water comes right to the surface, providing a rich feeding ground for numerous populations of diverse organisms.

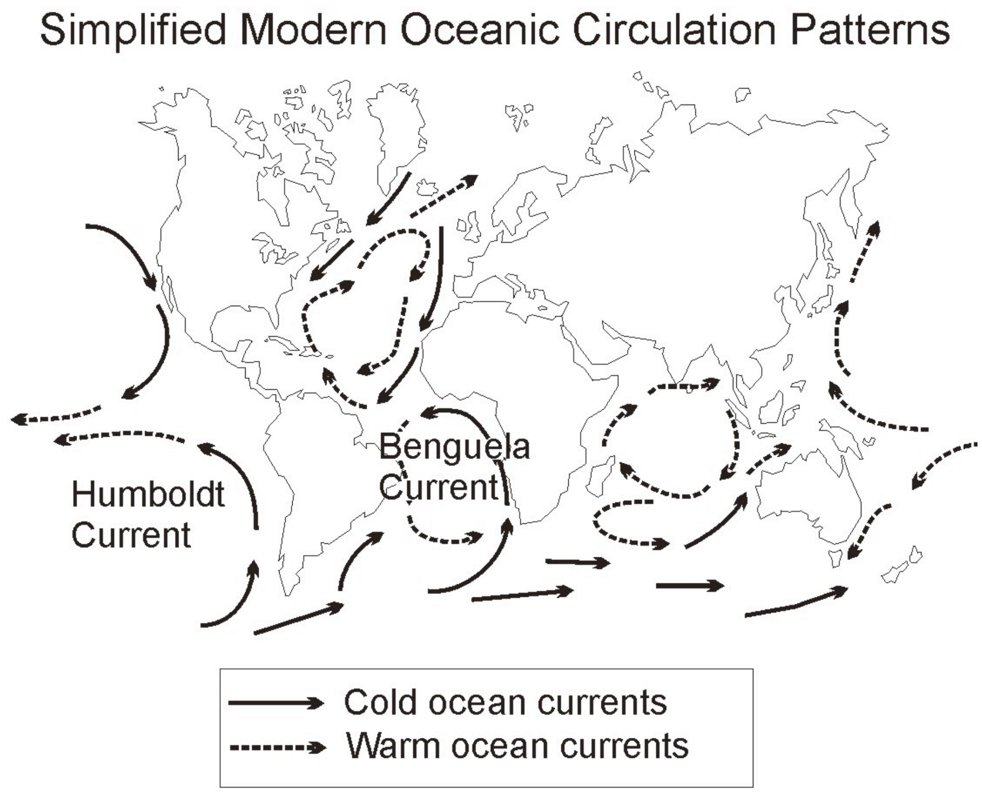


Figure 4.12. *Modern circulation patterns of ocean currents.*

During upwelling and mixing the deep cold waters warm up, depressurize, increase in pH and oversaturated with regard to phosphate. The nutrients supplied by this deep P-rich water produce algal blooms and high biological activity on the surface.

Upwelling zones make up less than 1% of oceanic surface area but produce over 50% of the total global marine biomass (Cook and McElhinny 1979). This intense biological activity leads to frequent deposition of organic and P-rich sediments. Many phosphorites are typically associated with biological sediments such as cherts (from algal blooms) and black organic rich sediments, which develop into black shales (Sheldon 1964b; Burnett 1977; Riggs 1979a; Bentor 1980; Glenn *et al*. 1994). Presently, major zones of upwelling and phosphate rich sediments occur along the western side of continents and also areas where major ocean currents like the Gulf Stream steer around major bathymetric highs and consequently produce some local gyres (Riggs 1984).

The correlation between phosphorite occurrences and trade wind-induced upwelling zones was first recognized by Kazakov (1937). Two modern examples of phosphate deposition in typical trade wind induced upwelling situations are the Benguela Current in southwestern Africa and the Humboldt Current in western South America (Veeh *et al*. 1973; Glenn and Arthur 1988; Bremner and Rogers 1990; Birch 1990).

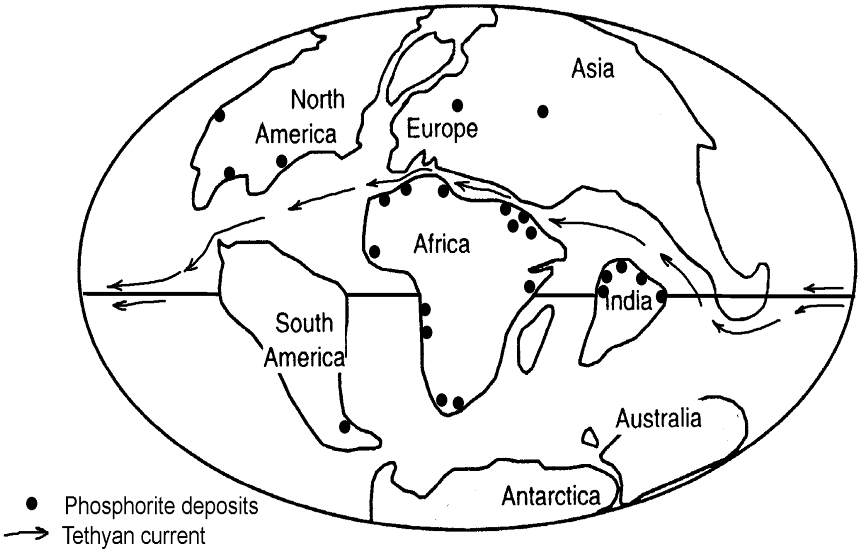


Figure 4.13. *Continental positions in the late Cretaceous showing the Tethyan current and the location of late Cretaceous phosphorite deposits (modified after Sheldon 1964b).*

There are however, very large Cretaceous and lower Tertiary phosphorites that are not associated with trade wind induced-upwelling zones (Figure 4.13), for example the deposits of India, Syria, Egypt, Tunisia, and Morocco. The deposition of these huge marine PR resources was likely related to a climate change-driven upwelling between large landmasses in equatorial areas (Sheldon 1980). Paleolatitude reconstructions have shown that phosphorites were deposited at specific sites in areas generally located about 5-45 degrees north and/or south of the equator (Sheldon 1964b).

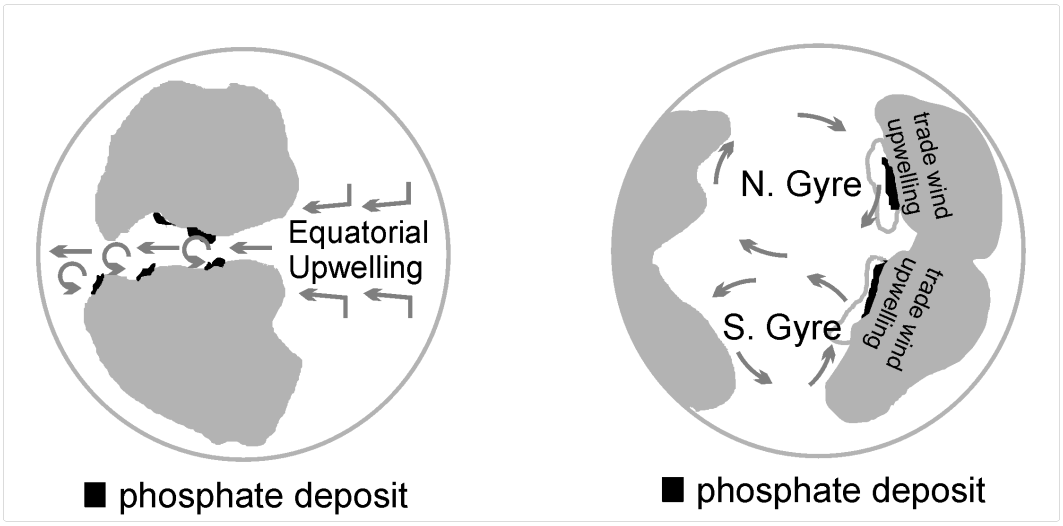


Figure 4.14. *Model of phosphorite deposition in upwelling zones (modified after Sheldon 1980).*

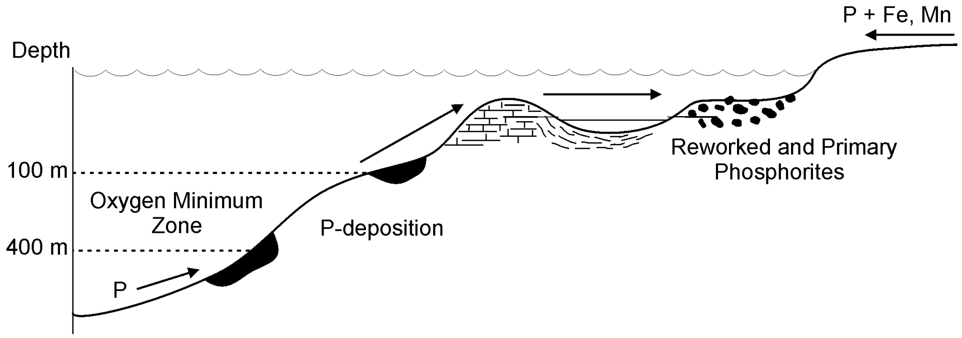


__Figure 4.15.__ Simplified model of sites of phosphorite deposition relative to water depth and oxygen concentrations.

A model showing potential zones of upwelling and phosphorite deposition (Figure 4.14) was developed by Sheldon (1980). He included both the trade wind related-upwelling and climate change-driven equatorial upwelling processes. According to Sheldon, P accumulation occurred at the ocean floors during long lasting periods of stable, warm, high level waters high seawater levels. These stable periods were interspersed with short periods of low water levels and actively circulating oceans with strong upwelling activities. In the transition between these periods the cold phosphate-rich water mixed with warmer shallow water in coastal areas and massive amounts of P were deposited in these upwelling zones.

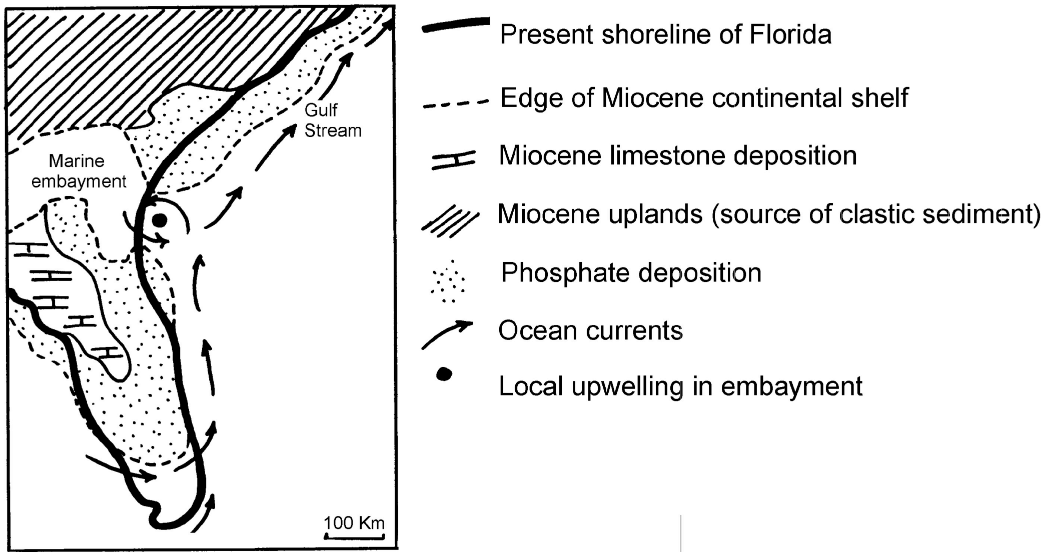


__Figure 4.16.__ Depositional model for the Florida and North Carolina phosphorites.

Upwelling currents also occur in marine embayments where P-rich terrestrial waters mix with sea water and which acted as sediment traps (Figures 4.15 and 4.16), for example in North Carolina (Riggs 1979b, 1994).

Not surprisingly, there are many different factors that affect the formation of phosphorites. Oxidation-reduction processes are thought to play important roles in the breakdown of organic matter, the liberation of phosphorus and the subsequent precipitation in pellets or replacement of siliceous or calcareous skeletons. Oscillations of oxidation and reduction processes, which are known to occur at the top and bottom of the oxygen minimum zones in upwelling zones, create ideal conditions for phosphogenesis (Figure 4.15) (Baturin 1972; Burnett 1977; Bentor 1980). Interstitial waters with high phosphate concentrations are usually associated with reducing environments (Bentor 1980).

Microbiologically mediated processes are also important for the breakdown of organic matter. Several models have been proposed that explain the role of microorganisms in interstitial water and the promotion of phosphate nucleation and resultant crystallization on mineral surfaces (Föllmi 1996). The origin and formation of phosphorites have been discussed in many publications including papers in recent years by Glenn *et al.* (1994), Jarvis *et al.* (1994); Krajewski *et al.* (1994); Föllmi (1996).

Extreme weather events can also affect P-deposition. Extensive phosphate deposits occur in areas where ocean currents and severe storms (?) removed large parts of the fine non-phosphatic muds leaving behind nodules, pellets and bones. In some cases the phosphates are reworked and concentrated in locations closer to the seashores.

Sea-level changes with subsequent transgressions (sea level rise) and regressions (sea level drop) are known to create a suitable environment for deposition of phosphatic sediments to shift seaward or landward (Figure 4.15). Transgression can cause reworking of pre-existing deposits, for example in Florida (Figures 4.15 and 4.16).

Phosphorite deposits are not created equal, and many differences exist in the geological settings of phosphorite deposits. Although the P contribution of phosphorites to the total P mass in oceans and continents is relatively small (Föllmi 1996), phosphorites are economically important.

Specific physico-chemical and biological conditions, as well as favourable global climatic conditions, chemical weathering rates, and sea level changes, may all affect global P cycling and the formation of phosphorites (Filippelli and Delaney 1994; Föllmi 1996; Compton *et al.* 2000; Shields *et al.* 2000). The timing of increased P fluxes to the oceans is frequently related to increased mechanical weathering and P fluxes during and after glaciation periods, for example at the Precambrian/Cambrian boundary (Cook and McElhinney 1979) as well as plate tectonics and associated major tectonic events (Guidry *et al.* 2000) and changes of global paleocurrents in the Tertiary (Stille 1992; Stille *et al.* 1996). Recent studies suggest that the timing of Tertiary phosphorite deposition (forming one of the largest phosphorite 'giants') might be related to epsisodes of increased uplift and erosion of the Himalayan-Tibetan Plateau (Compton *et al.* 2000; Shields *et al.* 2000).

Paleogeography of Phosphorite Deposition.

Phosphorites have preferred locations of formation but also a temporal distribution that shows a distinct periodicity of phosphogenic episodes (Cook and McElhinny 1979) (Figure 4.17). Thus, to find phosphorites it is necessary to have a good understanding of the paleogeography of the target area as well as the age of the sediments.

The Eocene and Miocene were periods when large volumes of phosphate deposition occurred globally. The Miocene was a time period of gradual warming of the global climate with a related transgression (possibly associated with melting ice caps) and a steady build-up of phosphate-rich sediments and finally the deposition of extensive PR deposits, for example in Florida and N. Carolina.

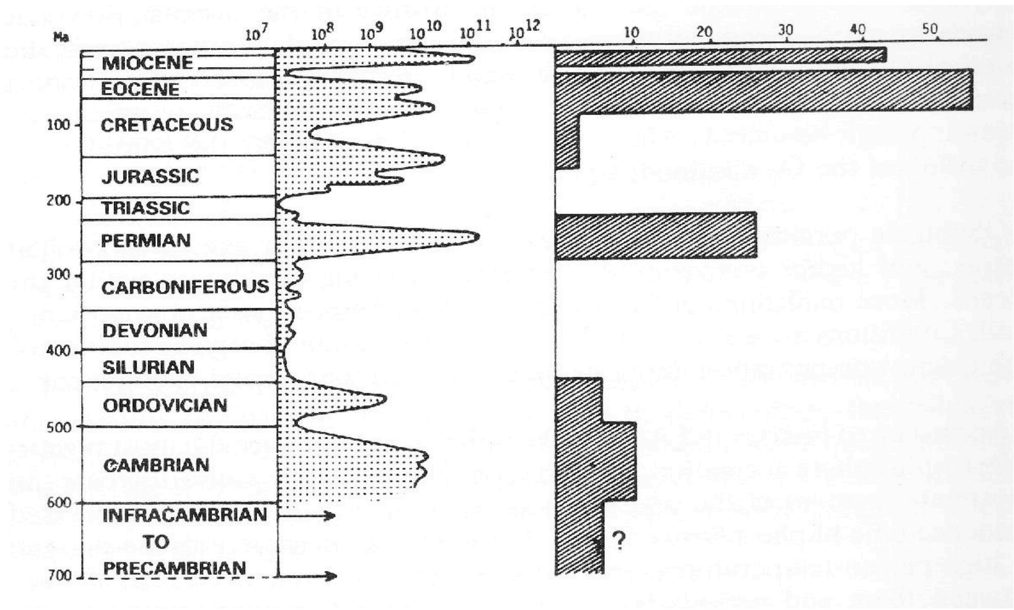


Figure 4.17. Distribution of major phosphate abundances and number of P deposits over time (after Cook and McElhinny 1979). Left: Geological time scale; Centre: Volume of phosphate ore; Right: Number of deposits.

Periods of rising sea level and low sediment deposition rates are thought to be important environmental factors for phosphate deposition. Sea level rise allows for the gradual build-up of phosphate rich sediments without erosion. The process of phosphate formation is likely to occur at the sediment water interface, or within pores in the sediments themselves, where oxygen-poor water with high P concentrations is found. Bacterial action in this environment forms phosphate-rich pellets (Figure 4.25) within the sediment that can be subsequently reworked and sorted by waves and currents to form high-grade phosphorites. A simplified section of the continental shelf with positions of P deposition is shown in Figure 4.15.

Except for the Cretaceous and lower Tertiary, the periods of phosphorite deposition largely coincide with periods of global glaciations (Cook and McElhinny 1979; Sheldon 1980). On the other hand, equatorial upwellings and associated phosphate formation occurred mainly during Cretaceous and Tertiary periods, during periods of high water levels in conjunction with East-West currents (Sheldon 1980), without apparent global glaciations.

How do we find sedimentary phosphates?

Phosphate discoveries usually follow two exploration steps. The first is target selection based on understanding the genesis of phosphate deposits. The second step is to utilize the best and most economic exploration tools to find and delineate phosphate-rich zones. These exploration tools are largely geological, geophysical and geochemical in nature. This combination of concept oriented surveys and detailed exploration led to a good number of discoveries over the last decades.

Table 4.8. *Uranium concentrations in phosphate rocks (from various sources).*

Rock type	Uranium Concentration (ppm = mg kg^{-1})
Non-marine phosphates	
Guano	< 30
Guano-derived rock	20-80
Igneous apatites	0.1-40
Marine phosphates	
Florida concentrate	110
average pebble	150
reworked, coarse	500
N' Carolina, (average)	60
Idaho,Wyoming,Montana (average)	90
Morocco	70-230
Turkey	40
Australia (average)	60
Peru	60
Colombia	80

Step 1 Target Selection

When exploring for marine phosphate-bearing sediments (phosphorites), the first action of an agrogeologist is to obtain a geological map and locate shallow marine sedimentary successions of an age that corresponds to worldwide phosphogenic episodes (Figure 4.17) (Cook and McElhinny 1979). For example, it would be prudent to investigate the availability and geological setting of marine sediments of the late Cretaceous and late Tertiary, but it would not be of much use to search for large phosphorite accumulations in sediments of Silurian, Triassic or Oligocene age because these time periods were by and large not phosphogenic episodes.

It is also important to reconstruct the paleogeography of the areas with shallow warm water marine sediments. Phosphorites occur in shallow marine sediments and thus an analysis of the sedimentary sequence and their location of formation can be crucial. Also, it is advantageous to know in which paleogeographic position, relative to the equator, the sediments were deposited. What were the relative positions of the continents to the equator at the time of deposition? What were the oceanic circulation patterns at the time, what was the geometry of the coastline, and where are local embayments or estuaries situated? Some of these questions are often not easy to answer without detailed geological analyses. Other researchers might have undertaken previous studies and paleogeographic analyses already and these data and analyses should be consulted before drawing up an exploration program.

Step 2 Specific Surveys

After selecting the target area using the conceptual approach, it is necessary to go to the field and carry out systematic surveys. But, again, some general exploration aids can make the search for phosphorites more effective. There are important and appropriate exploration tools that can be applied. First, the geologist looks for geological hints, such as ‘pathfinder’ minerals that occur close to phosphate deposits, for example the green sand mineral glauconite, or mineral assemblages that are indicative of environments of phosphorite deposition.

In the case of sedimentary phosphates, the agrogeologist will likely focus on the following shallow marine sedimentary associations, which are known to be potential indicators for finding phosphorites (Riggs 1986):

- Phosphate - black shale – chert,
- Phosphate - dolomite - Mg-rich clays (attapulgite/palygorskite),
- Phosphate - diatomite – tuff,
- Phosphate - dolomite – glauconite.

A useful tool in the search for phosphorites is the geophysical exploration method of gamma ray spectrophotometry, which involves detecting radioactive rocks and minerals. It is known that U^{4+} replaces some of the Ca^{2+} in the apatite mineral

(Altschuler 1980) (Table 4.7) and phosphorites contain varying concentrations of U (Table 4.8). The decay of this uranium is detectable by gamma ray spectrophotometers. Handheld x-ray spectrometers are very useful exploration tools in the search for phosphorites.

A commonly used technique to locate rocks by measuring radioactivity is to lower a radiometric detection device (probe) down pre-existing water, oil and gas boreholes to identify radioactive anomalies. The standard well logging technique of gamma-radiation in borehole logs is a rapid method of scanning thick sections of sediments. This geophysical exploration technique used in oil exploration proves to be a good tool for finding phosphorites as well.

A reliable colorimetric field test kit for estimating the presence of phosphate in rocks was developed at the US Geological Survey (Shapiro 1952). This simple field test provides a semi-quantitative estimation of P-concentration in those rocks that contain more than 3% P_2O_5. The test has been successfully applied in the search for phosphate enrichment zones in carbonatites (Borsch 1984; van Straaten 1995).

Exploring for sedimentary phosphates

Case History #1: Turkey

The discovery of the phosphorites in Turkey in 1962 was based on the combination of conceptual target area selections with well-focused ground surveys (Sheldon 1964a). The conceptual approach guided the selection of target areas, which were geological regions with shallow marine sediments, condensed profiles, Turonian-Senonian (upper Cretaceous) sediments, as well as areas with higher than normal radioactivity and black shale - chert lithologies, or associations with glauconite. Using geological and geophysical exploration tools, the ground surveys led to the discovery of the targeted phosphorite within a relatively short period of time.

The conceptual basis for selecting Turkey as a target area grew out of examining the causal relationship between upwelling waters and phosphorites. This concept was first forwarded by the Russian scientist Kazakov (1937) who identified that phosphogenic zones are often related to two kinds of wind systems and associated ocean currents, Trade Wind zones and East-West equatorial zones. The idea that there were upwelling zones at the edge of the Turkish landmass during earlier periods was formulated by one of the world's leading phosphate geologists, Richard Sheldon, during his visit to the area in 1962.

Case History #1: Turkey cont.

During the Upper Cretaceous to Lower Tertiary time period, Turkey was situated in the East-West equatorial zone of the Tethys, a narrow ocean strait between Africa and India in the south and Europe and Asia in the north (Figure 4.13). This was a relatively narrow East-West waterway which likely experienced strong currents and local upwelling zones. Sediments from this region correspond to the late Cretaceous–Eocene period, so the time period coincided with a known phosphogenic episode.

No known phosphorites had yet been found on the north shore of the Tethys, but paleogeographic reconstructions showed shallow marine sediments of back-arc basins ('miogeosynclines' in the old terminology) on the south shore of the Tethys and a deep fore-arc sedimentary basin ('eugeosyncline') to the north. Sheldon looked for shallow sedimentation sequences, with slow deposition (condensed profiles) and characteristic sediment associations such as black shale – chert.

Some of the characteristic rocks found in the general area of the south shore of the Tethys in the area of present-day Turkey were:

- Cherts: indicative of nutrient and silica rich upwelling waters (diatomite blooms),
- Black shale in shallow water environments: indicative of nutrient rich, cold upwelling waters, carrying large amounts of biomass in the form of plankton.

After developing the concepts, outlining the areas of potential phosphate deposition and then narrowing down the area of potential phosphate accumulation, a field party carried out ground surveys in designated areas with black shales and cherts. Because U can replace Ca in the apatite of sedimentary phosphates, particularly where phosphorites are associated with organic matter, measuring radioactivity in rocks proved to be a good tool for exploration.

In the end, a major discovery of phosphorites was made. The discovered phosphorites in Turkey have the following characteristics:

- Form: pelletal
- Colour: white to dark brownish grey
- Hardness: hard
- Associated fossils: fish teeth, bones, and scales
- Associated minerals: glauconite
- Associated lithologies: black shales, cherts.

Exploring for sedimentary phosphates -
Case History #2: Australia

Until 1961 only a few small phosphorite occurrences were known in Australia. They included small guano type deposits but no major marine sedimentary types.

In 1962, the Utah Development Corporation was granted licenses to explore 2.7 million square miles of unprospected shelf sediments. They started with a literature review using the resources of geological surveys and universities, and then analyzed various sedimentary rock suites gathered from university collections. This led to the ‘discovery’ of 30 significant phosphate deposits. In subsequent years, the Geological Survey of Australia carried out spectrographic analyses in these areas, which in turn led to the discovery of phosphorites in the Rum Jungle, Amadeus and Great Artesian Basin areas (Figure 4.18). These phosphorites were discovered in Ordovician, Permian and Cretaceous sediments and, as expected, none were found in Silurian, Devonian or Carboniferous rocks. The deposits found in Western Australia are associated with glauconite-rich sediments (Howard 1972, 1986).

In 1964, the Australian government granted ten more exploration licenses that permitted systematic searching for phosphates (Howard 1972). This search ended in 1966 with the discovery of extensive phosphate deposits in Middle Cambrian rocks of the Georgina Basin, west of Mt. Isa (Howard 1986) (Figure 4.18). Initially the licensed companies based their search on the following criteria:

- Cretaceous or Precambrian-Cambrian back-arc (miogeosynclinal) sediments,
- shallow shelf sediments and condensed sequences,
- sediments deposited in low paleolatitudes,
- black shale-chert lithologies,
- sedimentary controls, for example embayments, and
- high-energy environments with reworked sediments and no cherts.

In 1964, the company IMC entered the exploration race and took a different approach. First, they considered economic concerns and decided that any economically viable deposit should be less than 325 miles away from principal fertilizer consuming areas. Phosphates have great space value, meaning that proximity to the market is very important because of transport costs and other economic considerations.

Case History #2: Australia cont.

In order to delineate their exploration target area, the geologists carried out a geological analysis of paleogeography, basin stratigraphy and favourable lithologies. Once this had been completed they carried out a detailed search. They examined cores and cuttings from boreholes, specimens from universities and geological surveys and samples from paleontological collections. In addition, they performed simple colorimetric tests of rocks and conducted gamma-ray surveys of borehole logs from oil companies and water authorities.

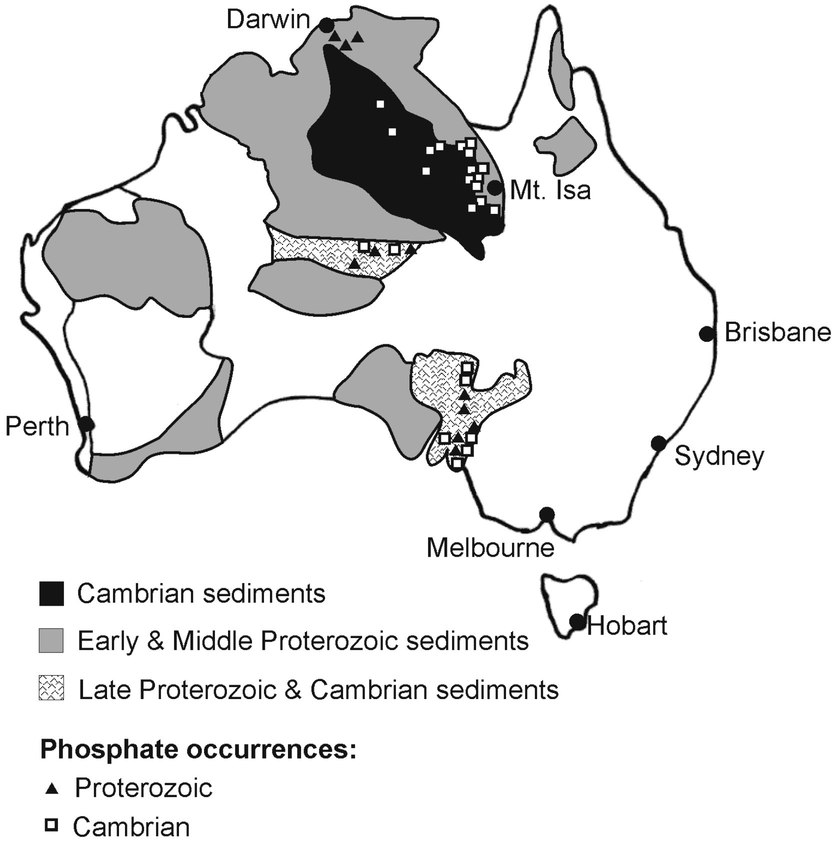


***Figure 4.18**. Distribution of Proterozoic sedimentary phosphate deposits in Australia (modified after Howard 1986).*

They narrowed the search down to certain areas and continued logging abandoned water boreholes. Eventually they found a good target in Upper Cretaceous sediments of the Perth Basin, Western Australia, but they had to abandon the area due to the unexpected great depth of the deposits and the associated high cost of extraction. In the Tasman geosyncline, they found the black shale-chert association, structural highs, oolites and nodular deposits of phosphorites, but these were too thin to be of economic interest and were also abandoned.

In 1966, Mid-Cambrian phosphorites were discovered in the Georgina Basin through chemical testing of cores and cuttings from stratigraphic oil wells (Howard 1972, 1986). The geologists found sediments with P_2O_5 grades of 7% in sediments over 80 feet thick, but the phosphorites were again located at a depth that was considered too deep for economic viability. Eventually, the closest area of lower-mid Cambrian outcrops was examined, and an economically viable phosphorite deposit was discovered after a short period of detailed prospecting. The Georgina Basin deposits were formed in shallow, partially restricted embayments, contemporaneous with deposits of offshore carbonates

The phosphorite ore found had the following characteristics:

- Age: lower-mid Cambrian,
- Form: consolidated pelletal-oolitic phosphorites,
- Lithology: interbedded with phosphatic-cherts and siltstones, limestones.

Other deposits were subsequently discovered in similar fashion using the same exploration model.

4.2.2 Igneous Phosphate Deposits

Major phosphate deposits of igneous origin have been discovered on all continents except Antarctica (Figure 4.19) (Notholt 1979; Cook 1984; Notholt and Highley 1986; Notholt *et al*. 1989, 1990). Most of the extracted igneous phosphate rocks come from Russia, South Africa, Brazil, Canada and Finland. In total, these deposits account for approximately 10 to 20% of current global phosphate production although generally they are of lower grade than deposits associated with sedimentary materials.

Typical rock associations in which these igneous PR accumulations occur include:

- Nepheline-synite complexes, specifically urtite and ijolite,
- Carbonatites,
- Biotite pyroxenite complexes,
- Anorthosite - gabbro complexes,
- Other, less economically important complexes.

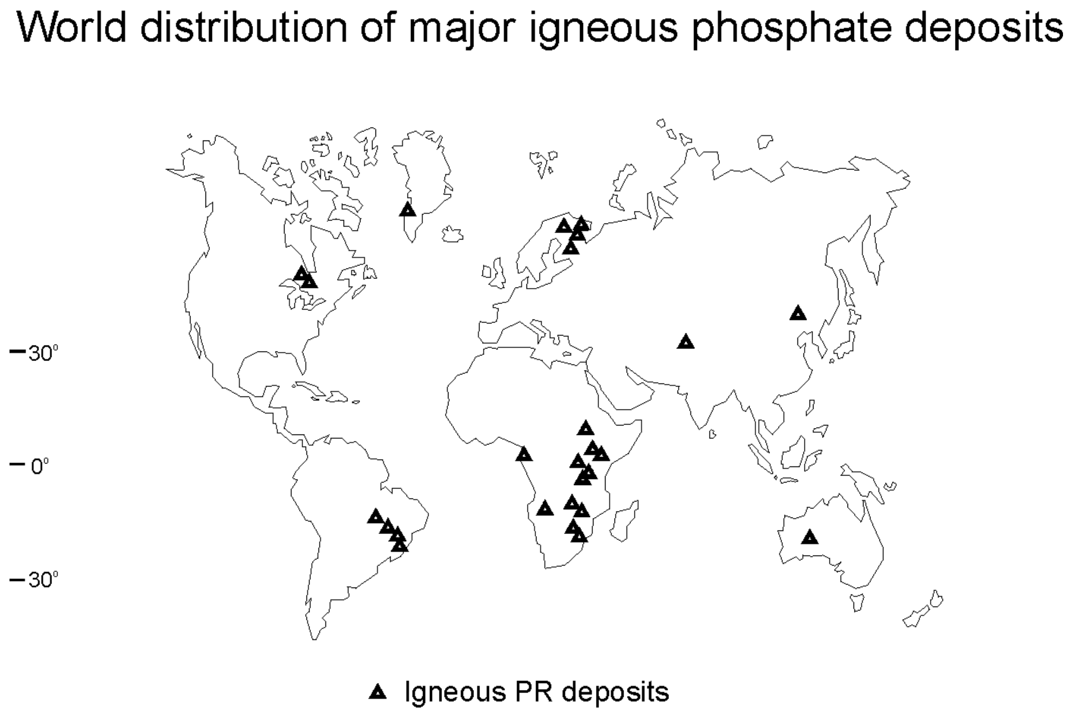


Figure 4.19. Distribution of major igneous and metamorphic phosphate rock deposits in the world.

Phosphate deposits associated with nepheline-syenite complexes

Nephelene-syenite is an igneous rock type consisting largely of nepheline and alkali feldspar. Most rocks of this type are pale colored, grey or pink, similar to granites, but some dark green varieties are also known.

Only one large phosphate-bearing complex associated with this type of rock is known (Notholt 1979). The Khibiny deposit, located on the Kola Peninsula in Russia, is one of the world's largest igneous phosphate rock resources. The Khibiny pluton is a ring complex, about 40 km in diameter, consisting of inward dipping sheets of nepheline-bearing rock types. The 100 m thick apatite – nepheline orebodies, traceable over a distance of more than 11 km, is restricted to a discrete zone of layered ijolitic rocks, consisting of the minerals nepheline, aegirine, apatite and sphene. Concentrations of 6 to 31% P_2O_5, from fuorapatite, are found in the ore. The ore also contains elevated concentrations of strontium (Sr) and Rare Earth Elements (REE). Reserves are estimated at 2700 million tonnes with an average grade of 18% P_2O_5.

Phosphate deposits associated with carbonatite igneous complexes

Carbonatites are igneous rocks, intrusive as well as extrusive, which contain greater than 50% (by volume) carbonate minerals (Woolley and Kempe 1989). Carbonatites are typically found outside extensive granitic cratons and folded belts (Figure 4.20). They are usually associated with repeatedly rejuvenated faults and shear zones, e.g. rift valleys (van Straaten 1995) and tend to have ring structures with diameters of 2-15 km. These ring structures can be detected easily from the air, by remote sensing techniques (Figure 4.21). The major carbonatite related igneous phosphate provinces are in Brazil, Eastern and Southern Africa (along the East African Rift Valley), Kola Peninsula (in Russia and Finland) and in eastern and central Canada (Notholt *et al.*1990).

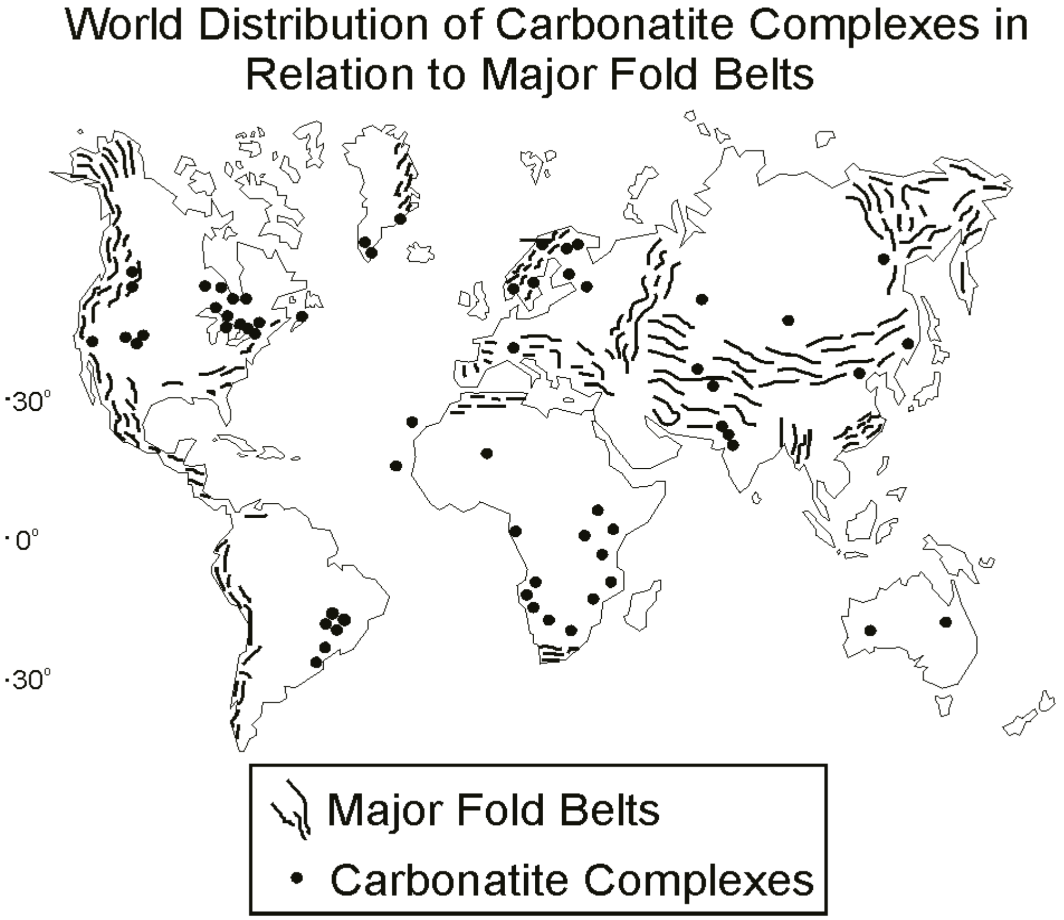


Figure 4.20. *World distribution of carbonatites in relation to major fold belts.*

There are four main carbonatite types, each representing a different phase of intrusion or extrusion: calcite ($CaCO_3$) carbonatite (sövite), dolomite ($CaMg(CO_3)_2$) carbonatite (magnesio-carbonatite), ferrocarbonatite with Fe-carbonates and natrocarbonatite containing rare Na-carbonates. However, natrocarbonatites are found only very rarely, partially because of their high solubility (Dawson 1989; Keller 1989). The formation of carbonatite rings follows a clear sequence. Geological field evidence shows that the sövite phase is the first to intrude, followed by magnesio-carbonatite and ferrocarbonatite phases. The cross-cutting intrusion of Barium (Ba), Rare Earth Elements (REE) and apatite-rich magnetite veins occurs in the final stages.

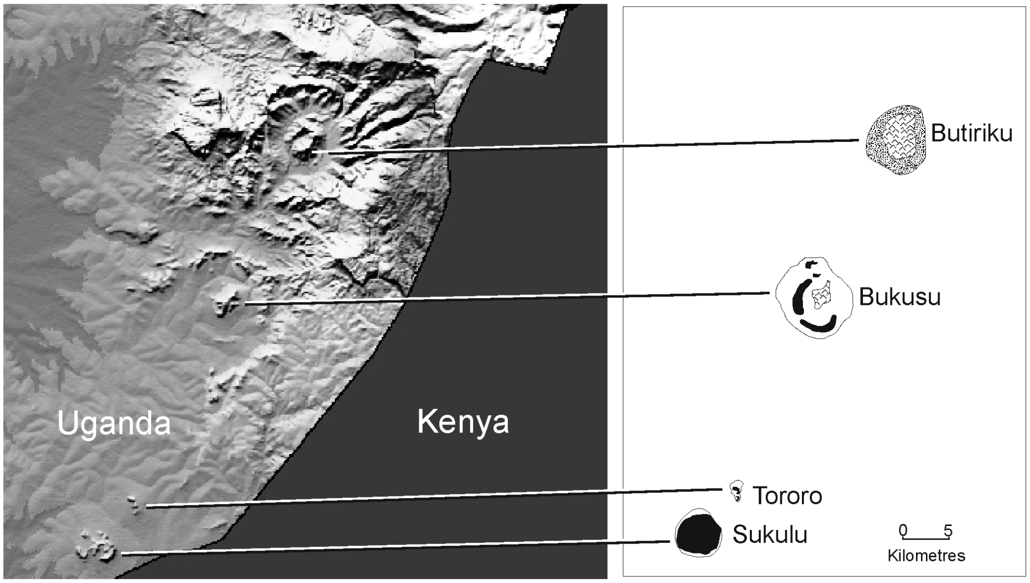


Figure 4.21. *Satellite image of Bukusu (lower) and Butiriko (upper) alkaline/carbonatite ring complexes in Eastern Uganda.*

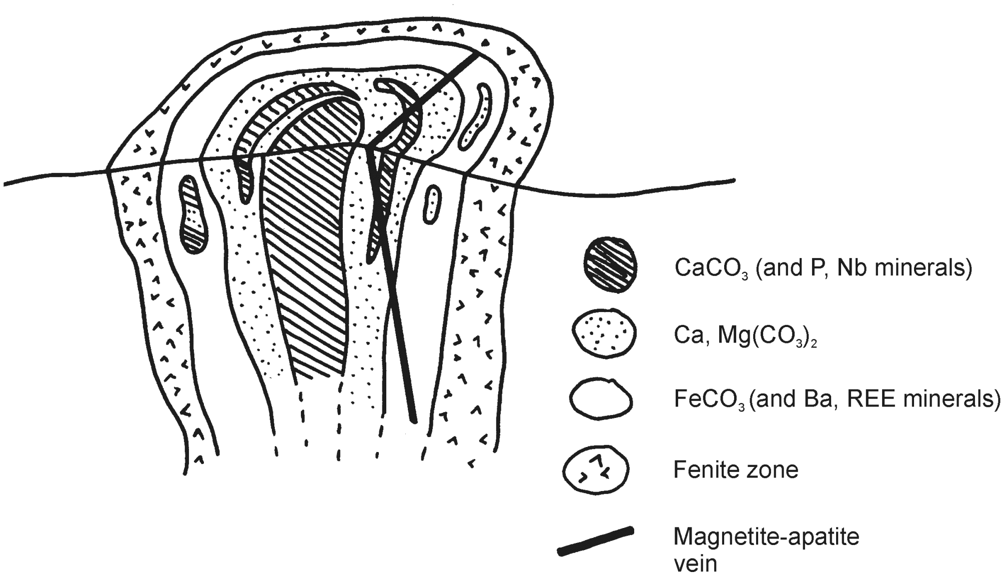


Figure 4.22. *Carbonatite ring complex showing the main carbonatite phases and associated mineralization.*

Concentrations of apatites occur mainly in the very early calcium-carbonate - rich (sövite) phase and in association with magnetite in late stage, cross-cutting veins. Apatite accumulations are also found at the contact of the carbonatite with the fenite zone, a zone of alteration associated with carbonatite intrusions. The distribution of phosphates and other minerals associated with carbonatite intrusions is depicted in the schematic diagram of Figure 4.22.

Phosphate deposits associated with biotite pyroxenite intrusions

Pyroxenite is an ultramafic igneous rock consisting mostly of minerals of the pyroxene group. When biotite, a common phyllosilicate mineral, is contained in pyroxenite, it is called biotite pyroxenite, which occurs as small round intrusions. Types of apatite rich ore typically associated with biotite pyroxenites include apatite–forsterite (olivine), and apatite-forsterite–magnetite (phoscorite).

Examples of this type of PR deposit are known to occur at Kovdor (Russia) and Phalaborwa (South Africa) (Deans 1966; Palabora Mining Company Ltd. 1976; Notholt 1979). The Kovdor ring complex (4 km x 5 km), which occurs on the Kola Peninsula, is an ijolite-pyroxenite intrusion, containing the P-bearing ore apatite in association with forsterite and magnetite. The dimensions of this ore body are about 1300 x 100-800 m, containing on average 50% magnetite and 16% apatite (6.6% P_2O_5). The deposit was mined primarily for iron, and about 700 million tonnes of Fe-ore was extracted. PR was considered at the time of mining to be ‘wastes’, but the tailings from this deposit were found to contain 12.5% P_2O_5 and subsequently have been identified as a valuable P resource (Notholt 1979).

Phosphate deposits associated with anorthosite - gabbro complexes

Anorthosite is a light-coloured coarse-grained intrusive igneous rock made up largely of plagioclase feldspar. Gabbro is a dark-coloured coarse-grained, intrusive igneous rock chemically equivalent to basalt. These two rock types often occur with one another as anorthosite-gabbro. There are very few phosphate deposits associated with anorthosite-gabbro intrusions, and only a small number of apatite-bearing anorthosite-gabbro intrusions have been found to contain sizeable P-resources. These complexes are typically Mid-Proterozoic in age and consist of rhythmically ‘layered’ anorthosite-gabbro intrusives or ultramafic-gabbro intrusives. The typical association of P-Fe-Ti (with the minerals apatite, ilmenite and Ti-magnetite) occurs in well-differentiated (‘pseudo-stratified’) intrusive complexes, the ore being commonly confined to the lower part of the intrusive body (Philpotts 1967; Kolker 1982). A small igneous phosphate rock deposit has been delineated in hornblendites associated with gabbro-anorthosites in Ethiopia (Abera 1994).

Phosphate deposits associated with hornblende-bearing syenite intrusions

Syenites are light-coloured coarse grained, intrusive igneous rocks consisting of feldspars, small amounts of quartz and one or more mafic minerals, for example hornblende. When these rock types contain considerable amounts of hornblende they are called hornblende-bearing syenites. Only few PR deposits containing concentrations of igneous apatites are found in geological environments associated hornblende-bearing syenites. Reported deposits include the Chilembwe PR deposit in Zambia which is found associated with hornblende-bearing syenites bordering extensive granite intrusive complexes (Sliwa 1991). This PR deposit is not large in size but locally important.

How do we find igneous phosphates?

Finding igneous phosphate accumulations is quite a challenge, as phosphate minerals are not very conspicuous in appearance. Consequently, most igneous phosphate deposits have been discovered during geological and geochemical surveys for other minerals. In carbonatite complexes, igneous phosphate accumulations are often found during the search for niobium (Nb), REE, vermiculite and Cu. In small biotite-pyroxenite complexes, apatite accumulations have been found during the search for Fe, Cu or vermiculite. For example, accumulations of apatites associated with syenite were discovered during the search for Cu in Zambia (Sliwa 1991), and apatite accumulations in gabbro-anorthosite complexes were found while looking for Fe and Ti accumulations in Ethiopia (Abera 1994).

When looking specifically for igneous phosphate accumulations the agrogeologist will generally follow the same two-step approach used to find sedimentary phosphates. The first step is target selection in order to reduce the area that will be surveyed, and the second step requires various specific surveys in the selected target area.

Step 1.Target selection:

In order to discover new PR resources the agrogeologist has to look for specific rocks and specific rock associations. The geological environments in which igneous PR resources are concentrated include alkaline complexes (e.g., nepheline-syenite complexes, specifically with urtite-ijolite phase), biotite pyroxenite complexes, carbonatites and anorthosite-gabbro complexes. There are also specific structural clues to look for. For example, carbonatites, as mentioned before, exhibit typical ring structures and occur in close proximity to continental rift areas or deep structural fault and shear zones (Figure 4.23).

Step 2. Specific Surveys:

Geological surveys involve studying existing geological maps or carrying out mapping in target areas. In addition to structures (ring complexes) and rock types (carbonatites) of interest, it is necessary to search for known deposits of ‘pathfinder minerals’, for example magnetite, vermiculite, fluorite, pyrochlore and REE minerals. High concentrations of magnetite and vermiculite are quite often found in the weathering environment of these complexes. Furthermore, geological observations of shattered contact metamorphic zones and fenite zones surrounding carbonatite complexes (Figure 4.22) are conspicuous as they contain minerals that are not very commonly associated with metamorphosed limestones.

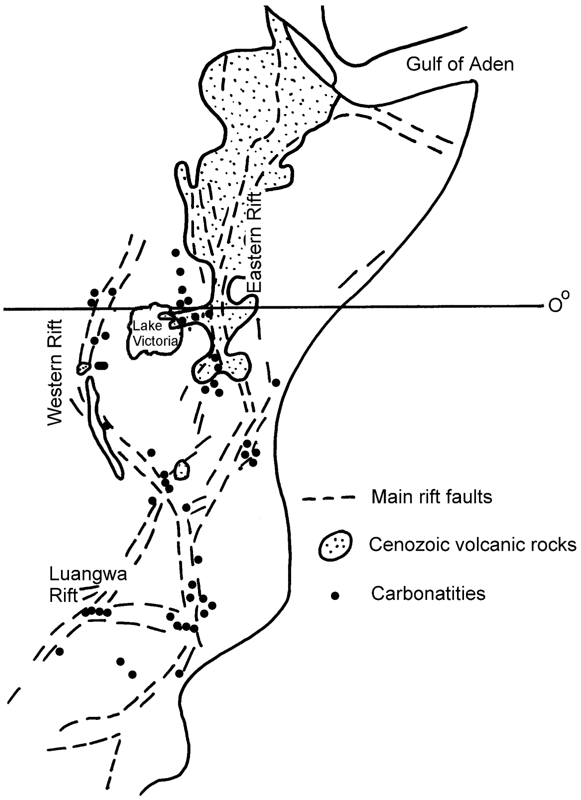


Figure 4.23. *East African Rift system showing locations of carbonatites.*

Remote sensing surveys can delineate ring structures but will not identify rock types and P mineralization. For example, carbonatites are found as ring complexes and oval shaped complexes, commonly 2-6 km in diameter. Remote sensing techniques have proven very useful in the search of carbonatites, to determine structural features such as radial drainage patterns, differences in vegetation cover, etc. However, airborne surveys can only outline structures of these potential phosphate-bearing complexes. There are no remote sensing examples so far that show the delineation of the actual apatite rich zones within these complexes.

Geophysical surveys are useful in areas of good airborne geophysical coverage. The geophysical signatures to look for are strong magnetic anomalies, strong radiometric anomalies and especially an overlap of both (van Straaten 1995a). These types of surveys have proved to be very useful exploration tools, especially in outlining structures and lithologies with potential for phosphate accumulations, e.g. carbonatites (van Straaten 1995). Geophysical ground surveys using magnetic and radiometric exploration techniques have also proved successful in many areas.

Vegetation surveys, such as geobotanical surveys and biogeochemical surveys have been used to indicate underlying geological features and structures. Biogeochemical surveys in which plants are collected and chemically analyzed can reflect chemical differences in the soil and the underlying rocks. Geobotanical surveys, the visual survey of vegetation, include the recognition of specific plant communities and the identification of malformed or discoloured plants or plant parts. Geobotanical surveys can also reveal compositional changes in the soils and the underlying rocks because the vegetation derives nutrients from these geological materials. For example, a geobotanical survey across the Ngualla carbonatite in SW Tanzania showed a distinctly different and more luxuriant plant community over the carbonatite than over the surrounding silicate rich country rocks, with various species occurring exclusively on one type of rocks and soils and not on others (van Straaten 1995a).

In Finland, the recognition of a specific plant, heather (*Hylocomium myrtillus*) was used as a reliable indicator of carbonatites. When this heather is found growing over carbonatites, it is healthier and has a higher water content than heather growing in the surrounding area. The moist heather, in turn, has a higher spectral reflectance than the vegetation surrounding the carbonatite, and this pattern can be discerned using remote sensing techniques (Talvitie 1979).

Geochemical surveys of soils and stream sediments can also be important exploration tools, as exemplified by discoveries in Finland, Tanzania, Uganda, and Zambia (Paarma 1970; Reedman 1974, 1984; Sliwa 1991; van Straaten 1995a). Geochemistry can be an especially important indicator to differentiate a metamorphic limestone from a carbonatite. Geochemically, many carbonatites contain relatively high concentrations of Sr, Ba, REE, and Nb (Mariano 1989; van Straaten 1989). Geochemical 'pathfinders' in stream sediments and soils such as Nb, Sr, Ba, Zn, Rare Earth Elements (REE) and of course, P from apatite itself are often useful in finding igneous PR deposits (van Straaten 1989).

4.2.3 Metamorphic Phosphates

Most apatite mineralizations in metamorphic rock occur in skarns or in metamorphosed carbonates. Skarns are carbonate-rich, porous rocks formed in proximity to igneous intrusions in which chemically active brines migrate through the carbonate rock, resulting in apatite and other minerals crystallizing together with calcite and dolomite. Associated minerals involved in the crystallization are fluorite, titanite and phlogopite, among others. These deposits are generally small but may be locally important.

Metamorphosed carbonate sequences with large accumulations of apatite have been reported from Mozambique (Manhica 1991) and Sri Lanka (Dahanayake and Subasinghe 1988). The origin of these resources is, however, unclear. In the case of the Evate complex in Mozambique, it is speculated that the PR resources are in fact metamorphosed phosphorites (Manhica 1991). It is interesting to note that both major deposits (in Sri Lanka and Mozambique) contain large quantities of relatively rare Cl-apatites.

4.2.4 Residual phosphates

There are many economically important apatite deposits in the soils or regolith overlying carbonatites and other igneous phosphate deposits. Commonly, the mineralogy of these deposits is limonite–magnetite–apatite. These occur due to tropical weathering of carbonatites resulting from the decomposition and leaching of more soluble minerals such as the carbonates, leaving behind apatite, magnetite and other Fe-oxides as residual materials. An example of the soft friable nature and easy extractability of phosphates from weathered, residual carbonatite related deposits is depicted in Figure 4.6. Many of the large igneous phosphate deposits in tropical countries (Brazil, Uganda, Sri Lanka, Mozambique, Gabon) and also in Canada (Cargill, Martison) (Erdosh 1979) are actually residual phosphate deposits, derived from igneous and metamorphic PR deposits.

4.2.5. Guano Phosphates

There are two types of guano phosphate deposits: insular guano and cave guano. Insular guano is commonly formed from bird excrements and cave guano consists largely of bat excrements. The word ‘guano’ actually originated from the local Quichua word *huano*, written phonetically in Spanish as guano meaning ‘droppings of seabirds’. Strictly speaking, it is a misnomer to refer to bat dung as guano, but in modern usage, guano describes both bat and sea bird manure. While bat guano deposits are commonly of low tonnage, accumulations of bird guano can form extensive deposits (Figures 4.24).

Insular guano is relatively easy to find, easy to extract (mine) and can be easily transported as most deposits are located close to the sea. Although there were once substantial insular guano deposits in Peru and small tropical islands around the world, production is now steadily declining due to overexploitation of these resources and a low renewal rate.

A dramatic example of this pattern was demonstrated by guano overexploitation on the island of Nauru, located in the South Pacific. A booming economy was supported by guano excavation on this island from 1920 to 1980. However, when the ore was exhausted the economy completely crumbled. The complete stripping of the island also changed the environment leaving behind a scarred and barren wasteland.

Historically, Peru was one of the largest producers of bird guano, found on islands along the upwelling zone related to the cold Humboldt Current off South America. During the peak of the guano era (1840-1860), Peru exported large quantities of guano to Britain (200,000 t in 1850, and >300,000 t in 1858). In the 1850s guano was Peru's leading export and its largest source of revenue. Powerful business interests in Peru, Britain and the USA managed to maintain a supply of bird guano for farmers in Europe and North America until the late 1870s when other P and N resources came onto the market. Currently, with the widespread use of industrially synthesized fertilizers and depleting guano resources, consumption of guano has slowed considerably, but still remains a valued nutrient resource for organic growers and local farmers.

An interesting renewable guano recovery technique has been developed in Namibia. Here, guano is produced and harvested from artificial roosting platforms. Production of guano from these platforms in Namibia averages about 2,000 t of guano every year (van Straaten 2002).

Insular guano

Insular guano is formed primarily from accumulations of bird excrements. The Incas are famous for using seabird guano, which they collected on the rainless Pacific islands and arid coastal areas of Peru, and used for agriculture. The Guano Islands, located off the coast of Peru, are teeming with birds. This is due to the Humboldt Current that flows northward along the western coast of South America. As the cold ocean current strikes the shelf, there is an upwelling of nutrient-rich waters. This supports an enormous population of plankton, which in turn serves as food for a huge population of fish. The fish attract all kinds of birds: boobies, cormorants, pelicans and terns, which produce large amounts of guano. The arid climatic conditions in these areas ensure a very sparse vegetation cover and minimal loss of nutrients through leaching. Consequently, the large deposition of bird manure and the low leaching rate resulted in guano accumulations.

Bat guano

Cave guano is formed primarily of bat excrements containing insect and fruit remains. Bat guano also contains the bones of dead bats. Fresh bat guano contains 10-12% N and 2-3% P_2O_5. As the deposit ages, much of the N is lost through volatilization and leaching and the remaining material is enriched to about 8% P_2O_5. Because the deposits are relatively small, they are only of local importance and only viable for a limited length of time. They can also be health hazards for the miners of bat guano as their excavation can liberate high levels of NH_3 and fungi that cause the fungal disease *histoplasmosis* (also responsible for ‘the curse of the mummies tomb’). Although the incidence of infection is relatively low, the effects of *histoplasmosis* are serious, similar to tuberculosis, and can lead to death.

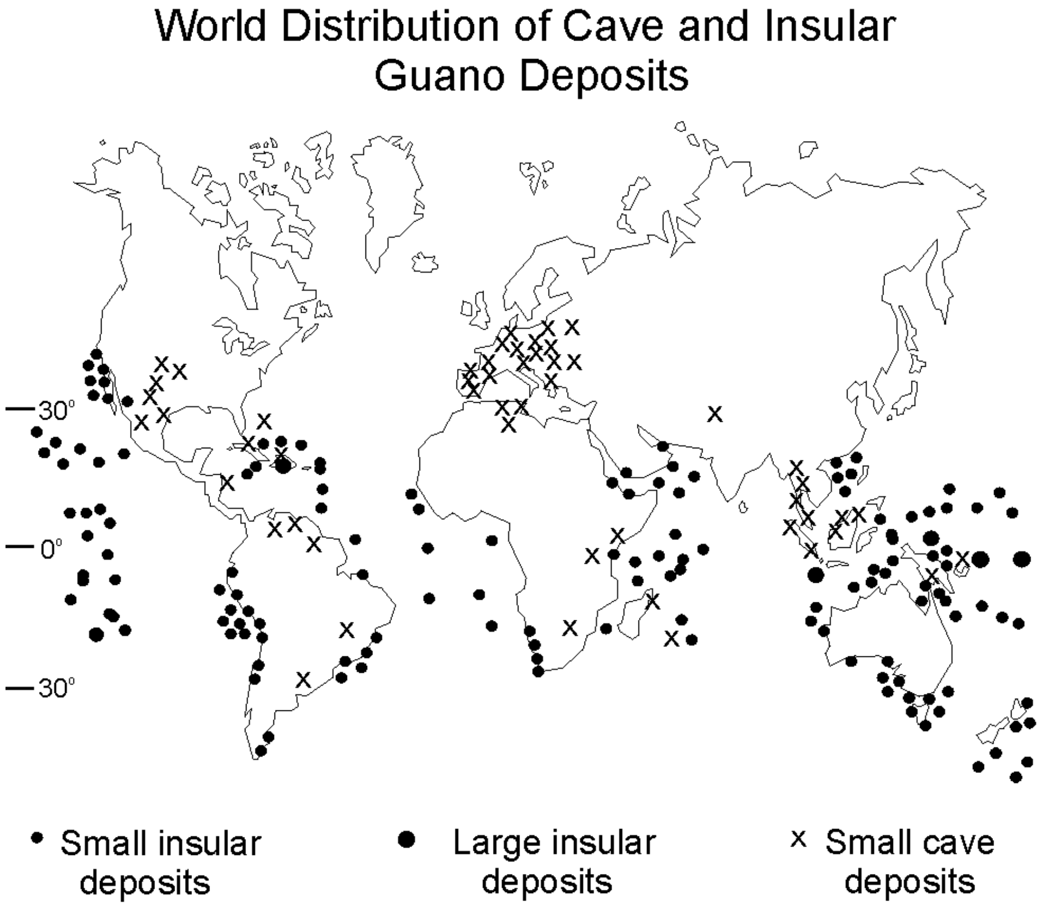


Figure 4.24. *World distribution of insular and cave guano deposits (after Cook 1984).*

4.3 Extraction, Beneficiation, and Further Processing

Following the discovery of phosphate rich rocks by geological, geophysical, geochemical and other means, a feasibility study is conducted to determine the economic viability of mining the deposit. On a global scale, phosphate rock resources are mined with grades as low as 4% P_2O_5 to grades as high as 39% P_2O_5.

Among the factors that determine the economic viability of a PR deposit are:

- geological and mineralogical parameters,
- geographic location,
- proximity to market,
- availability of other raw materials, e.g. sulphur, power,
- labour and a suitable legislative climate.

If the deposit is deemed economically viable the development of the mine site and the extraction of the ore will commence. The extracted ore is then usually put through the process of beneficiation, the physical upgrading and concentrating of ore by separation of ore from waste. Beneficiation of ore is then usually followed by "further processing."

4.3.1 Evaluation

During the evaluation process, the geologist measures and evaluates the shape and extent of the ore body through 'definition drilling' to determine tonnage and grade of the deposit. The geologist should also compile structural, hydrological and environmental details and should collaborate with the mining engineer to provide plans and practical aspects of mining the deposit.

In general, each deposit has it's own characteristics, and many are geologically complicated, requiring geological, geotechnical and environmental assessments and planning before they can be extracted. For easy and economic extraction of large deposits through open pit mining, mining engineers generally prefer flat-lying and thick unconsolidated homogenous PR resources with minimum structural, hydrological and potential environmental complications. A thick overburden requires costly stripping of the overlying soil with heavy earth-moving equipment.

The feasibility of mining the PR deposit is further influenced by the ease with which the ore can be physically extracted (mined) from the ground. Phosphates interbedded with other sediments require potentially costly separation processes to remove unsuitable 'waste' material.

Other important considerations at the onset of a mining venture relate to planning of the management of waste disposal and provision of closure plans after the resources have been exhausted. In many countries with active mining operations these aspects are standard parts of best management practices.

Transportation costs must also be factored in. Transportation costs are commonly high in remote areas but can be reduced if local industry has sufficient demand. Other factors such as infrastructure, availability of labour and legal aspects of extraction (mining code) are all part of feasibility studies that precede the actual mining. Land tenure is another very important issue in phosphate mining and processing. Land tenure is often complicated and controversial.

Fantel *et al.* (1985) estimated the costs of mining, processing and transportation for a selection of large-scale phosphate mines as ranging from US$ 26 to 70 per tonne. Because of these high costs, only large, near-surface deposits are usually extracted by mechanical means, for example with large earth-moving equipment and draglines. Smaller and lower grade deposits are seldom of interest to large companies. However, it is a geological truism that for every large deposit there are several small deposits. These smaller and lower-grade PR deposits are often worked by manual or semi-mechanical means and are potentially important for local resource development.

Appleton (1994) provides examples of small-scale phosphate extraction operations in India, Sri Lanka, Bolivia and Malawi, and demonstrates that semi-mechanized, appropriate technology can contribute to a cost effective supply of indigenous phosphates to be used directly in nearby agricultural communities. Production costs including extraction, crushing and grinding, bagging, transporting and overheads of phosphates used for direct field application in India, Colombia, Bolivia and Sri Lanka fluctuate from US$ 22 to 60 per tonne, with most of them in the range of US$ 30 to 40 per tonne. The actual blasting and opencast mining costs range from US$ 2 to 6 per tonne.

While the extraction and beneficiation costs in local semi-mechanized operations are generally lower due to the use of semi-mechanized approaches and low labour costs, large-scale operations enjoy the benefit of the ‘economy of scale’ using large excavators and handling large volumes. On a tonne by tonne basis of phosphate concentrate, the total production costs of extraction and beneficiation into phosphate concentrates is in the same order of magnitude in large-scale and medium-scale operations.

4.3.2 Phosphate Extraction (mining)

There are several methods to extract (mine) phosphate-bearing rocks from the ground depending on size, shape, depth below the surface and physical nature of the ore. The most common conventional extraction technique is by open pit mining. To start, the overburden, mostly soil, but also other rock layers, is removed and stored at designated sites beside the open pit. The overburden ranges commonly between 1 to 20 m. The ratio of ore to waste typically ranges from 1:5 to 1:10. Environmental concerns related to these activities include surface disturbance due to the removal of overburden and ore, and disruption of land use.

After the overburden is removed, the actual excavation proceeds with loosening-up of the phosphate ore. The method used depends on the hardness of the ore. Loose material can be scooped up by excavators and draglines and loaded directly onto large trucks that haul the material out of the pit to a processing site. Other surface extraction methods can involve the loosening up of unconsolidated ore by ‘monitors’, high-pressure water jets, and the subsequent pumping of the slurry to the processing site.

Other methods involve dredging, a method which involves removal of unconsolidated material from underwater deposits. The machines used for this type of extraction range from bucket-ladder dredges to suction dredges.

At present, most phosphate extraction of large deposits is carried out by conventional mining methods. However, many small phosphate deposits are mined by semi-mechanized methods, using manual means to loosen the material and transporting it by truck for processing. Manual extraction using pick and shovel is generally carried out only at very small phosphate deposits.

Very few phosphate deposits are mined by conventional underground methods. A proposed novel method of extracting unconsolidated phosphate ore from greater depth is that of ’borehole mining’. This technique entails drilling into the deposit, lowering monitors (high-pressure water jets) down the borehole and loosening unconsolidated phosphates at depth by remotely directing the water jet to the unconsolidated ore. The loosened materials is then pumped up the borehole as slurry and transported by pipeline to the processing facilities. The primary advantage of this system is that deep deposits of unconsolidated material can be safely extracted where conventional mining would be too dangerous. In addition, the environmental impact is generally lower because there is no removal of overburden and tailings can be put back into the excavated cavities. The expected disadvantages include possible changes in water quality near the mine and the potential for land subsidence, as the roofs of these cavities could potentially cave in. This extraction technique has been tested but is not yet in use in present day operations.

4.3.3 Phosphate Beneficiation (physical upgrading)

Following the extraction of the ore, the next step is beneficiation, which is the physical upgrading and separation of ore from waste. Phosphate rock resources are mined with grades as low as 4% P_2O_5. After beneficiation, the grade of the concentrate is usually 30 to 38% P_2O_5; close to 42%, the theoretical P_2O_5 content of fluorapatite.

After extraction from the mine, the ore is commonly stored in large piles and blended to provide a constant feed grade to the subsequent crushing and grinding units of the mill. The ground phosphate materials consist of a range of grain-size ore materials, the finest of which are commonly discarded and pumped into ‘slime ponds’. The coarser material is physically treated to separate phosphatic minerals (usually apatite) from unwanted accompanying ‘gangue’ minerals, such as quartz, calcite, and dolomite and iron minerals.

Gangue minerals occur either as exo-gangue, minerals that are distinct and not intergrown or are not coating the desired minerals, or as endo-gangue, minerals that are intergrown or as core to the desired mineral or as coating. The nature of the accompanying gangue influences the difficulty of beneficiation. Obviously, the value of a PR deposit is influenced by the ease with which the ore can be beneficiated and processed into a form that is optimal for the end user, the farmer.

The physical separation of the phosphatic minerals from the exo-gangue minerals is done by various methods, including gravity separation, magnetic separation and flotation. Of these, only flotation involves the use of chemical reagents e.g. the use of fatty acids and various oils. These separation techniques facilitate changes to the surface characteristics of ore particles in such a way that apatite minerals can be selectively removed from the exo-gangue minerals. This process is quite sophisticated and needs fine-tuning to be effective (Walker 1990). The liberation of endo-gangue minerals is even more difficult and requires even more sophisticated separation techniques. The example of Figure 4.25 from a phosphate ore of Ecuador (Hemmings 2003) illustrates the intimate mixture of various minerals within pellet-like phosphate grains before it can be processed.

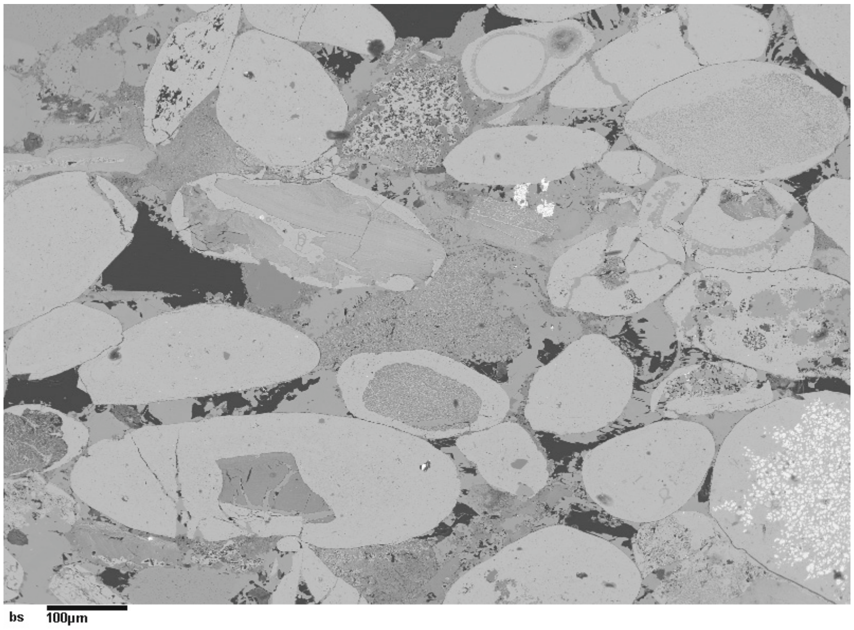


Figure 4.25. *Phosphate grains with inclusions from the Napo Formation, Ecuador. Light grey = apatite, dark inclusion (bottom) = quartz, light inclusions within apatite (left corner) = pyrite, grey (upper left corner) = calcite. (Hemmings, 2003, with permission).*

Various gangue minerals provide specific difficulties for the beneficiation and acidification processes.

- Silicate rich ores, especially ores with unreactive quartz (SiO_2), pose mainly physical dilution problems and no chemical problems. However, if the silicates are made up of acid soluble silicates or clays, they may require gravity and size separation, physical 'desliming' processes or calcinations, as well as heat treatment (Notholt 1994).

- PR ores high in magnetic Fe oxides, for example igneous phosphate deposits, are upgraded with relative ease with low intensity magnetic separators. On the other hand, Fe-oxides and hydroxides like hematite and goethite (limonite) pose a challenge, as low intensity magnetic separation alone is not effective. Upgrading through high intensity magnetic separation techniques or flotation are needed to reduce the combined Fe_2O_3 and Al_2O_3 content to less than 5% as required by the conventional wet-process acid production (Notholt 1994). If the ore is to be considered for partial acidulation processing, the Fe_2O_3+Al_2O_3 content is crucial for the agronomic effectiveness of the product. Concentrations of >10% Fe and Al oxides considerably reduce the effectiveness of partially acidulated PR (Hammond *et al.* 1991).

- The presence of Mg in carbonate and other forms constitutes a major problem in the traditional processing of phosphate rock with the wet acidulation process. Process engineers require MgO concentrations of less than 1.5% in the ore, as magnesium compounds (commonly in the form of dolomite) create high viscocities in phosphoric acid and easily precipitate when ammonium is used to produce liquid ammonium based phosphate fertilizers (Notholt 1994).

- Phosphate ores with high organic matter content also create problems for the conventional acidulation process through the formation of undesirable foams. To remove the organic matter the PR is usually calcined through oxidation (Notholt 1994).

- Phosphate rock ores high in Fe-sulphides, mainly pyrite, are considered unsuitable for conventional acidulation processes and therefore pyrites are removed by various gravitational or roasting processes. However, Lowell and Weil (1995) demonstrated that a mixture of PR and small amounts of pyrite can have considerably positive effects with regards to in-situ PR acidulation and S nutrition.

- PR ores with carbonate matrix, especially calcite and dolomite, pose a special problem for the conventional acidulation process. Considerable amounts of acid will be spent to remove the calcite before the acidulation of apatite, the mineral of interest. Several operations use flotation methods to reduce the carbonate content in the PR concentrate. This requires fine-tuning of the flotation process using various organic and inorganic additives to achieve surface modification for floating the apatite minerals. This is more easily achieved using fluorapatite ore of igneous origin rather than sedimentary phosphate ores. Conventional phosphate beneficiation plants aim at reducing the MgO content in the concentrate to 0.5-0.6%.

- Chlorine (Cl) as the chloride ion (Cl^-) is undesirable because it causes corrosion of the processing equipment, so any potential phosphate ore is required to contain less than 0.1-0.2% Cl (Notholt 1994). Chlorides occur in some phosphate ores from salts and can easily be washed out.

- Ores high in Al and Fe phosphates are commonly found in the weathering environment of many phosphate deposits, for example in Senegal. These aluminum-phosphates (crandallite and millisite) are only calcined and marketed as fertilizers and animal feed (Flicoteaux and Hameh 1989). Also, the use of calcined calcium-iron-phosphates in flooded rice fertilization bears some promise (IFDC 1998).

Phosphate rock resources have highly variable mineralogical and chemical characteristics that require tailored beneficiation to be effective in the classical acidulation processes commonly applied by the phosphate industry. If other processes are used they should be judged according to their suitability in addressing the mineralogy and chemistry of the phosphate rock, their geographic location, infrastructure availability, capital investment and the energy required to produce appropriate P-based fertilizers best suited to the local soil conditions. However, in the end it is most important that the phosphate rock fertilizer be affordable and acceptable to the farmers.

4.3.4 Phosphate Processing: Acidulation

Following beneficiation, the phosphate concentrate is dried, stored and further processed into soluble P-fertilizers. In large-scale P-fertilizer operations this is done using the wet-process acid (WPA) and standard process technology (Young and Davis 1980) which transforms the concentrate into a soluble form. The principal process is that of acidulation, using various kinds of acids. The primary acids used in conventional WPA production systems are sulphuric or phosphoric acids, but nitric and hydrochloric acids are also used in some plants (Figure 4.26).

These acids are reacted with PR concentrates (commonly 30-38% P_2O_5) derived through the beneficiation processes described above. Impurities in the starting materials can cause considerable processing problems as described above (McClellan and Gremillion 1980). Variations on this process are used to produce a variety of P fertilizers including single superphosphate (SSP), triple superphosphate (TSP), mono-ammonium phosphate (MAP), and di-ammonium phosphate (DAP).

Sulphuric acid is produced from various S-sources, either from elemental S (‘brimstone’), which is almost pure S, or from pyrite (FeS_2). The use of pyrite poses some potential environmental problems, particularly problems with elevated concentrations of various heavy metal elements that are often associated with pyrite.

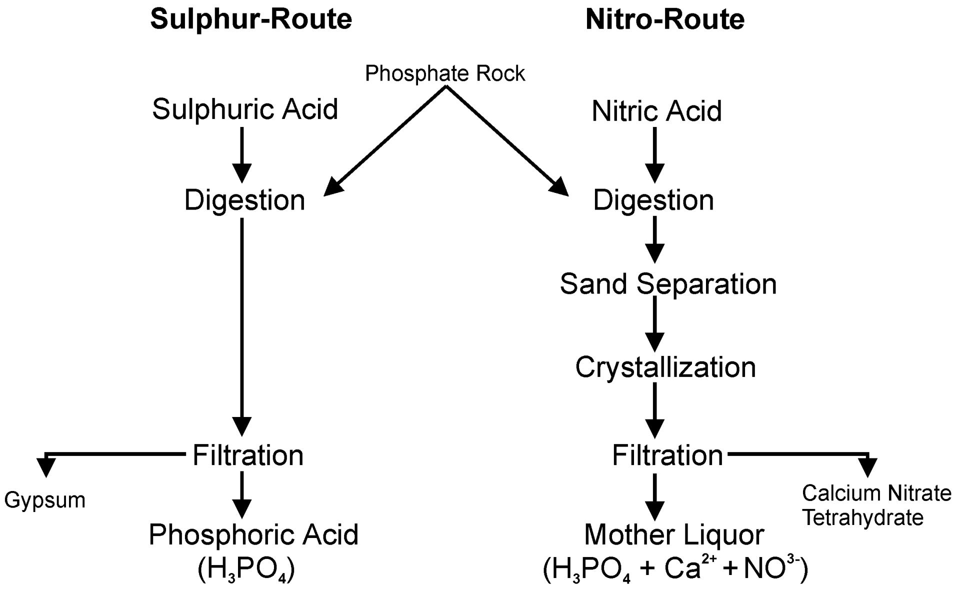


Figure 4.26. *Acidulation of phosphate rock with sulphuric and nitric acid (modified after Conradsen and Kongshaug 1993).*

An increasing percentage of the world's phosphate fertilizers are the so-called nitro-phosphates are derived from nitric acid-based processes (Støren 1992), which use nitric acid instead of sulphuric or phosphoric acid. These processes were developed in Norway in the 1930's and are used in recent years mainly in Europe. A simplified flow chart detailing comparing nitric acid-based processes to suphuric acid-based processes is shown in Figure 4.26. It should be noted that the nitro-phosphate process does not create any gypsum waste.

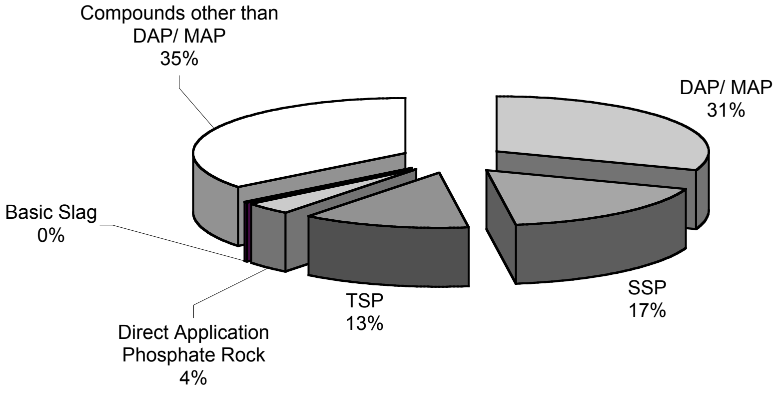


Figure 4.27. *World phosphorus fertilizer use in 1990 (after Schultz 1992).*

Production of P-Fertilizers

Figure 4.27 shows the global P fertilizer usage in 1990 according to composition (Schultz 1992).

Production of Single Superphosphate (SSP)

The production of single superphosphate (SSP) is achieved by reacting apatite concentrates with sulphuric acid. The reaction of apatite with sulphuric acid is as follows:

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 17H_2O \Leftrightarrow 3Ca(H_2PO_4)_2{\cdot}H_2O + 7CaSO_4{\cdot}2H_2O + 2HF \quad \text{(equation 4.2)}$$

F-apatite sulphuric acid monocalcium phosphate gypsum

The resultant product SSP contains a mixture of the soluble P source, mono calcium phosphate (MCP) in the form of $Ca(H_2PO_4)_2{\cdot}H_2O$ as well as gypsum ($CaSO_4{\cdot}2H_2O$) at a ratio of 1:1 (50% MCP, 50% gypsum). SSP contains about 17 -20% P_2O_5, of which 90% is water soluble (as MCP) and about 16% S (in gypsum).

Production of Triple Superphosphate (TSP)

The production of triple superphosphate (TSP) is a two-step process. It starts with the production of phosphoric acid by reacting apatite with sulphuric acid according to equation 4.3, followed by the reaction of the phosphoric acid produced in step one with apatite (equation 4.4).

$$7Ca_{10}(PO_4)_6F_2 + 70H_2SO_4 + 140H_2O \Leftrightarrow 42H_3PO_4 + 70CaSO_4{\cdot}2H_2O + 14HF \quad \text{(equation 4.3)}$$

F-apatite sulphuric acid phosphoric acid gypsum

$$3Ca_{10}(PO_4)_6F_2 + 42H_3PO_4 + 30H_2O \Leftrightarrow 30Ca(H_2PO_4)_2{\cdot}H_2O + 6HF \quad \text{(equation 4.4)}$$

F-apatite phosphoric acid monocalcium phosphate

The final product contains 44-52% P_2O_5, almost 100% of which is water soluble, without any S. The two-step process of TSP production results in a highly concentrated, highly soluble form of P. However, in the process, large amounts of gypsum (phospho-gypsum) are left behind, considered to be ‘waste’. If nitric acid is used instead of sulphuric acid in the first step, gypsum is not produced as a waste material (Figure 4.26).

The spot price for bagged TSP, free on board (f.o.b.), in North Africa was US $186 in March 2005.

Production of N & P fertilizers

The widely used N and P fertilizers Mono- and Di-Ammonium phosphates (MAP and DAP respectively) are produced by a reaction of phosphoric acid with various amounts of ammonia. The equations for the production of MAP and DAP are shown below.

Mono-Ammonium Phosphate (MAP)

$NH_3 + H_3PO_4 \rightarrow (NH_4)H_2PO_4$ (equation 4.5)

MAP contains 52-55% P_2O_5, and 11% N_2. The cost and freight (cfr) of MAP (for example from the US to Argentina) was US $280 per tonne in July 2005 (The Market, Fertilizer News July 2005). MAP is best suited for calcareous soils where the short spike in local acidity keeps the P in solution longer, delays precipitation of insoluble Ca–P species and increases the availability of micronutrients.

Di-Ammonium Phosphate (DAP)

The process involved in the production of DAP is similar to that for MAP. The difference is that instead of 1 unit NH_3 reacted with phosphoric acid (for MAP), there are 2 units of NH_3 reacted with phosphoric acid according to equation 4.6.

$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4$ (equation 4.6)

DAP contains about 46% P_2O_5 and 18% N_2 and is not acid producing (pH = 8).

The spot price of DAP at the U.S. Gulf, in July 2005, was US $252-256 per tonne, bulk, free on board (f.o.b.) (www.fertilizerworks.com/html/themarket.pdf). DAP can be used effectively on many soils.

Nitro-phosphates

The nitrophosphate process uses nitric acid for digestion according to equation 4.7 and flow diagram (Figure 4.26).

$Ca_{10}(PO_4)F_2 + 20HNO_3 \rightarrow 6H_3PO_4 + 3HF + 10Ca(NO_3)_2$ (equation 4.7)

The principal inputs of nitrophosphate based fertilizer production are phosphate rock, nitric acid, ammonia, CO_2, water, energy and air. The principal outputs of the process are various complex phosphate fertilizer products, $CaCO_3$, sand, process condensates, energy and air (Støren 1992). It should be noted that no phospho-gypsum is produced, avoiding by-product disposal problems. Also, the process is independent of sulphur inputs. Environmentally, lower amounts of solid, liquid and gaseous effluents are discharged into the environment during the nitrophosphate process than by sulphuric-acid based processes. The lack of solid wastes and lower emissions makes this process environmentally more advantageous and acceptable in the European Union. However, the integrated nitrophosphate processes are technically complex, contributing to higher production costs than the traditional wet-process acid (WPA) production used in the United States and many other countries.

4.3.5 Lesser known processes

There are several lesser-used modification processes that aim at making low reactive PR resources more plant available (Table 4.9). They can be summarized as physical, physico-chemical, chemical and biological modification processes.

Table 4.9. *Phosphate rock modification processes.*

Type of modification	Method
Physical	Fine grinding
	Mechanical activation
Physico-chemical	Thermal processes
Chemical	Acidulation
	Partial acidulation
	Mixing with Sulphur
	Heap leaching
	Blending and granulation
	Ion exchange
Biological	Phospho-composting
	Green manuring
	Biosolubilization with microorganisms
	Use of coir dust
	Mycorrhizal inoculation

Physical modification

Fine Grinding

Crushing and fine grinding of the PR ore are common processes that precede almost all other processes. Crushing and grinding are very energy intensive processes. Crushing and grinding can be done by various primary and secondary crushing processes followed by grinding with ball and rod mills, semi-autogenous grinding (SAG) mills, or in the case of low-tech processes, by local ball mills, or other grinding equipment.

Lim *et al.* (2003) demonstrated that ‘mechano-milling’ with ball mills and high-energy inputs induced physical and chemical reactions in finely ground PRs. The grinding increased the proportion of amorphous material and subsequently the effectiveness of PR. The results of laboratory experiments with 6 different PRs indicate that the fertilizer’s relative effectiveness (FRE) increased sharply with only short milling times of one hour or less. For some of the PRs (from Egypt and Queensland/Australia) the effectiveness tripled (Lin *et al.* 2003).

Mechanical Activation

Another way of processing low reactive PR is that of mechanical activation using rotary-chamber vibrating mills (Gock and Jacob 1984) or other mills with and without grinding aids to prevent agglomeration. According to Gock and Jacob (1984), dry milling techniques not only reduce the grain size of the PR but also open up defect sites in phosphate minerals, and subsequently change the solubility parameters of the PR as a function of milling time. X-ray diffraction and infrared data supported by citrate solubility tests over time provide evidence for mineralogical changes that enhance solubility of the PR (Gock and Jacob 1984). Citric acid tests of mechanically activated Togo PR showed increasing solubilities with increased energy inputs for grinding.

Physico-Chemical Modification

One of the better-known physico-chemical modification processes is through thermal processes resulting in thermophosphates. There are three different processes: calcination, sintering and fusion.

- Calcination is a thermal process that takes place at elevated temperatures, but well below the fusion temperature. This process breaks down carbonates and drives off CO_2. Calcination processes are also used to promote the transition of francolitic phosphates to more stable but unreactive fluorapatites (Lehr 1980).
- Sintering involves the agglomeration of small particles to form larger ones without reaching the melting point.
- Fusion involves subjecting minerals, ores, concentrates and other inorganic matter to thermal energy above the melting point. In the case of phosphate rock, fusion would require heating the PR to high temperatures above the melting point.

Thermophosphates include Rhenania phosphate, Fused Magnesium Phosphate (FMP) and calcined Al-phosphates. The best-known thermal phosphates are Rhenania phosphates and Fused Magnesium Phosphates (FMP).

Rhenania phosphates

In the Rhenania process, soda ash (Na_2CO_3) is mixed with PR and silica and subjected, in the presence of steam, to temperatures between 1100^{o}C and 1200^{o}C. The resultant sodium-silicophosphate is thereafter quenched with water and ground to a fine powder.

$$\underset{\text{F-apatite}}{Ca_{10}(PO_4)_6F_2} + \underset{\text{soda ash}}{4Na_2CO_3} + SiO_2 \underset{1200^{o}C}{\rightarrow} \text{Ca-Na silicophosphate} + NaF + CO_2 \quad \text{(equation 4.8)}$$

Rhenania phosphates have high solubilities and are suitable for tropical soils. In particular, Rhenania phosphates are agronomically effective in high P-sorbing soils of Brazil, Nigeria, Ethiopia and Congo. In western Kenya, the Rhenania phosphates were produced and used in the 1950s using Busumbu PR from Uganda and soda ash from Lake Magadi in Kenya (Mathers 1994). The main disadvantages of Rhenania phosphates are the high costs of production, largely due to high-energy requirements and their reliance on the availability of soda ash and large amounts of water for quenching.

Fused Magnesium Phosphate (FMP)

Fused Magnesium Phosphate (FMP) is formed by mixing concentrated PR sources with Mg-silicate sources such as olivine or serpentine. The mix is then fused at furnace temperatures of about 1500-1600°C. Immediately after fusion, the fused glass is quenched and then finely ground (Cekinski and da Silva 1998).

$$\text{Apatite + Mg source (olivine, serpentine or dolomite)} \underset{\text{electric furnace temperature = }1500^{o}C}{\rightarrow \text{ glass } \rightarrow} \text{quenching with water}$$

Fused Magnesium Phosphate has the advantage of being a slow release Mg phosphate fertilizer that is effective in tropical soils, but it has the limitation of having high energy and water requirements (25-30 tonnes of water per tonne of FMP). To successfully operate a FMP operation, a source of cheap electricity is required as well as large amounts of cheap water. However, efficient water recycling and use of energy resources can reduce the costs of FMP considerably. Another advantage is that the scale of the operation of FMP can be varied, from large scale to small scale. FMP is currently produced in Japan, Brazil and China.

In New Zealand several alternative techniques with the fusion of phosphates were tested in the past, during shortages of sulphur. The production of fused phosphate fertilizers using phosphate rocks, glauconitic greensands and dolomite requires fusion at approximately 1250°C, and subsequent quenching with water (Cornes 1948). Other experiments, using phosphate rocks from the Pacific island of Nauru and locally available Mg rich silicate rocks like dunite and serpentinites, were conducted in the early 1950s (Billinghurst and Nicholson 1956).

Calcined Al-phosphates

Another type of thermophosphate is calcined Al-phosphate. Al-phosphates such as crandallite, wavellite or millisite are calcined at temperatures of about 550°C. The calcined product contains 32% P_2O_5 and has a high citrate solubility (>12%). In Senegal, the locally produced calcined Al-phosphates are largely used for animal feed production. Direct field application of calcined Al-phosphates for crop production has shown positive yield results on P-deficient, neutral to alkaline soils. Under these conditions the solubility of calcined Al-phosphate increases with increasing soil pH. The International Fertilizer Development Center (IFDC) conducted experiments between 1996 and 1998 and demonstrated that some thermally treated Al-phosphates (e.g. from the Christmas Islands) are 83-93% as effective as TSP for flooded rice under alkaline soil conditions (IFDC report 1998).

In Brazil, locally available aluminum phosphates were tested using the locally available Al-phosphates as source material. A modern fluidized bed reactor was used to calcine the Al-phosphates (Guardani *et al.* 1989).

Chemical modification

Full acidulation

Full acidulation is the so-called wet-process acid (WPA) production described earlier using the methods and materials used to produce single superphosphates (SSP) and triple superphosphates (TSP).

Partial acidulation

Partial acidulation of phosphate rock (PR) is a method developed over the last few decades that is different from ‘full’ acidulation. In the ‘full’ acidulation process with sulphuric acid (to produce SSP) and phosphoric acid (to produce TSP) the theoretical stoichiometric quantity of acid is used to fully convert insoluble phosphate rock (principally apatite) to water soluble mono calcium phosphate (MCP). For the production of partially acidulated phosphate rock (PAPR), only a portion of the quantity of acid to convert PR into MCP is used and the remaining unreacted P will only be slowly released (Hammond *et al.* 1986). The percentage of acid used to prepare PAPR, relative to the quantity of acid, which would be required for full acidulation, is expressed as % PAPR (Hammond *et al.* 1986). Part of the MCP (with a pH of 1-2) is thought to react with the unacidulated part of the PR, resulting in added P being released.

The technology is most effective when using PR material that is low in Fe and Al oxides (Hammond *et al.* 1989, Chien and Hammond 1989). In pot and field trials, Bationo *et al.* (1990) could show that the $Fe_2O_3 + Al_2O_3$ content played a major role in the effectiveness of partially acidulated sedimentary PR resources. Partially acidulated Fe+Al-poor phosphate rocks were agronomically more effective than Fe+Al-rich phosphate rocks. A similar finding was made by Butegwa *et al.* (1996) who tested the agronomic effectiveness of unacidulated and partially acidulated phosphate rocks from a carbonatite in Uganda. Partial acidulation of an unreactive igneous PR with a low Fe + Al-oxide content was agronomically more effective than partial acidulation with Fe and Al-oxide rich P rocks. The study concluded that the partial acidulation technique is most successful and effective with PR materials that have low Fe+Al oxide contents.

Advantages of this method include the requirement for less acid, and the ability to use P rocks that are chemically less suitable for full acidulation. The robustness of the technology and the possibilities of low-tech applications have been demonstrated in Zambia, where a local cement mixer was used for the partial acidulation of an igneous unreactive PR (Borsch 1993). So far, however, the major barrier of this technique is the unavailability of inexpensive locally available sulphuric or phosphoric acid.

Although successful in many field trials in many countries, PAPR is only slowly gaining acceptance. A 150,000 t capacity PAPR plant started operating in Venezuela in 1999 (Casanova 2003).

Mixing and coating with sulphur

Bromfield (1975) demonstrated that mixing phosphate rock with sulphur was as effective as superphosphate in the Alfisols of Northern Nigeria. Coating apatite grains or granulating apatite with S has also been tested by Swaby (1975), Rajan (1982, 1983, 1987) and Schofield *et al.* (1981). The basic process is acidulation of the phosphate rock. But instead of acidulating the PR ore in the fertilizer plant, acidulation takes place ‘in-situ’, in the soil. Sulphuric acid is produced in the soil by oxidation of S, probably mediated by micro-organisms, and in turn the sulphuric acid acidulates the apatite in the PR. In the product ‘Biosuper’ (Rajan 1982), PR is granulated with S and then inoculated with *Thiobacillus ssp*. bacteria that enhance the oxidation of S. The reaction of apatite with the in-situ produced sulphuric acid will transform the apatite into $Ca(H_2PO_4)_2{\cdot}H_2O$ (mono calcium phosphate monohydrate) and gypsum.

Heap Leaching

Heap leaching of phosphate rocks is a technique that has been suggested as a cheap method to recover P from waste heaps of the phosphate industry or from low grade PR resources (Habashi 1989, 1994). Heap leaching is an extraction technique already practiced on an industrial scale for the recovery of low-grade gold, uranium and copper ores. In this method, the low-grade ore or ‘waste’ material is stockpiled into heaps on large impermeable plastic sheets, where it is subjected to slowly percolating solvents. The leach solution is collected for further processing. In the case of phosphates, low-carbonate or carbonate-free PR ores are piled in heaps with an impermeable liner at the bottom. Nitric acid at 20% strength, or hydrochloric acid at 10% strength is then added to percolate through the heap. The phosphate minerals dissolve during the acid’s passage through the heap and P in the form of mono calcium phosphate will leach out at the bottom of the heap and can be evaporated into marketable products. Products that can be formed by processes using dilute HNO_3 or HCl include:

- $Ca(H_2PO_4)\cdot Ca(NO_3)_2\cdot 2H_2O$ (with HNO_3 leaching), or
- $Ca(H_2PO_4)\cdot CaCl_2\cdot 2H_2O$ (with HCl leaching).

This unique technique has been tested so far only in laboratories in Montreal, Canada, but not yet on an industrial scale (Habashi 1989, 1994). The same research group also proposed to use in-situ leaching techniques to extract P from underground phosphate ores (Habashi 1989). Biological heap leaching techniques (bioleaching) using organic acids produced by micro-organisms requires more testing.

Blending and granulation/compaction

In order to enhance the agronomic effectiveness of unreactive or low reactive phosphates, Chien *et al.* (1987, 1996), and Hammond *et al.* (1989) conducted experiments using a blending and compacting technique whereby PR is blended with water-soluble phosphates, commonly TSP, and compacted. Chien *et al.* (1987) demonstrated that small amounts of water-soluble phosphates act as a starter dose for the plants until P from the PR becomes available to the plants. It is thought that the starter dose of the water-soluble TSP will stimulate root development and the denser root system will then increasingly utilize the remaining PR (Chien *et al.* 1996). This technique, with various blending ratios, has shown promise in many agronomic tests (Chien *et al.* 1987, 1996; Govere *et al.* 1995; van Straaten and Fernandes 1995; Mnkeni *et al.* 2000).

In practice, the technique employs either compacting the water-soluble P source (e.g. TSP) with PR on a dry base, or pelletizing the mix in a rotary pelletizer on a wet base (Lupin and Le 1983). With this technique, not only PR and TSP can be mixed, but several more water-soluble components can be added as well, for example, urea and KCl (Chien *et al.* 1987; Chien and Menon 1995a). Compaction techniques have low capital and energy requirements and can be carried out in units of various scales. The other technique, pelletizing TSP with PR, is also a low capital, low energy requiring technique which has been tested in several places in Africa (van Straaten and Fernandes 1995) and Indonesia (Kharisun, 2002, pers. comm.). In Uganda, the laboratory and field tests with compacted blends of igneous PR and TSP at a ratio 50:50 (with 5% urea as a binder) showed high citrate solubilities of P and a very high relative agronomic effectiveness of above 88% (Butegwa *et al.* 1996). These data suggest that blending and compacting can improve the effectiveness of low reactive phosphate rocks and that this technique has the potential to be used as an effective substitute for water-soluble P fertilizers. Similar results have been achieved in several countries (Chien *et al.* 1987, Chien and Menon 1995a; Mnkeni *et al.* 2000). Detailed studies of pelletized phosphate rock blends in Zimbabwe showed some of the underlying principles of in-situ acidulation as a result of the reaction of apatite with hydrolyzed TSP (van Straaten and Fernandes 1995).

All of the modification techniques described above are based on low-cost alternatives to conventional water-soluble phosphate fertilizers. Most of the methods described are based on local resource utilization and appropriate technologies. While the products from these modification techniques might not be of the same quality compared to imported water-soluble P fertilizers, they provide some promise for local utilization by small-scale farmers in tropical and sub-tropical countries and in remote locations. Many of the techniques and products have been studied in pot and field trials in developing and developed countries. Each process, however, has distinct place value, as the available raw materials differ from place to place, and technologies appropriate in one location might not be appropriate in another.

PR dissolution process based on ion exchange

The ion exchange phosphate process is an ion exchange process that has been tested by Lai and Eberl (1986). This process is based on the principle that a zeolite sink can sequester Ca ions released during the dissolution of PR, and exchange them with ammonium in the NH_4-exchanged zeolite. This will further the dissolution of PR and, at the same time, release NH_4^+ (Lai and Eberl 1986). The activity of Ca^{2+} in the solution will be lowered and more PR will dissolve (Lai and Eberl 1986). The ion exchange phosphate process has the advantage of slowly releasing NH_4^+ and $H_2PO_4^-$ as well. The PR dissolution process is based on the following reaction (equation 4.9).

$$\text{Phosphate rock} + NH_4^+\text{-exchanged zeolite} \Leftrightarrow \text{Ca-zeolite} + NH_4^+ + H_2PO_4^- \quad \text{(equation 4.9)}$$

Biological modification processes

There are several modification processes that make use of biological processes, including phospho-composting, biosolubilization with microorganisms, green manuring and mycorrhizal optimization of phosphate uptake. The principal processes in these biological modification processes of P rocks are acidulation and strong bonding with organic molecules, chelation, of Ca^{2+}.

Phospho-composting

Phospho-composting, that is the incorporation of PR into compost heaps with the aim of making the insoluble PR more soluble, has been successfully tested in many places, mainly in India (Singh *et al.* 1983; Bangar *et al.* 1985; Singh and Amberger 1990, 1991, 1998). During the decomposition of organic matter, acids are produced that can enhance PR dissolution. As microorganisms in the compost pile require P as a nutrient for growth, they convert the inorganic mineral P into more plant available forms. Ca-chelation by organic functional groups or anions produced during composting can contribute to increased PR dissolution (Bangar *et al.* 1985).

Not all composting systems favour PR dissolution. In many composting systems the pH is alkaline and these conditions do not faviur dissolution of PR. For example, trials in Zimbabwe using unreactive phosphate sources from the Dorowa carbonatite complex and composted cattle manure showed insignificant solubilization of F-apatite (Chirenje 1996). It is speculated that two factors contributed to this very low solubilization: the nature of the phosphate rock (igneous fluorapatite), and the high pH (8-9) of the cattle manure based composts, which were not conducive to apatite dissolution.

In contrast to the findings that PR dissolution was very low in composts using cattle manure alone, Mathur *et al*. (1987) demonstrated that composting can substantially solubilize igneous PR into plant available P when low pH composts are used, for example composts containing low pH peat. The most effective solubilization was achieved by composting igneous PR of Kapuskasing, Northern Ontario, Canada, with farmyard manure and peat, or liquid manure and peat under aerobic conditions. After composting the farmyard manure plus peat plus PR and liquid manure plus peat plus PR for 2-4 months, 63.9% and 74.4% respectively of the igneous PR was solubilized into a plant available form (Mathur *et al*. 1987).

Research in Zimbabwe using a pelletized blend of 30-50% PR from Dorowa and 10 -50% locally produced TSP (with acidifying properties) subsequently incorporated into cattle manure and composted showed enhanced crop response. This intervention resulted in yield increases by a factor of 2- 4 (Dhliwayo 1999, Tagwira 2003). This method is successfully used by hundreds of resource-poor farmers on small farms in communal areas of Eastern Zimbabwe (Mbwera pers. communication, 2006).

Combination with green manure

Research with green manure has been carried out in various developing countries in an attempt to increase PR dissolution. A major success was achieved in Western Kenya with the direct application of PR in combination with green leaf manures especially *Tithonia diversifolia*, a common shrub grown along roadsides and fields. The combined application of PR with the *Tithonia* biomass resulted in increased yield of corn/maize, the staple food in Kenya (Sanchez *et al.* 1997; Jama *et al.* 2000; Jama and van Straaten 2006). One of the explanations for the increased agronomic effectiveness of PR + *Tithonia* is related to the role of organic anions that compete with phosphate ions for adsorption sites in the soils. Investigations in other tropical countries indicate that under certain conditions, green manure of legume crops, for example cowpea and *Crotolaria,* in combination with low reactive PR resources is suitable as a preceding crop for corn/maize, resulting in higher yields (Muleba 1999).

Biosolubilization with microorganisms

The process by which insoluble apatite in phosphate rocks breaks down is known as phosphate solubilization. This process is carried out by microorganisms that excrete metabolites, mainly organic acids. Microbiologists conducted research to increase plant-available P by utilizing biological processes to extract P, a less energy intensive and less costly method than conventional P-fertilizer production. In laboratory and batch-type experiments as well as initial field experiments, microorganisms, especially filamentous fungi, principally *Penicillium* and *Aspergillus* species were inoculated into plant residues together with phosphate rock material (Kucey 1983, 1987, 1988; Asea *et al.* 1988; Cerezine *et al.* 1988; Kucey *et al.* 1989; Nahas *et al.* 1990; Vassilev *et al.* 1995; Nahas 1996; Bojinova *et al.* 1997; Goenadi *et al.* 2000; Narsian and Patel 2000; Sahu and Jana 2000; Gyanschwar *et al*. 2002; Welch *et al.* 2002; Kpomblekou-A and Tabatabai 2003). The plant residues (for example residues from sugar cane processing and cassava 'wastes') provided the carbon and energy sources for phosphate solubilizing fungi. These fungi (e.g. *Aspergillus niger*) produce organic acids (predominantly citric acid), which in turn react with PR and produce P in the plant-available form.

Experiments in Brazil, Indonesia, Japan and Spain as well as in Canada have shown that this innovative method has a great potential to produce inexpensive biological P fertilizers using local PR resources and locally discarded plant wastes (Kucey 1983, 1987, 1988; Asea *et al.* 1988; Cerezine *et al.* 1988; Kucey *et al.* 1989; Nahas *et al.* 1990; Vassilev *et al.* 1995; Nahas 1996; Bojinova *et al.* 1997; Goenadi *et al.* 2000; Narsian and Patel 2000; Sahu and Jana 2000). Research at the University of Guelph, Canada, is currently underway to optimize this method of biomobilization and bioextraction of P from PR for potential application in sustainable agricultural systems (Schneider and van Straaten 2005; Arcand and Schneider 2006).

The acidulation of phosphate rocks by organic acids produced during fermentation of agricultural residues is a strategy with some promise in environments where PR deposits are remote, where the importation of expensive acidulating reagents is prohibitive, and where no other modification techniques are available. Characterization studies and research need to be carried out on the suitability of various local organic acid producing agricultural wastes, such as cassava wastes, banana wastes, etc. On an industrial scale, it is possible to produce various organic acids from sugar cane wastes and banana wastes (Mane *et al.* 1988; Sassi *et al.* 1991).

Combination with coir dust

Another method that has some merits is the use of PR in combination with a waste product from the coconut industry – coir dust. This is a solid organic residue obtained after the extraction of coconut fibres from coconut husks. Coir dust is discarded in numerous coconut processing operations in South and Southeast Asia, as well as in some parts of Africa. Coir dust, largely made up of lignin, cellulose and hemicellulose with low Ca and low Fe concentrations, has a pH of 5.5 - 6.0, a high surface area and a high cation exchange capacity (Verdonk 1983). Experiments with unreactive PR from Sri Lanka and coir dust showed increased rates of dissolution (Perera 1995). This increased PR dissolution is thought to be related to the low exchangeable Ca concentration in the coir dust, which could act as a sink for Ca-ions and thus enhance the dissolution of PR.

Innoculation with Mycorrhizae

Mycorrhizae, which literally means 'fungus-root', refers to the symbiotic relationship between plants and the fungi that colonize the plant roots during active plant growth. This relationship is beneficial to both parties, as the plant receives increased nutrients and water, and the fungi gain plant produced carbon sources. It is well known that mycorrhizae can enhance P-acquisition in P deficient soils by extending the root system and exploring more soil volume for P and other nutrients (Marschner and Dell 1994). However, there are conflicting reports as to whether mycorrhizae will actually increase the release of P from PR.

Recent findings indicate that the growth of mycorrhizal plants can be enhanced when PR is applied. There seems to be a synergistic interaction between mycorrhizae and P-solubilizing microorganisms, such as phosphate-solubilizing rhizobacteria (Barea *et al.* 2002). Research in P-deficient boreal, temperate forest soils has shown that ectomycorrhizal fungi are important for the acquisition of P by trees and that apatite stimulated mycelial growth (Wallander 2000; Landeweert *et al.* 2001; Blum *et al.* 2002; Hagerberg *et al.* 2003). No research has been carried out as yet on ectomycorrhizal fungi and P acquisition from apatite in forest and savannah environments of the tropics.

Other PR dissolution methods

Other dissolution techniques to break down PR into more soluble and plant available forms include mixing PR with pyrite and embedding PR in low pH peat, both indirect acidulation techniques. The oxidation of pyrite produces sulphuric acid that can theoretically enhance PR dissolution. Laboratory studies have shown that PR incubated with pyrite can enhance P release (Lowell and Weil 1995). When a mix of pyrite and Mussoorie PR from India was incorporated into decomposing cattle manure, the agronomic effectiveness of the P- and S-enriched manure was enhanced (Gupta *et al.* 1988). Experiments in Sri Lanka have shown that PR embedded into high-sulphur peat showed a gradual increase in P-release over time (Dahanayake *et al.* 1991).

4.4 Reactions of P-fertilizers in soils

The principal problems of *P-fixation* in soils, especially on Fe-Al rich and volcanic soils as well as Ca rich calcareous soils have been studied over the last half century by many researchers (see review articles by Sample *et al*. (1980) and Hedley and McLaughlin (2005)). The reactions of soluble P-fertilizers like TSP (made up of 80 -95% monocalciumphosphate - MCP ($Ca(H_2PO_4)_2 \cdot H_2O$)) in soils received special attention.

In the second half of the last century, a group of scientists around W.L. Lindsay studied the fundamental chemical reactions of P compounds in soils (Lindsay and Stephenson 1959, Lindsay *et al*. 1962 and Lindsay and Vlek 1977). This research demonstrated the complexities of reactions when soluble P compounds are dissolved by soil water and reacted with soil constituents in the immediate surrounding of the applied P fertilizer granule. The main P-compounds in fertilizers and reaction products are summarized in Table 4.10.

An example cited by many researchers is that of the dissolution of granules of monocalcium phosphate - MCP (the main constituent in TSP) in soils. Upon application of soluble MCP granules into moist soils, MCP attracts water from the soil and reacts according to equation 4.10.

$$Ca(H_2PO_4)_2 \cdot H_2O + H_2O \rightarrow CaHPO_4 \cdot 2H_2O \text{ (DCPD)} + H_3PO_4 \text{ (phosphoric acid)} \quad \text{(equation 4.10)}$$

The dissolution of triple superphosphate (TSP) with its main component of MCP ($Ca(H_2PO_4)_2 \cdot H_2O$) results in the formation of metastable triple point solution (MTPS) with a pH of about 1.5. When MCP has reacted with soil water it becomes DCPD + soluble P compounds that migrate into the soil. The reaction product - DCPD - remains as a ‘shell’ in the soil and many people mistake this as ‘unreacted TSP’. These reaction products, which are in fact slowly reacting DCPD ‘shells’, are found in the soil several months after the TSP (MCP) has reacted. The sparingly soluble P compound DCPD that remains in the shell represents approximately 20 -34% of the applied P.

The acid P-solution that moves out of the granule and dissolves Fe, Al and Mn compounds in the immediate surrounding of the granule are either taken up by plants or form – over time - insoluble Fe, Al, and Mn phosphates.

The strongly acidifying effects of the application of MCP (TSP) granules are only temporary in the immediate surrounding of the applied granule. After placement of MCP the range of the migrating P in solution is generally restricted to 20-40 mm from the granule surface. The range of the outward migrating P solutions depends on the composition of the soil. In particular, the outward movement of P is strongly restricted in lateritic soils due to the high sorption capacity of the Fe-Al rich soils

(Benbi and Gilkes 1987).

Sparingly soluble Ca-phosphates are formed when MCP is applied to neutral or alkaline soils. After about a month the reaction product - DCPD ($CaHPO_4 \cdot 2H_2O$) - hydrolyzes to form octocalcium-phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$).

The application of ammonium phosphates to soils changes the pH in different ways. MAP ($(NH_4)H_2PO_4$) can locally produce acid soil conditions (pH of 3.5) around the fertilizer granule when applied to the soil. In contrast, the application of DAP ($(NH_4)_2HPO_4$) raises the pH in the immediate surround of the granule to 8.

In general however, these pH effects are temporary, only involving a small portion of the total soil volume, and therefore do not have a significant overall effect on soil pH. The reaction of MAP and DAP resulted in the precipitation of a wide variety of P compounds.

Table 4.10. *Highly water-soluble and sparingly-soluble P compounds.*

Compound	Formula	Common name	pH
Highly water-soluble P compounds			
Monocalcium-phosphate (MCP)	$Ca(H_2PO_4)_2 \cdot H_2O$	TSP	1.0
Metastable triple point solution (MTPS)	Meta-stable		1.5
Mono-ammonium phosphate	$(NH_4)H_2PO_4$	MAP	3.5
Di-ammonium phosphate	$(NH_4)_2HPO_4$	DAP	8.0
Sparingly-soluble P compounds			
Dicalciumphosphate	$CaHPO_4$ (monetite)	DCPA (di-calcium phosphate anhydrite)	6.5
Dicalciumphosphate dihydrate	$CaHPO_4 \cdot 2H_2O$ (brushite)	DCPD (di-calcium phosphate dihydrate)	6.5

4.5 Direct application of phosphate rock

The easiest form of P-fertilization is through the direct application of phosphate rock. This method has many advantages, including:

- Independence of import of P-fertilizer products from abroad,
- Low cost of production,
- Technology amenable to minimal, low tech processing techniques,
- No requirements for imported acids,
- Small transport costs as processing is done close to PR deposit,
- Provision of jobs and secondary benefits to the local communities.

The costs for producing phosphate rock concentrates for direct application on a dollar per P_2O_5 unit basis are considerably lower than the costs for chemically processed phosphate rocks. Studies by Schultz and Lee (1988) show that the per unit P_2O_5 price for Direct Application P-fertilizer (30% P_2O_5) is US$ 323 at the factory gate and US$ 407 at the farmgate in comparison to US$ 607 and US$ 663 for factory and farmgate prices respectively for TSP.

In practice, the ‘processing’ of PR for direct application only requires fine grinding. Finely ground indigenous PR resources provide a low-cost alternative to costly conventional water-soluble P fertilizers, particularly in situations where the import of fertilizers is prohibitively costly, or further processing involving imported acids is impractical. Finely ground indigenous PR sources as direct application P-fertilizers have been tested in many places around the world. But unfortunately, there are only a few PR resources that are reactive enough for direct application. Most PR resources require some form of modification to become agronomically effective.

The agronomic responses vary strongly between directly applied PRs, from negligible to comparable with TSP (Figure 4.30) (Léon *et al.* 1986). The direct application of low reactive phosphate rock has generally resulted in little or no agronomic response in the first year, although it may have some residual effects in the long term. Field research has shown that inappropriate soils or crops are often responsible for the low agronomic effectiveness of this type of P-fertilizer. In addition, for many farmers, who want to see immediate responses for their investment, this method is not seen as a viable option and is seldom used.

In general, the agronomic effectiveness of PR for direct application is determined by the following factors:

- The nature of the phosphate rock (the rock factor),
- The soil conditions (the soil factor),
- The type of crop (the crop factor),
- Soil management practices (the management factor).

The greatest agronomic effectiveness will be achieved when all four factors are optimal.

The rock factor

The agronomic effectiveness of the rocks depends on a number of rock-related factors. The PR grade is one major factor. Commercially viable concentrates are normally in the 30-35% P_2O_5 range, but direct application can make use of lower grade PR resources as well.

The type of apatites used for direct application is another, very important factor. Prior to applying phosphate rocks to soils, it is important to determine the type of apatite (francolite or fluorapatite). This can be done by a number of methods including x-ray diffraction (XRD) (Holland and Redfern 1995). The measurement of the crystallographic properties, specifically the so-called 'unit-cell a-value', is a measure of the distribution of elements within the crystal structure, and in part reflects the substitution of carbonate (CO_3) for phosphate (PO_4) (Smith and Lehr 1966; McClellan and Lehr 1969; McClellan 1980; McClellan and Van Kauwenbergh 1990; Bolland and Gilkes 1997; Van Kauwenbergh 2003).

The unit-cell a-values of francolites change with the degree of carbonate substitution. Francolites with the highest carbonate substitution have unit-cell a-values of 9.320 Å (Ångstrom); francolites with the lowest carbonate substitution have unit-cell a-values of 9.370 Å (McClellan 1980). Apatites with a-values between 9.370 and 9.420 Å are not francolites but belong to a series of fluor- to hydroxy-apatites (McClellan and Lehr 1969; McClellan and Gremillion 1980). Higher carbonate substitution results in higher reactivity. The lower the unit-cell a-value, the higher is the 'reactivity' of the PR, hence these data can be used to predict the agronomic effectiveness of the phosphate rock.

The age of the phosphorite can also be an important factor. Unit-cell a values in sedimentary phosphorites change over geological time, the youngest having the most favourable and most reactive unit-cell a-values in comparison to older phosphorites (McClellan 1980; McClellan and Saavedra 1986) (Figure 4.28). This age relation is largely a function of post depositional alteration. Francolites are less stable than fluorapatites and are altered over time through a combination of effects of weathering and metamorphism. Francolites from older sedimentary successions commonly contain less carbonate substitution than younger, less altered francolites. This variation of carbonate substitution in francolites over time, from Precambrian to Tertiary, was shown by McClellan (1980) and McClellan and Saavedra (1986).

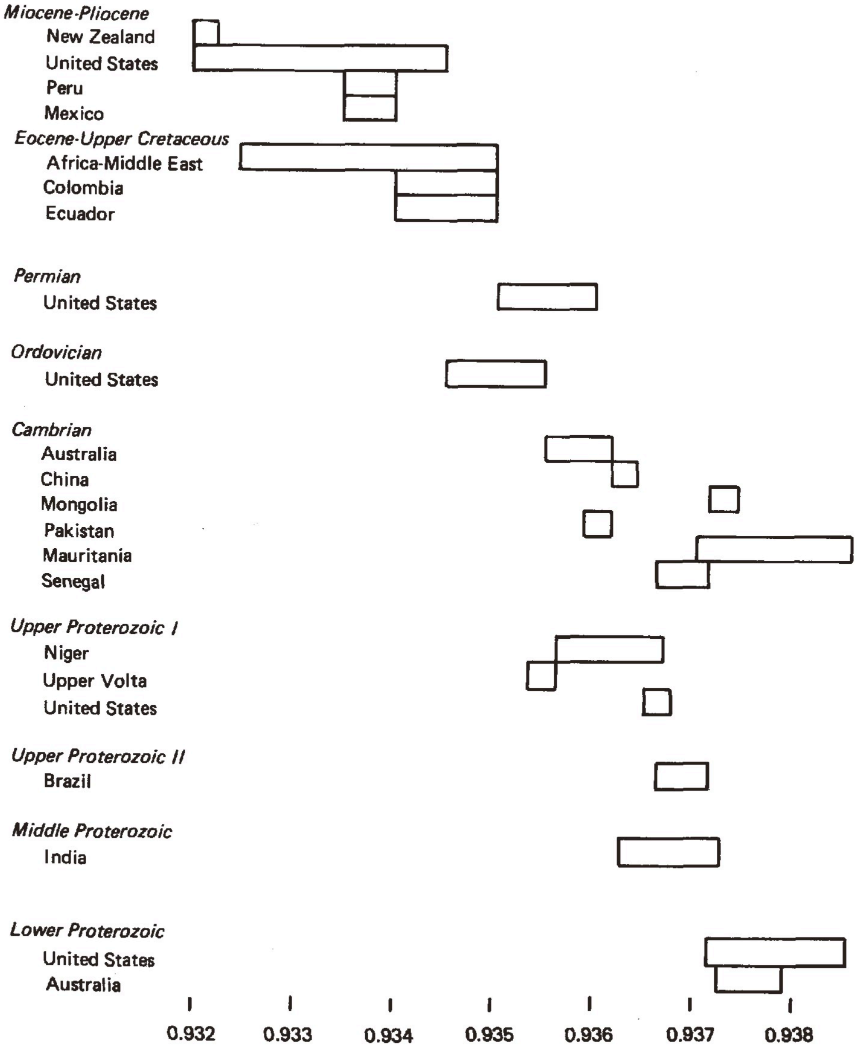


Figure 4.28. *Variation of unit-cell a-values (on horizontal axis) in phosphorites as a function of age (McLellan 1980; McClellan and Saavedra 1986).*

Another important factor to be considered when directly applying phosphate rocks to soils is solubility. Solubility is generally determined through extraction methods with various acids, for example 2% citric acid, or the ammonium citrate extraction method (Chien and Hammond 1978, Mackay *et al.* 1984). Hammond and Leon (1983) proposed a system of four solubility rankings (high, medium, low and very low) largely based on laboratory work analyzing phosphate rock solubilities in extraction media. Laboratory methods for predicting the agronomic potential of PR have been described by Chien and Hammond (1978). Other analyses that should be conducted are the determinations of concentrations of other nutrients such as Ca, as well as concentrations of potentially toxic elements (F, As, Cd, etc.).

Classification of Phosphate Rock for Direct Application

Rock potential	Neutral ammonium citrate	Solubility (% P_2O_5) Citric Acid	Formic acid
High	>5.4	>9.4	>13.0
Medium	3.2-4.5	6.7-8.4	7.0-10.8
Low	<2.7	<6.0	<5.8

Relative Agronomic Effectiveness

Soluble P_2O_5 in neutral ammonium citrate % P_2O_5	RAE	Solubility Ranking
>5.9	>90	High
3.4-5.9	90-70	Medium
1.1-3.4	70-30	Low
<1.1	<30	Very Low

$$\text{RAE \%} = \frac{\text{(yield of ground rock) - (yield of check)}}{\text{(yield of TSP) - (yield of check)}} \text{ X } 100$$

Figure 4.29. *Classification of PR for direct application (after Hammond and Leon 1983).*

Numerous pot and field trials in South America have shown a clearly differing yield response of guinea-grass to the application of PR from various parts of the world (Léon *et al.* 1986) (Figure 4.30). Some of the phosphate rocks (e.g. from North Carolina, Peru (Bayovar) and Tunisia (Gafsa)) had similar yield responses and agronomic effectiveness to that of chemical triple superphosphates. These very reactive and agronomically effective phosphate rocks are all of sedimentary origin.

Other phosphates (for example from Brazil, Tapira and Catalão) from igneous sources have proved largely ineffective when applied directly to the soils. This is consistent with the measurements of unit-cell a-values of these igneous F-apatites. Some of the more reactive sedimentary PR resources are quite young, geologically speaking, and formed during the late Cretaceous to Tertiary.

In addition, it has been shown that the grain size of the applied PR plays a major role (Kanabo and Gilkes 1988). Fine grinding has been found agronomic effectiveness of PRs (Khaswneh and Doll 1978; Anderson *et al.* 1985).

Hedley and McLaughlin (2005) concluded that direct application of PRs is probably most effective on perennial crops and pastures rather than on short-term annual crops.

Despite its economic and agronomic promises, the production of PR resources for direct application has declined in recent years. In the former Soviet Union alone, the production has dropped from 900,000 t in the 1980s to 350,000 t in 1991 (Van Kauwenbergh and Hellums 1995).

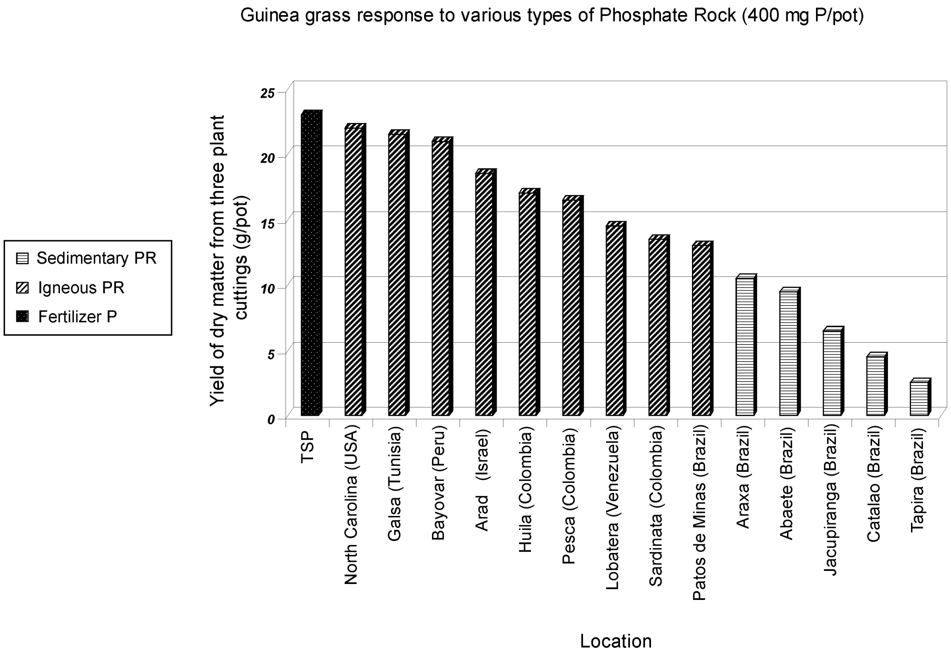


Figure 4.30. *Yield response of guinea grass to various types of phosphate rocks (modified after Leon et al. 1986).*

The soil factor

The application of phosphate rocks, even the most reactive phosphate rocks, will not be very effective if certain soil conditions are not met. Phosphate rocks dissolve faster in low pH soils, in soils low in Ca, and soils low in P. Elements in the soil such as Fe, Al and Mn contribute to 'fixation' of P from solution.

Prior to the application of PR, the soil should be analyzed for pH, and exchangeable Al, Fe as well as P and Ca concentrations. The total and available P concentrations should be determined in order to calculate how much P is required. Biological activity in soils, including mycorrhizae, bacteria, fungi and phosphatase activity, is important as well as a low pH in the rhizosphere (this depends on root exudates or type of N supply) (Figure 4.31).

The dissolution of apatite is optimal when the soil moisture is adequate (free-draining field capacity) (Kanabo and Gilkes 1988).

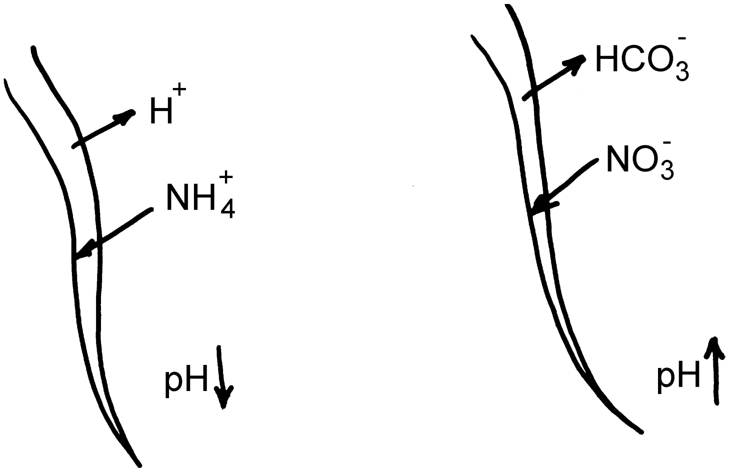


Figure 4.31. *Rhizosphere pH related to nitrogen supply.*

The crop factor

Crops vary in their ability to use P from PR sources mainly because the mobilizing capacity of P from various P rocks varies with crop species (van Ray and van Diest 1979; Flach *et al.* 1987; Bolan *et al.* 1990; van Diest 1991, McLenaghan *et al.* 2004).

The best known plants with relatively high P-mobilizing capacities are:

- ○ Buckwheat (*Fagopyrum esculentum*),
- ○ Clover (*Trifolium ssp.*),
- ○ Kale, or rape (*Brassica napus*),
- ○ White Lupins (*Lupinus albus*),
- ○ Cabbage (*Brassica oleracea*),
- ○ Pigeon pea (*Cajanus cajan*).

Other legumes and some crops of the *Brassicaceae* family are also effective in enhancing phosphate rock solubilization. Most cereal grains and cotton have low P-mobilizing capacities.

One of the mechanisms with which certain plants acquire P is through the excretion of organic acids from their roots. For example, the roots of the leguminous pigeon pea (*Cajanus cajan*) release piscidic acid that can complex iron and enhance the availability of iron-bound phosphorus (Ae *et al.* 1990). Also, the roots of *Lupinus albus* are known to excrete large quantities of citrate ions, which have been reported to increase P acquisition of plants (Gardner *et al.* 1983). Hoffland *et al.* (1989a,b) and Hoffland (1992) could show that P-deficient rapeseed plants (*Brassica napus*) acidify parts of their rhizosphere by exuding malic and citric acids. The dissolution and uptake of soluble P is enhanced through these acid root exudates, by the formation of extensive and fine root hairs, and increased P uptake through mycorrhizae (Leyval and Berthelin 1989).

Other plants, like buckwheat (*Fagopyrum esculentum*), can enhance P uptake through high uptake of Ca and, probably, root exudation of hydrogen ions (Ma *et al.* 1997).

The management factor

Management practices, such as placement of phosphate rocks, timing of application, as well as lime application, can influence the effectiveness of phosphate rocks or water-soluble P-fertilizer.

The placement of PR in soils influences the rate of P release. Studies in many parts of the world have shown that the method of broadcasting and incorporating the PR into the soil directly increases the effectiveness of PR. Banding of PR is less effective.

Timing of the application of phosphate rocks is important in terms of how effective they are when it comes to plant growth. Phosphate rocks need to be incorporated into the soils well in advance (several weeks) before the onset of the rains.

Liming is a management option to increase pH and reduce exchangeable Al^{3+} concentrations, especially for crops that are sensitive to Al. However, when increasing the pH through liming, the dissolution of phosphate rock is decreased due to an increase in Ca concentration (the common ion effect).

Direct application of phosphate rock: summarizing remarks.

To maintain and enhance the productivity of soils and food crops it is necessary to extract, process and apply phosphates from naturally occurring PR deposits. Significant mineralogical and chemical differences exist between the various apatite minerals in phosphate ores, with some phosphate resources more suitable for direct application than others. Except for the reactive sedimentary phosphate rocks, like North Carolina PR (Figure 4.30), which are generally relatively young (formed in the Late Cretaceous, Tertiary until Recent), many of the naturally occurring PR resources require processing to be agronomically effective in the initial growing season. However, as shown above, there are a great variety of processes available to transform the inorganic P in apatite into more plant available forms.

4.6 Environmental Issues

There are basically three major production related activities with which environmental problems are associated:

- ○ Extraction (mining) of PR,
- ○ Beneficiation (physical upgrading) of PR,
- ○ Conventional processing (acidulation) of PR.

4.6.1 Main environmental problems related to extraction

The main problem associated with extraction is related to the large environmental footprint of surface mining and disposal of wastes. Large-scale open pit operations inevitably create large topographical surface disturbances through land clearance and consequent loss of natural ecosystems and land for other uses.

The amount of water used in the process of extraction and separation is also significant. For example, the friable phosphatic ores of Florida and North Carolina are extracted by large high-pressure water jets, so-called ‘monitors’, which deliver 37,000 to 45,000 L water per minute at a pressure of 1.45×10^6 Pa (Mislevy *et al.* 1990a). Although up to 90% of the water is recovered or re-used, the water requirements are still considerable.

Open pit extraction frequently requires a lowering of the water table in order to excavate unconsolidated phosphate deposits by backhoes and other conventional equipment. Pumping to lower the water table at the mine site can cause substantial lowering of the water table in the surrounding area, leaving farmers with ‘dry wells’ and drying up local rivers and lakes. However, careful planning can generally limit the scale of the drawdown and minimize the environmental impact.

Some parts of the large scale phosphate operations in Florida have shown that, with concerted efforts and best management techniques, these ‘moonscapes’ can be partially reclaimed and turned into pasture land, orchards, wetlands, or wildlife management areas after closure of the mined out land (Morris 1992).

4.6.2 Main environmental problems related to beneficiation

The main problem related to PR beneficiation (physical upgrading), is the disposal of very fine particles. In the beneficiation process, the phosphate ore is washed, screened, and particles greater than 1 mm in size are used for further processing. Particles smaller than 1 mm (as much 1/3 of the ore) are discarded by pumping them into the fines ponds (also called ‘slime’ ponds) to allow for settling. These fines ponds generally require a large amount of land, covering between 40% and 60% of the mined land area (McFarlane 1992).

The natural settling rate for the fines in these ponds is extremely slow and was once considered 'one of the most difficult problems associated with reclamation' (Mislevy *et al.* 1990a). It was calculated that it would take 10-15 years for 50% of the alumino-Mg-silicate clay mineral palygorskite (attapulgite) and other clay minerals to settle out (Mislevy *et al.* 1990a).

In recent years, major progress has been made to accelerate settling rates and convert waste sites into farmland and land for other uses. Various rapid dewatering and flocculation processes of the phosphatic clays have been developed and particularly the blending techniques using sand and clays have become successful reclamation techniques.

The dried out phosphatic clay ponds are very fertile and are deemed as valuable land for high biomass production, which could also be considered an energy source for methane gas production (Mislevy *et al.* 1990a). However they are of limited agricultural use for forage and crop production because of radioactive minerals that reach the settling ponds with the fines.

These radioactive minerals are generally not in concentrations high enough to be phytotoxic but may still be problematic (Mislevy *et al.* 1990a,b). For example, in Florida, ^{226}Ra concentrations in perennial grasses growing on dried out phosphatic clay ponds were nearly six times higher than the same grass species growing on unmined ground. A long-term study examining the quantity, quality and uptake of nutrients and ^{226}Ra showed increased levels of ^{226}Ra in forage crops (Mislevy *et al.* 1990b). It was calculated that if these plants were consumed by animals, the beef and milk from these animals would contain less than 1.0 mrem yr^{-1}, which is the annual effective dose equivalent corresponding to the Negligible Individual Risk Level (Mislevy *et al.* 1990b).

4.6.3 Main environmental problems related to processing

The chemical processing of most sedimentary phosphate rocks with acids produces contaminated water and build-up of radioactive material. The major problem associated with the wet-process phosphoric acid production route is the disposal of the by-product gypsum, phospho-gypsum. During processing using the wet-acid phosphoric acid route approximately 1.5 tonnes of phospho-gypsum are produced per tonne of phosphate concentrate (i.e. 5 tonnes of phospho-gypsum per tonne of P_2O_5). The volumes of this material in solid form are huge; by some estimates they reached 1 x 10^9 tonnes by the year 2000 in Florida alone.

Phospho-gypsum ponds are used to receive the gypsum produced during the production of phosphoric acid, as well as all of the water contaminated during the process. This results in a mass disposal problem along with the problem of accumulations of toxic materials in gypsum ponds (Rutherford *et al.* 1994).

The gypsum and other ‘wastes’ released to the gypsum ponds during the wet-process phosphoric acid processing not only creates a quantitative problem, but the phospho-gypsum in the waste ponds (and stacks, after drying) also represent a potential hazardous waste issue and a public health concern (Rutherford *et al.* 1994).

The water in the ponds commonly has elevated F and P concentrations. However, contamination of groundwater with F and P is a concern that is addressed in modern operations by installing liners at the bottom of the gypsum tailings storage area. The problem arises mainly at old gypsum storage sites that do not have efficient liners at the bottom of the piles.

The pond solutions commonly have a very low pH (1.0-1.5), which is of concern especially in the case of dam failure, collapse of the substratum, or overflow during rainy seasons.

Higher concentrations of ^{226}Ra are also found in these ponds when the ore is derived from sedimentary PR. During acidulation, ^{226}Ra mainly follows the Ca-pathway and ends up in the gypsum ponds and piles (Rutherford *et al.* 1987). ^{226}Ra decays to ^{222}Rn (Radon), a radioactive gas with a short half-life (3.8 days), which can pose health hazards and make the land difficult to rehabilitate.

In 1990, the US Environmental Protection Agency (EPA) estimated that phospho-gypsum from 11 out of 21 US production facilities could be classified as hazardous waste on the basis of leachate toxicities. Based on the assessment of ‘hazardous’ wastes, the environmental compliance cost would be in the range of US $114 per tonne of P_2O_5. By reclassifying the phospho-gypsum as ‘special waste’, the environmental costs would change to US $28 to 36 per tonne P_2O_5, depending on the site-specific management options (Schultz 1992).

The closure of phospho-gypsum stacks requires a cover or barrier to prevent runoff of contaminated water and gypsum. Phospho-gypsum stacks in the USA reach a height of up to 60 m. The closure of a typical stack costs up to US $10 million. Fertilizer companies are required to monitor the closed stacks for up to 50 years (UNEP 1996).

In Europe, most phosphoric acid plants have been closed in recent years due to environmental concerns and stringent environmental regulations. The costs involved in meeting the discharge limits influenced the industry to pursue alternative non-conventional process routes, mainly using nitric acid instead of sulphuric and phosphoric acids.

Other solid waste products from conventional phosphate processing that have potential harmful effects are spent vanadium catalytic converters used in the production of sulphuric acid and Fe-rich shales. The latter are found in residues from pyrite roasting (required for the production of H_2SO_4), which contain considerable amounts of sulphides and have a low pH.

It is important to point out that most environmental concerns are related to the processing of sedimentary phosphate rocks due to their inherent elevated trace element and radionucleide concentration. Igneous phosphate rock deposits contain in general much lower concentrations of harmful trace elements and radionucleides than sedimentary phosphate rocks.

Potentially toxic trace elements in phosphate rocks

There are many elements in phosphate rocks that are not essential to plants, human or animal nutrition or are toxic. Elements of environmental and health concern are As, Cd, Cr, Co, Pb, Mn, Ni, Se, Zn as well as radionuclide elements. Of these elements, only As, Cd, Se and the radionuclides need special attention. It is clear that the input of most of the other elements is low in comparison to the natural concentration in soils.

One of the toxic trace elements commonly associated with phosphate rocks and pyrite is arsenic (As^{III} = toxic, and As^{V} = less toxic). Charter et al. (1995) evaluated As concentrations in 12 PRs from various deposits in Africa and the Americas. The eman As concentration in these rocks was 9.6 mg kg $^{-1}$, ranging from 3.2 to 32.1 mg kg $^{-1}$. The maximum permissible concentration of As in phosphate ore is 40 mg kg $^{-1}$. As seen from Table 4.11, the As concentrations vary in PRs from source to source (Van Kauwenbergh 2001).

Cadmium is non-essential to the growth of plants and animals, but its toxicity to humans gives cause for concern. Elevated Cd intake affects many bodily functions and specifically kidney functions. Geochemically, Cd is closely related to Zn in minerals and rocks. The average concentration of Cd in the continental crust is 0.098 mg Cd kg^{-1}, with granitic rocks containing on average 0.1 – 0.2 mg Cd kg^{-1}, shales 0.8 mg Cd kg^{-1}, and limestones 0.035 mg Cd kg^{-1}. Cadmium is naturally enriched in coal as well. The global average content of Cd in uncontaminated soil is 0.62 mg Cd kg^{-1} (Ure and Berrow 1982).

Table 4.11. *Arsenic concentrations in phosphate rocks (various sources).*

Origin of phosphates	Arsenic (mg kg^{-1})
Morocco	9
N' Carolina	17
Araxa, Brazil	17
Togo	27
Idaho	40

Phosphate rocks, especially phosphates of sedimentary origin and guano, can contain elevated concentrations of Cd (Table 4.12), and since about 60-70% of the Cd will form part of the P-fertilizer product upon processing, the issue of Cd in fertilizers, plant uptake, bioaccumulation and human nutrition has been the subject of many studies (Mortvedt *et al*. 1981; Hutton 1982, Hutton and Symon 1986; Rothbaum *et al.* 1986; Jones *et al.* 1987; Mortvedt 1987; McGrath *et al.* 1988; Rutherford *et al.* 1994; Singh and Myhr 1998; Alloway and Steinness 1999) and new technologies have been developed to reduce potential contamination in soils.

Technically, Cd can be removed using various solvent extractions, ion exchange, co-precipitation, as well as calcination (Van Kauwenbergh 2001). However, so far none of the processes to reduce Cd ('decadmiation') from the P fertilizer product have been proven economic on an industrial scale as yet and research is continuing to find economically viable technologies to reduce Cd concentrations in P fertilizers.

Another element of environmental and health concern is Selenium (Se). Elevated concentrations of Se have been found in some sedimentary phosphates and associated shales in the Western United States (Perkins and Foster 2004; Presser *et al*. 2004). The PR deposits of the Permian Phosphoria Formation contain 30 to 300 mg Se kg^{-1}. In the Fe-sulphide pyrite the Se concentration can be enriched 10-100 times. The Meade Peak Member of the Phosphoria Formation contains up to 1200 mg Se kg^{-1} (Presser *et al*. 2004). Igneous PR deposits on the other hand contain generally very low concentrations of this element. Environmental effects of Se from the disposal of Se-rich phosphorites are described in Chapter 8.

Another potential issue of environmental and health concern is the concentration of radioactive elements, especially U and Ra in naturally occurring phosphorites. Uranium found in phosphorites originates from seawater and is incorporated into the apatite lattice during the decomposition of organic matter, as well as during reduction processes at the sediment seawater interface (Barnes and Cochran 1993).

The U concentrations in naturally occurring phosphorites generally vary from 5 to 200 mg U kg^{-1} by weight (Altschuler 1980; Jarvis *et al.* 1994). Concentrations of U in PR are shown in Table 4.8. It should be pointed out that U in igneous phosphates is very low, commonly below 2 mg U kg^{-1}.

The average U concentration in soils is 2.18 mg kg^{-1} (Ure and Berrow 1982). Uranium accumulations in soils that received long-term fertilization with superphosphates have been described by Rothbaum *et al.* (1979).

The radioactive element of concern in the processing of P fertilizers is Radium (Ra), especially the isotope Radium-226 (^{226}Ra), a daughter product of the Uranium -238 (^{238}U) decay series and a precursor of the carcinogenic gas Radon-222 (^{222}Rn)

(Roessler *et al.* 1979; Dixon 1985; Sam and Holm 1995). During the wet acidulation process of P fertilizers, Ra is partitioned and largely follows the Ca pathway into the phospho-gypsum ponds. It is thus less of a concern in the phosphate fertilizer product than in the phospho-gypsum 'wastes'.

Table 4.12. *Cadmium concentrations in PR concentrates before processing into P-fertilizers (compiled from Van Kauwenbergh 2001 and other sources).*

Origin of phosphates	Cadmium (mg kg $^{-1}$)
Sedimentary phosphates	
Morocco	12 - 26
North Carolina	38-50
Gafsa, Tunisia	40-43
Taiba, Senegal	86-97
Thies, Senegal	101
Togo	48-67
N' Florida	6-8
E' USA (average)	14
W' USA (average)	61
Igneous phosphates	
Araxa, Bazil	2-3
Phalaborwa, South Africa	1-1.6
Kola, Russia	0.3-2
Guano	
Christmas Islands	43
Nauru	100

From the human standpoint, the main radiological concern is the exposure of persons involved in extraction and handling of Ra and Rn rich phosphorites to Rn gas. The occupational risk for individuals exposed to Rn through inhalation of Rn gas and Ra-rich dust has been extensively studied (Makweba and Holm 1993; Hussein 1994; Olszewska-Wasiolock 1995; Khan *et al.* 1998; Bigu *et al.* 2000; Khater *et al.* 2001; Papastefanou 2001) and compared to radiation exposure of the general public. In general, the occupational exposure needs to be assessed on a case by case basis but in comparison is commonly lower than the exposure of professionals working in the medical field and nuclear energy industry, and often comparable to the exposure of airline pilots and flight crews (ICRP 1990).

While ^{226}Ra largely follows the pathway into the gypsum ponds, U follows the phosphoric acid path and finally ends up in the phosphate fertilizer product (Roessler *et al.* 1979). The removal and recovery of U from phosphate ores is possible, however, with the very low concentrations and the current low price of U, this option is not attractive economically.

Air emissions

Air emissions during beneficiation and processing include dust (often rich in P) and Fluorine (F). While the dust can be removed through various filters (bag filters, wet scrubbers or dry cycloning devices), the HF produced during the common acidulation process must be treated before being released into the atmosphere. If SiO_2 is present in the ore, SiF_4 (Silicon-tetrafluoride) is formed which can be reduced by scrubbing with H_2O (hydrolysis) according to equation 4.11. Modern plants with efficient 'best available techniques' are able to reduce the air emissions and F release, primarily through scrubbing and neutralization, to about 0.02 kg F t^{-1} (50 mg Nm^{-3}) (UNEP 1996).

Hydrolysis: $3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$ (equation 4.11)

4.6.4 Environmental Issues Related to Phosphate Fertilizer Use

Phosphorus is a relatively immobile nutrient in the soil. It does not generally leach into the ground water because it easily sorbs onto soil particles containing Fe-oxides and Ca. Phosphorus is lost from the fields mainly as adsorbed components of soil particles, mostly through soil erosion.

Phosphate fertilizers are applied to land at various quantities, commonly between 10 and 50 kg P ha^{-1}. From this, only a small portion (5-30%) of the soluble P fraction is recovered by the plants in the first growing season. The residual fertilizing effect of the remaining 70-95% of P in the soil and it's uptake by subsequent crops is much lower than in the first growing season. The fate and nutrient use efficiency of P from various P-sources including P-fertilizers has been discussed by many scientists including Gilkes and Lim-Nuez (1980), Bolland and Gilkes (1998), Baligar *et al*. (2001).

The amount of P that is lost through drainage from agricultural non-point sources has changed over the years as a result of better management of nutrients. In the past, some areas in the Great Lakes region of North America reported a considerable loss of P from agricultural application of fertilizers, manures etc., into the drainage system and finally into fresh water and river systems causing eutrophication. In recent years, however, the loss of P via soil erosion has been reduced significantly due to better soil management (e.g. buffer strips along the fields). In Canada, municipal wastewater - largely human waste - is the largest point source of N and P releases to the aquatic environment. With advanced techniques of P removal at many municipal wastewater treatment plants the P discharges to fresh waters has been reduced dramatically in recent years (Chambers *et al*. 1997).

The budget of P utilization (input vs. output) varies considerably from region to region in the world. Some countries, especially in the northern hemisphere, have a surplus of P, leading to a general surplus of P accumulating in soils. More P from fertilizers, manure and crop residues is put into the soil than is harvested in the form of crops and crop residues. In contrast, in many tropical developing countries there is a general negative balance (deficit) of P. This negative nutrient balance contributes to the steady decline in soil fertility in many tropical countries and is a major concern for sustainability of agriculture in these areas (Sanchez *et al.* 1997).

Detailed studies in Kenya have shown that the nutrient balance between P inputs (mineral fertilizers, organic inputs like manure and plant residues, atmospheric deposition, sedimentation by irrigation or natural flooding) and outputs (harvested product, crop residue removal, leaching, runoff and erosion) is negative. Fertilizers and manures do not replenish the entire quantity of nutrients that are exported through the harvest of crops and plant residues, as well as lost through runoff and eroded sediment. In the case of P, the rate of nutrient depletion is > 6.6 kg P ha^{-1} per year (Smaling *et al*. 1997).

Trace Element Concerns in Phosphate Fertilizers

The main trace element concern in phosphatic fertilizers is Cd. Most of the Cd inherently contained in PR remains in the P-fertilizer during processing. Sedimentary phosphates as source material for P-fertilizers have generally high but variable Cd concentrations (Table 4.12). For example, phosphate rocks coming from the eastern USA contain about 15 mg Cd per kg P_2O_5 or less, while those from the western United States can contain more than 60 mg kg^{-1}. Some phosphate ores contain large concentrations of Cd (> 100 mg Cd kg^{-1} P_2O_5) and the producers have problems finding markets for these high Cd phosphate raw materials in the wake of directives from the European Union to gradually reduce the Cd content in phosphate products. In some EU countries, the allowable Cd content has been lowered to 60 mg Cd per kg P_2O_5. As phosphate fertilizers produced from sedimentary PR ores and bird guano contain considerably higher Cd concentrations than fertilizers produced from igneous sources, there is a trend in the P-fertilizer industry to switch from the relatively high cadmium containing sedimentary phosphates of Morocco, Togo and Senegal to the lower Cd products from igneous phosphate rock resources of Finland, Russia, Brazil, Canada and South Africa, or to blend sedimentary and igneous phosphate concentrates in order to lower the Cd concentrations of the product (Table 4.12).

Although the amount of Cd applied to the soils through the application of P-fertilizer each year is small, it can pose a health risk if applied at high rates and year after year. Cadmium is not very mobile in the soil and it is not easily leached, but rather accumulates in soils and in plants. Health concerns arise if the plants taking up large concentrations of Cd are used for human consumption. Cadmium bioavailability and uptake by plants can be higher in P-fertilized acid soils due to the increased solubility of Cd in low pH soils. However, the intake of Cd by humans through the consumption of crop products is enhanced only when several factors come together: The region in which the crops are grown has acid soils with low cation exchange capacities, the fields have received significant amounts of Cd from certain P fertilizers originating from sedimentary or guano PR resources, and the crops grown are leafy vegetable crops. Leafy vegetables such as lettuce and spinach are known for their enhanced Cd uptake (Hutton 1982). Tobacco also takes up considerable amounts of Cd. Other crops, such as barley, are not significantly affected by elevated Cd concentrations in soils (Singh and Myhr 1998).

Cadmium input into soils from various sources has been studied for a long time (Hartvedt *et al.* 1981; Rothbaum *et al.* 1986; Jones *et al.* 1987, and others, compiled in Alloway and Steinness 1999). The annual Cd inputs into soils for P-fertilizer application range from 2 g Cd ha^{-1} yr^{-1} in the UK (Jones *et al.* 1987) to 20 g Cd ha^{-1} yr^{-1} in New Zealand (Rothbaum *et al.* 1986). Most soils receive 2-4 g Cd ha^{-1} yr^{-1} from P-fertilizers (Alloway and Steinness 1999). The potential application of large volumes of phospho-gypsum containing 3-4 mg Cd kg^{-1} into soils could contribute to additional Cd loading of soils (Alcordo and Rechcigl 1995). Other anthropogenic inputs of Cd to soils include sewage sludge, which may contribute as much as 150 g Cd ha^{-1} yr^{-1}, and wet/dry deposition from metal smelters, which may contribute anywhere from 25 to 1000 g Cd ha^{-1} yr^{-1} (Alloway and Steinness 1999).

Chapter 5

Potassium

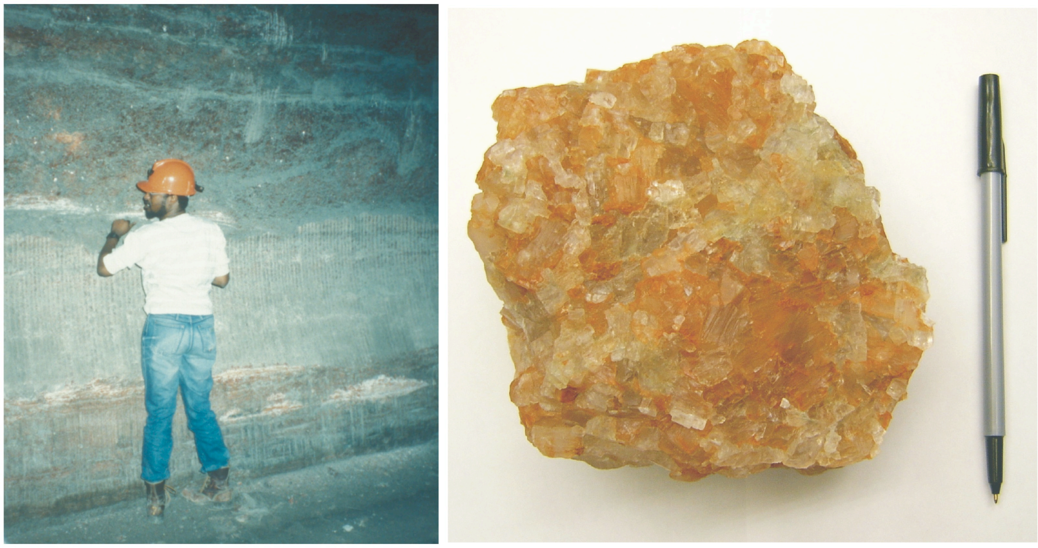


Figure 5.1. *(left) Horizontal sylvinite beds in underground potash deposit near Saskatchewan, Canada; (right) coarse-grained specimen of sylvinite (mixture of sylvite KCl -pink- and halite NaCl –white) from Saskatchewan, Canada .*

Potassium (K) is a macronutrient that is essential for the growth of plants. It is required in quantities similar to that of nitrogen. It promotes and regulates enzyme activation, supports the translocation of carbohydrates, increases water use efficiencies and resistance to effects of drought and diseases. More K is required by plants in the early stages of growth than in maturity stages. Potassium is commonly more concentrated in stems and leaves than in seeds. However, K is not part of any plant tissue but rather a constituent of the fluids that fill internal plant tissues as K^+. It is highly mobile and moves widely within plants.

Potassium is particularly important as a nutrient for the production of crops like potatoes, sugar cane, sugar beet, grapes, fruit, as well as cereals. Root and tuber crops commonly contain more K than N. In tropical countries, considerable quantities of K are required for plantation crops such as oil palm, coconut, cacao and rubber. In high-yield, intensively managed agricultural systems, it is used in large quantities by crops. In low-yield crop production agriculture K is used only sparingly.

Potassium in the form of carbonates and hydroxides occurs in wood ashes and was used in this form as a fertilizer long before it was recognized (in 1840) as an essential nutrient in plant growth. Today, K-fertilizers account for about 95% of the total K-consumption. Other applications include the manufacture of K-based chemicals such as KOH and K_2CO_3. It is also used in medicine, food processing, pharmaceuticals, oil field drilling, chemical reagents and various other industrial uses (Harben and Kužvart 1996).

***Table 5.1**. Potassium as a nutrient, its forms in plants and in common minerals.*

Nutrient	Uptake form	K in plants	K in minerals
Potassium (K)	K^+	Constituent of internal cell fluids (cytosol); ionic K^+ transported in xylem and phloem	Silicates: K-feldspar, mica, leucite, glauconite, illite (clay mica); K-salts: Sylvite, carnallite, kainite and langbeinite.

Potassium occurs in a variety of forms in soils. Common silicate rocks and minerals make up the largest proportion of K in soils. However, in this form K is generally firmly bonded in a silicate lattice and is usually not available to plants. The available portion of K in soils includes K in exchangeable forms and K in solution.

For crop production, the addition of K to soils is important in soils that are naturally deficient or depleted by harvesting and other anthropogenic actions. Potassium cannot be captured from the air, like nitrogen. Instead, it is slowly released from rocks and minerals through the process of weathering. Other sources of K for plant uptake are of organic origin, for example animal manures, plant residues and other forms of organic matter.

Common silicate minerals found in soils like feldspars and micas can contain more than 10% K. While the K in the common feldspars (e.g. in K-feldspar) is largely unavailable to plant roots, other silicates release K more easily, for example the mineral leucite and, to some extend, the dark micas phlogopite and biotite. So far, no K-rich silicate minerals have been mined for the purpose of replenishing K in soils.

Soluble-K occurs in high concentrations in K-salts, which are found in large salt (evaporite) deposits in various parts of the world. The main K-fertilizers marketed in the world are extracted (mined) from these naturally occurring soluble K-salt deposits. These K fertilizers are not only very soluble and easily available to plants they are also easily leachable nutrient sources, especially in sandy soils with little clay and organic matter. Based on environmental and economic considerations, interest in slow-release alternatives is growing.

In the following chapter we will discuss the functions of K in plants and the forms and uptake mechanisms of K from soils. The geology and mineralogy of K-bearing rocks and minerals will be discussed as will methods of processing of K minerals and the ways geologists discover K resources. Finally, we will discuss environmental issues related to potash mining, processing, disposal of wastes, and the use of K fertilizers in agriculture.

Facts about K

The chemical symbol for potassium (K) is derived from the Latin and German word 'Kalium' which means potassium. 'Kalium' may itself be derived from the Arabic word 'Qali', which means alkali.

Potassium is often equated with potash, a term derived from earlier times when the ashes of land plants (mainly trees) were leached and the solutions were boiled in large iron pots to crystallize into soluble potassium salts. The collected salts in pots were called: pot-ash. Today, potash means potassium-bearing salts and processed K products, mainly KCl, muriate of potash.

In 1840, the German chemist, Justus von Liebig (1803-1873) discovered the role of potassium as a plant nutrient.

In 1857, the first potassium-bearing salts were discovered in Stassfurt, Germany, in 260-255 million years old salt bearing rock formations. They were subsequently mined.

There are three naturally occurring K-isotopes, ^{39}K (93.1%), ^{40}K (0.01%) and ^{41}K (6.88%).

5.1 Potassium in plants

No plant can grow and complete it's life cycle without potassium. Plants take up K primarily from soil solution as the cation K^+. Vegetative portion of crops contain more K than the seeds. Plant membranes are highly permeable to this ion, allowing it to move freely throughout the plant. However, K is neither a constituent of plant parts nor is it part of any specific plant compound. In its cationic form, K^+ moves in the plant freely in internal cell fluids, and in xylem and phloem. Potassium is very mobile in plants.

The role of K in plants is mainly *regulatory* in nature. Major regulatory functions of K include:

- Enzyme activation to promote carbohydrate metabolism, which includes the formation, breakdown and translocation of starches,
- Promotion of nitrogen metabolism and the synthesis of protein in green plants, resulting in increased seed and grain size,
- Control of stomatal movements, which reduces water loss when hot, dry and windy conditions are prevalent,
- Regulation of water uptake and loss, which is essential during stages of rapid growth as it is linked to the cells ability to swell and grow and helps to stiffen straw and stalk due to increased turgor pressure,
- Control and regulation of activities of other essential nutrients.

Many of these functions are complementary and together provide an important influence on the efficiency of the vital process of photosynthesis, the translocation of amino acids and photosynthates, mainly sucrose (Mengel and Kirkby 2001), as well as the synthesis of proteins in leaves and starch in roots. In addition, K also assists in the neutralization of various organic acids and is an antidote to nitrogen excess.

Plants will take up K in excess if it is available in the soil. It is this mechanism of luxury uptake of K that can be detrimental to the uptake of other cationic nutrients needed in plants, e.g. magnesium (see Chapter 7).

Adequate K supply is important for plants to regulate water-use efficiency. Sufficient K supply in the guard cells of stomata is important as they control the opening and closing of stomata and thus the loss or conservation of water and exchange of various gases. Potassium deficiencies cause plants to be sensitive to drought, disease and frost. In temperate climates, it is common to apply K fertilizers in the fall/autumn to increase cold hardiness.

Most K is supplied to plant roots via the mechanism of diffusion, the movement of nutrients from the zone of higher concentrations to the zone of lower concentration (Barber 1995). At the root surface, there is sometimes an uptake competition between K and Mg such that if too much K is available there is the possibility of an Mg deficiency. Problems can arise if a proper balance between these two elements is not maintained, for example, mulch with high K content often induces Mg deficiencies.

Monocotyledons (monocots), such as grasses and many cereals, take up large amounts of K from the soil, through their extended root system. The roots of monocots may even remove K from interlayer positions in clay minerals (Mengel *et al.* 1998). Dicotyledons (dicots) can also exhibit high K demands and compete with monocots for K resources in the soil (Mengel *et al.* 1998). Nitrogen availability may also affect K uptake; when leguminous and non-leguminous crops are grown on identical soils with low K concentrations, non-leguminous crops commonly contain more K than leguminous crops.

Because the synthesis of starch is greatest when K is abundant, the availability of K is important for the production of starchy foods like bananas, potatoes, sugar beets, cassava, and other root crops. Other high K-consuming crops include tomatoes, sunflowers, pineapple, oil palm, coconut palm and many tropical fruits. K is also important for the formation of stimulant crops, such as cacao and tobacco.

Figure 5.2. *(left) Potassium deficient leaf of maize/corn; (right) K-deficient banana leaf with necrotic leave edge on right, healthy banana leaf on left side of the plant).*

K-deficiency symptoms on corn/maize plants include yellowing or browning along the edges of leaves, especially the older leaves (Figure 5.2). In bananas, K deficiencies are recognized by necrotic leave edges (von Uexküll 1985). In recent decades, K has received increased attention due to intensive cropping practices, as well as an increase in K-depletion problems in soils.

5.2 Potassium in soils

The average K_2O concentration in soils is similar to the crustal average, approximately 2.20% K_2O (Ure and Berrow 1982). However, soil concentrations vary widely depending on the underlying parent material. Soils with the highest K-concentrations are derived from highly micaceous rocks, such as mica schists and phyllites, as well as river alluvium (Portela 1993). Soils developed from ultramafic rock types, such as dunites, peridotites and serpentinites generally have low K-concentrations.

Portela (1993) studied twenty surface soils in Portugal representative of different parent material and demonstrated that varying K concentration of soils depends on the composition of the parent materials and the degree of weathering. Soils overlying carbonatite complexes in East Africa, show a strong contrast between the high-K concentration of soils overlying K-rich feldspar bearing silicates and the low-K concentration of soils overlying calcite- and dolomite-rich Ngualla carbonatite in Tanzania (Figure 5.3). Similar contrasts between soils overlying carbonate rocks and silicate rocks have been reported from Zambia (pers. communication V. Shitumbanuma 2006).

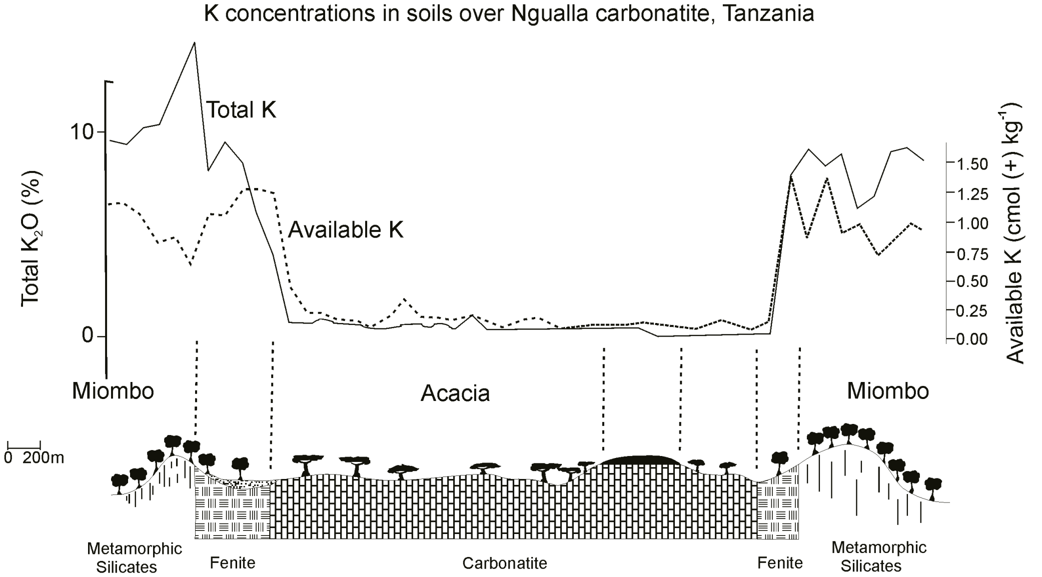


Figure 5.3. *Relationship between bedrock, vegetation and K concentrations (total and available K) in soils covering the Ngualla carbonatite, SW Tanzania.*

The intensity of weathering to which a soil is subjected also affects the soils' potassium concentration. Young soils, such as many volcanic soils, as well as soils resulting from extensive continental glaciations and associated deposits, or soils derived from wind-transported sediments, are generally rich in K^+ (Mengel *et al.* 1998). Loess, a soil which is made of thick layers of wind-blown silt (particles 2-

64 µm in diameter), is particularly rich in K. Geographically, loess is found in large regions of Europe, Asia, and the Americas, bordering areas of partial continental glaciation. In contrast, the highly weathered soils typical of many tropical regions generally have low total K concentrations, some of them a low as 0.03% (Mengel and Kirkby 2001). The generalized soil fertility map of China (Figure 5.4) also illustrates the distribution of soils and clay minerals, from dry, arid and temperate climates in the North of China to tropical climates and highly weathered soils in the tropical South. The area covered by the Loess Plateau in central Asia can also be seen.

Soils in arid and semiarid regions of the world commonly contain higher potassium concentrations than soils with similar texture in humid climates due to the fact that there is insufficient moisture to leach out K down the soil profile.

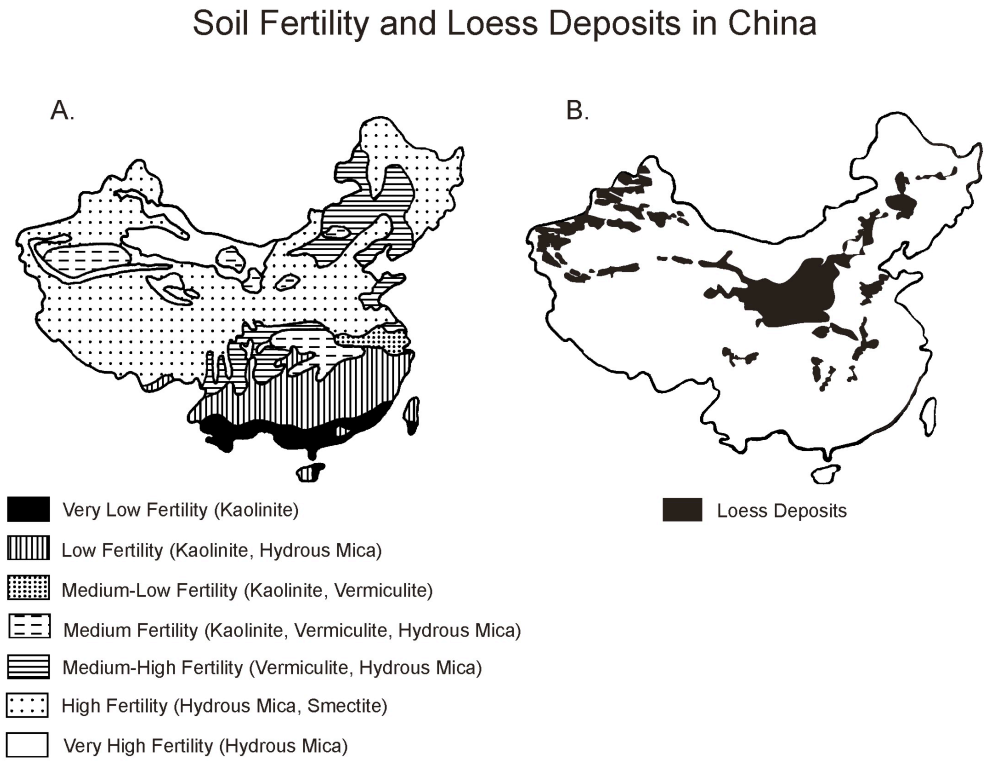


Figure 5.4. *Simplified soil fertility map of China showing A) the K status and predominant clay minerals of soils. Notice the differences of clay mineral composition, from North to South, and B) the distribution of the fertile loess deposits.*

The K availability in soils largely depends on the composition of the rocks and minerals underlying the soil, on buffering capacities of K, and soil management parameters. Sandy soils have lower K-buffering capacities than clay-rich soils, especially soils rich in illite (clay mica) or smectites. The amount and type of clay in the soil can have a large effect on the amount of K that is available to plants. Kaolinitic clay, which is common in tropical regions, tends to have particularly low K concentrations, while other clays generally have high K concentrations (Table. 5.2).

Table 5.2. *Potassium content and CEC of clay minerals (from various sources).*

Clay Mineral	K (%)	CEC (cmol (+) kg $^{-1}$)
Biotite	7-10	0-10
Hydromica	6-8	30
Illite (clay mica)	4-6	50
Vermiculite and smectite	0-2	100-150
Kaolinite	0	2-15

Most K in soils is tied up in primary minerals, such as K-feldspar and micas or secondary minerals such as illite, clay mica.

There are four forms of K in the soil:

○ the unavailable mineral form,

○ the non-exchangeable form in fine-grained micas,

○ the exchangeable form on clay and organic matter surfaces, and

○ K^+ in soil solution.

Unavailable mineral K

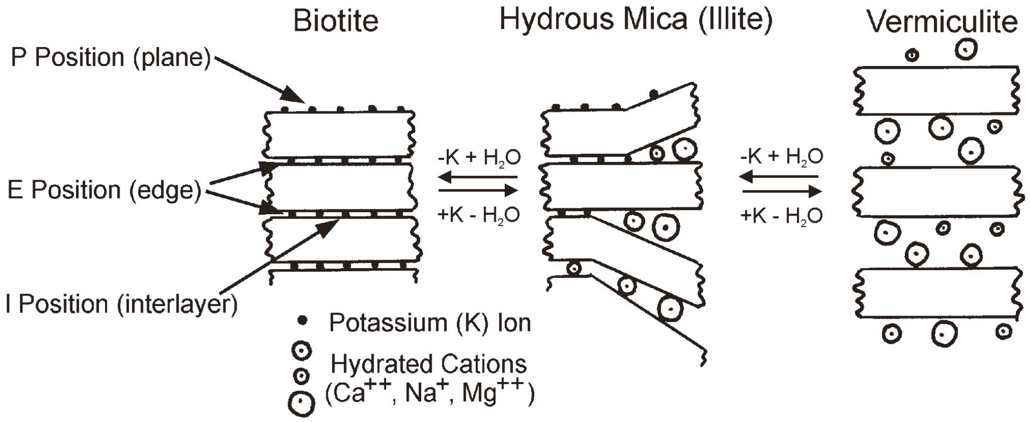
Approximately 90-98% of K in soils is in a relatively unavailable primary mineral form. Potassium occurs mainly in the framework silicate K-feldspars and in micas. In K-feldspars, the K-ion is tied by strong, covalent bonds and it requires a large amount of energy to release K from this mineral. However, despite their very low solubility, K-feldspars in the sand fraction of soils may provide a more continuous supply of K to soil solution than previously thought (Sparks 1987).

‘Non-exchangeable’ K

In fine-grained micas, the K-ion is largely in the ‘non-exchangeable‘ form, whereas the non-hydrated K-ion is sandwiched between silicate layers. The non-hydrated K in the interlayer space is not readily available to plants, but can become available through the opening of the interlayer space during weathering when hydrated cations such as Na, Mg and/or Ca open up the lattice and replace K. The process of opening the mica lattice starts from the edges and progressively expands the interlayer space with the concurrent replacement of the unhydrated K with large, hydrated cations Ca, Mg and/or Na (Figure 5.5).

Exchangeable K

In micas, K is found in three principal positions, the p-position (planar), the i-position (interlayer) and the e-position (edge) (Figure 5.5). During weathering, K is replaced by other cations, for example H^+ and the hydrated cations Ca^{2+}, Mg^{2+} and Na^+. The replacement of K is energetically easiest from the planar position, followed by the edge, and last from the interlayer position (Rich 1968). The opening of the mica starts from the edge with hydrated cations replacing the non-hydrated K (Figure 5.5). This process is dependent on factors such as charge density, moisture content, and the concentration of competing ions. With the progression of soil weathering, the K-content in the minerals decreases, and the CEC of the soil increases to a maximum of about 150 cmol (+) kg^{-1} in vermiculites (Table 5.2). Beyond this point, further weathering of clay minerals to kaolinite results in a decrease in CEC.



K Content (%)	10	4-6	<1
CEC	0	30-50	150

Figure 5.5. *Simplified illustration of the weathering of biotite mica to hydrous mica (illite) and vermiculite.*

Soil solution K

Typically, about 1-2% of the total K in soil is in the plant-available form, either directly available from soil solution or from exchangeable K. Soil solution K and exchangeable K exist in a dynamic equilibrium such that when the concentration of soil solution K is reduced due to root uptake, some of the exchangeable K is desorbed from the exchangeable sites, replenishing the soil solution K. When K is added to the soil in the form of K-fertilizer or other forms of soluble K, the soil solution becomes enriched and K from the soil solution can be adsorbed onto the exchange sites of clays and organic matter.

The dynamic equilibrium relation of the different forms of K can be summarized as follows:

- ○ Mineral K (e.g. in K-feldspar and mica),
- ○ Non-exchangeable K (e.g. in illite and biotite),
- ○ Exchangeable K (on clays and organic matter),
- ○ Soluble K (in soil solution).

Figure 5.6 shows a general picture of K gains and K losses in the rock-soil-plant continuum. Figure 5.7 illustrates, in a simplified manner, the release and exchange of K^+ in the soil and root environment.

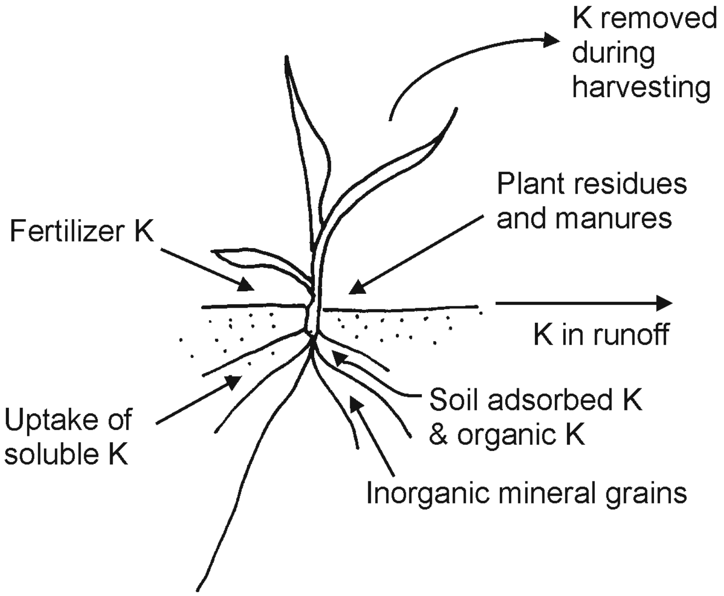


Figure 5.6. *Gains and losses of potassium in the rock-soil-plant continuum.*

The reverse process of K release in soils is the fixation of newly added K sources. When soils are degraded, and K resources are depleted, the micas are transformed into 2:1 clays, specifically vermiculites. Potassium ions add to 2:1 clays, through the addition of K-fertilizers or manure, can be captured, or ‘fixed’. Figure 5.5 illustrates both processes, showing the release of K from biotite (reading the process from left to right) and K-fixation (reading the process from right to left).

K-fixation is high in soils with high amounts of negatively charged vermiculites and illites (clay mica). These soils can fix considerable amounts of newly applied K^+. However, these vermiculite-rich soils not only 'fix' K^+ but NH_4^+ as well, which has a similar ionic size. This K^+ (and NH^+) fixation in vermiculite-rich soils can have large agronomic consequences for farmers, on rates of K-fertilization, and on the management of soil in general.

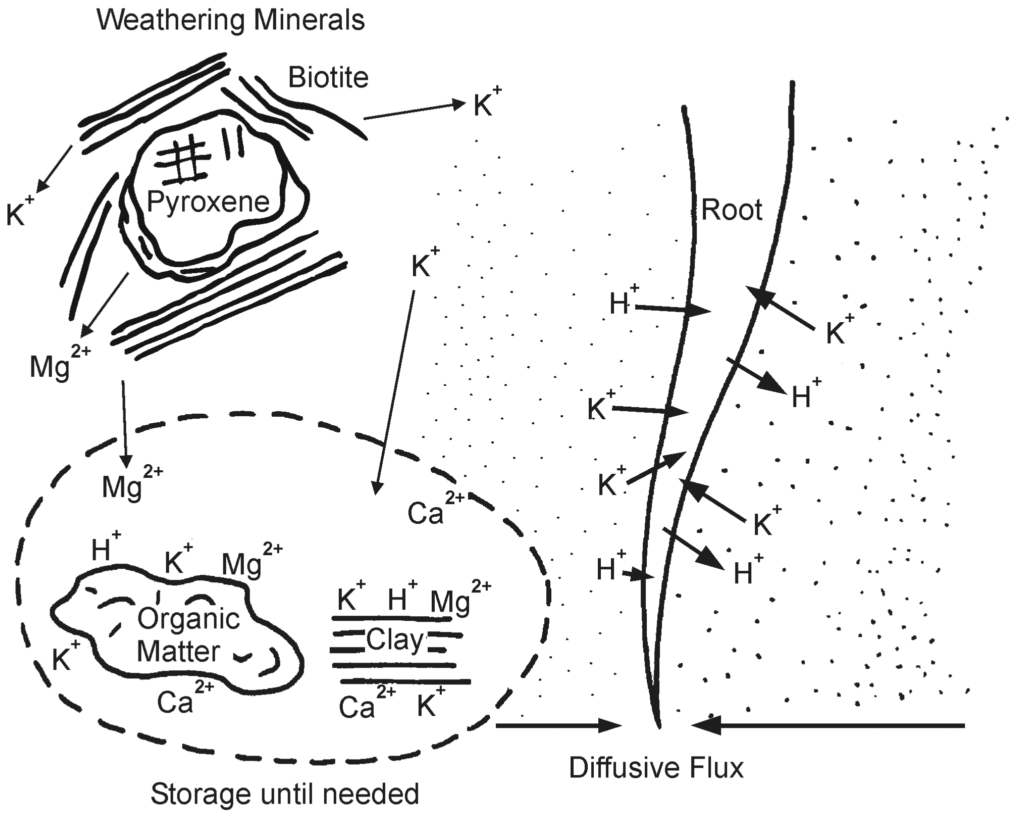


Figure 5.7. *Uptake of K^+ by plants. Diagram shows K^+ and other cations in solution, in exchangeable form on clay and organic matter and in weathering mineral grains (here biotite).*

Additional factors that influence the fixation of K are wetting and drying processes, as well as the CEC and pH of the soils. Alternate wetting and drying cycles enhance the release and fixation of non-exchangeable forms of K in vermiculites and illites. The Cation Exchange Capacity (CEC) is the ability of the soil to hold onto cations and prevent them from leaching beyond the roots. In soils where the CEC is elevated, more K^+ and other cations are adsorbed and thus fewer ions are available in the soil solution. The concentration of positive ions, which compete for exchange sites, also influences the fixation of K^+. Similarly, the pH is a measure of its H^+ concentration, so the fewer H^+ ions in the soil solution (in alkaline soils), the lower the competition for exchange sites. Liming increases soil pH (see Chapter 7) and consequently increases K-fixation. K deficiencies have been commonly observed on calcium-carbonate-rich, high pH soils.

Soil testing provides information on the sufficiency levels of soils for plant growth. Havlin *et al*. (1999) reports the K-sufficiency concentrations for soils on which maize/corn is grown (Table 5.3). K concentrations below 40 mg kg^{-1}, which is equivalent to approximately 0.1 cmol (+) kg^{-1}, are considered very low.

Soil test results must be interpreted with caution because laboratories, extraction methods, soil conditions and soil test interpretations vary strongly from place to place. Cox *et al*. (1999) showed that the conventional 1 *M* NH_4OAc-exchangeable potassium (K^+) soil test is inadequate in soils where non-exchangeable K^+ contributes significantly to crop nutrition.

Table 5.3. *K sufficiency levels and soil test K, measured with the 1 molar ammonium acetate method (source: Havlin et al. 1999). 39 mg kg^{-1} is equivalent to 0.1 cmol (+) kg^{-1}.*

Exchangeable K in soil (mg kg^{-1})	**Sufficiency level**
<40	very low
41-80	low
81-120	medium
121-160	high
>160	Very high

5.3 Geology of Potassium

The average concentration of K in the upper earth's crust is 2.8% K_2O or 2.3% K (Rudnick 2003). However the K-concentrations of different rocks and minerals vary considerably (Table 5.4). Granitic and rhyolitic rocks have relatively high total K-concentrations. However, most igneous rocks, such as basaltic rocks, contain considerably lower levels. Ultramafic rocks, such as dunites, peridotites and serpentinites, have very low concentrations of K (Ahrens 1965). On the other hand, ultrapotassic volcanic rocks contain relatively high concentrations of K (Gupta and Fyfe 2003).

Sedimentary rocks make up 5-8% of the earth's crust, but cover approximately 75% of the land surface (Pettijohn 1975). Some sedimentary rocks contain relatively high concentrations of K, especially those derived from clay-rich sediments (Table 5.4). Some glauconite-rich sediments, for example Eocene greensand marls from New Jersey, USA, contain between 3.5 and 7.8% K_2O (James 1966). Sediments lowest in K are carbonates, dolomites and calcitic limestones (Wedepohl 1970).

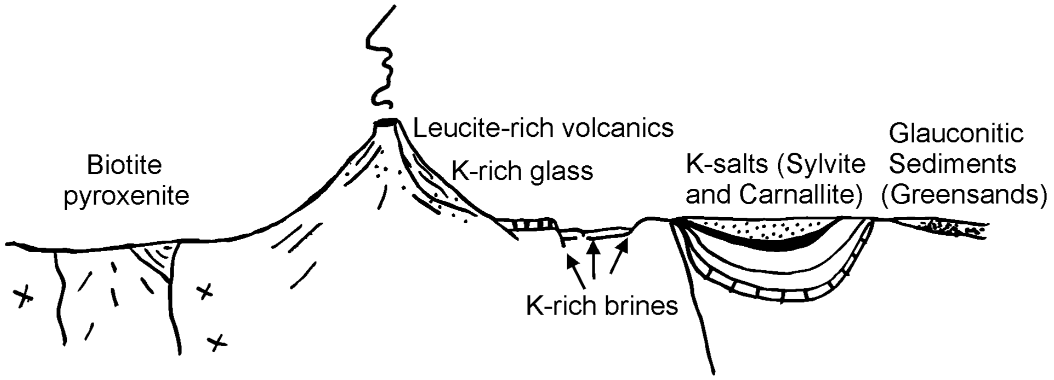


Figure 5.8. *Simplified cross-section of geological K resources.*

Table 5.4. *K_20 content of selected rocks and minerals. Sources: Ahrens (1965); Wedepohl (1970); Gupta and Fyfe (2003). Conversion factors shown on page vi.*

Rock type	Total K_2O content (%)
Granitic and Rhyolitic rocks	3.8
Andesitic rocks	3.2
Basaltic rocks	0.7
Ultamafic rocks (dunites, peridotites, serpentinites)	0.1
Ultrapotassic volcanic rocks	2-6 (in exceptional cases up to 10-14%)
Limestones	0.31-2.81 (clay-rich)
Carbonatic limestone	0.68
Dolomitic limestone	0.31
Sandstone	0.01-6.68 (average 1.48)
Shales	3.2
Gauconitic sediments (Eocene greensand marls from New Jersey, USA)	3.5-7.8
Evaporites (K-salts)	17-63

By far, the most abundant minerals in the earth's crust are silicates: quartz, feldspars, micas and other minerals such as amphibole, pyroxene, olivine and clay minerals. Most of the K in the crust is incorporated in silicate minerals. Most K-silicates are insoluble. Consequently, most of the K is not available to plants in the short run. However, the agronomic potential of specific K-silicates as slow-release K fertilizers, for example leucite, biotite/phlogopite, glauconite and some K-zeolites may be high and should be tested on K-responsive crops and tree species, e.g. plantation crops.

Table 5.5. Potassium content of some silicate minerals.

Mineral	% K_2O
Leucite	20-21
K-feldspar	8-15
Biotite	7-10
Phlogopite	7-11
Muscovite	7-11
Glauconite	6-8
Illite (clay mica)	4-8

The highest concentrations and most soluble forms of K in rocks and minerals are found in the chemically precipitated sedimentary rocks known as evaporites. These rocks are made up mainly of salt minerals, some of which contain very high K concentrations (Table 5.6). In current agricultural land management practices most of the soluble K and Mg inputs are derived from K-salts. Potassium fertilizers are mainly obtained from evaporite based potash deposits containing sylvite (KCl) or complex K-Mg chlorides and sulphates.

***Table 5.6.** The most common K-bearing minerals in bedded (sedimentary) salt deposits.*

Chemical Formula	Mineral	K_2O Content
KCl	Sylvite	63%
$KCl \cdot MgCl \cdot 6H_2O$	Carnallite	17%
$4KCl \cdot 4MgSO_4 \cdot 11H_2O$	Kainite	19%
$K_2SO_4 \cdot 2\ MgSO_4$	Langbeinite	22%

The presently used K and Mg fertilizers are very soluble and the released nutrients are easily available to plants. This soluble characteristic of K-salts makes them easily leachable, especially in sandy soils with little clay or organic matter. In addition, many of these soluble K and Mg sources are salts containing chlorine, which are unsuitable for salt sensitive crops such as potatoes and tobacco. Based on environmental and economic considerations, interest in slow-release alternatives to these highly reactive, soluble fertilizers is growing.

5.3.1 K-salts

Potassium bearing salts (potash) are finite, non-renewable resources in many parts of the world. The global potash production in 2004 was 30 million tonnes of K_2O equivalent (US Geological Survey 2005). About 95% of the potash produced is used in the fertilizer industry (Williams-Stroud *et al.* 1994). The remaining 5% is used in the manufacture of K-based chemicals (Harben 2002). Canada, Russia, Belarus and Germany are the main producers of K-fertilizers followed by Israel, Jordan and the United States. The 2004 world potash production, on a country-by-country base, is illustrated in Figure 5.9. The distribution of major potash deposits in the world is shown in Figure 5.10.

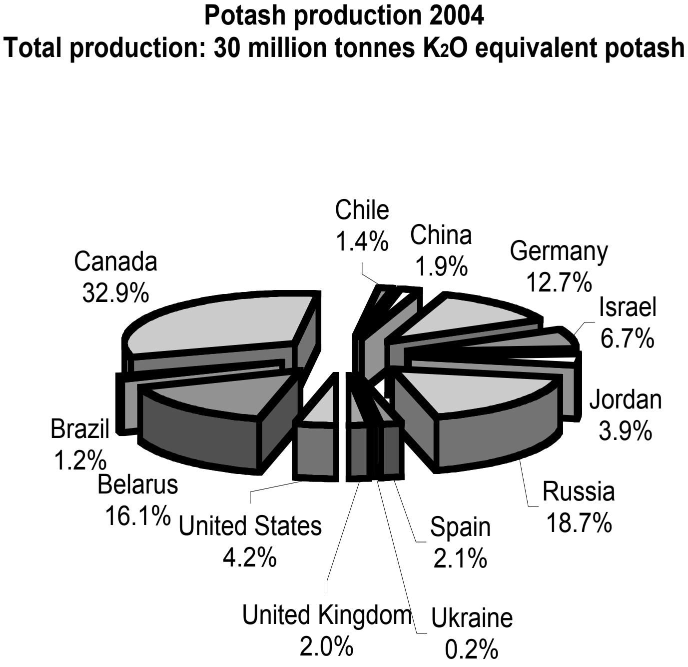


Figure 5.9. *Global potash production (source: US Geol. Survey 2005).*

The main naturally occurring soluble K-salt is sylvite, KCl, which in the fertilizer industry and farming communities is known as 'muriate of potash' (MOP). Other naturally occurring soluble K-minerals include carnallite, kainite and langbeinite (Table 5.6).

Global reserves of potash are estimated at 8.3 billion tons K_2O equivalent. Global resources total about 250 billion tonnes K_2O equivalent (US Geological Survey

2005). Based on the reserve figures and using current production rates, current 'reserves' will last more than 270 years. Taking the 'resource' figures into account, the lifetime would be several thousand years.

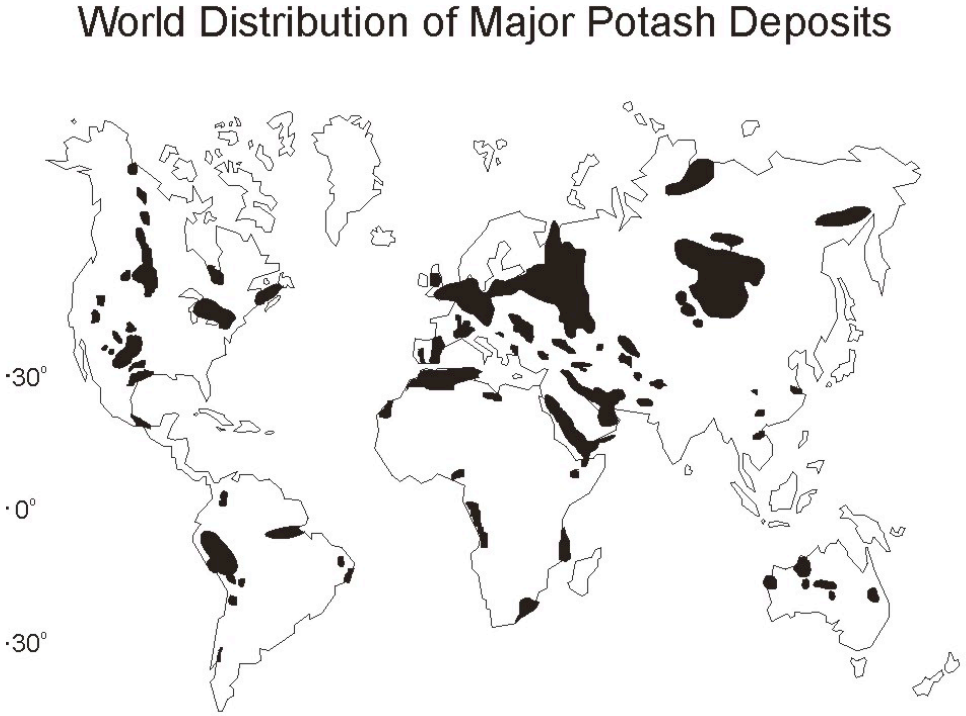


Figure 5.10. *Distribution of major K-deposits in the world (source: Adams 1975).*

In addition to the naturally occurring K-salts, some K-salts are synthesized. The potash fertilizer 'sulphate of potash' (K_2SO_4) is a synthesized fertilizer, produced through a reaction of KCl and sulphuric acid. This K fertilizer is the principal non-chloride source of potassium and is widely used in high value crops such as fruits, vegetables, coffee, ornamentals and tobacco. The second most important non-chloride K fertilizer used in special horticultural applications is KNO_3, which is manufactured at nitrate plants in Chile's Atacama Desert. The process to produce K-nitrate involves the reaction in solution:

$$NaNO_3 + KCl \rightarrow KNO_3 + NaCl \qquad \text{(equation 5.1)}$$

The formation of K-salt deposits

Naturally occurring K-salts are formed in restricted marine basins during periods of high evaporation rates, high temperatures and low relative humidity. Salt basins are restricted to arid areas of low latitude. The formation of K-salts is generally related to increasingly concentrated sea water brines or from mixing of sea water with brines. Bedded-salt deposits are generally of marine origin and form when sea water is trapped in structural basins, cut off from the open sea. Sea level changes or uplifting of the land are commonly the reason for the changing configuration of inland basins. When the sea level is high, water can circulate freely into oceans and basins, but once the sea level falls, the circulation in the basins becomes increasingly restricted. The specific gravity of the sea water plays an important role in circulation within the restricted basins (Figure 5.11).

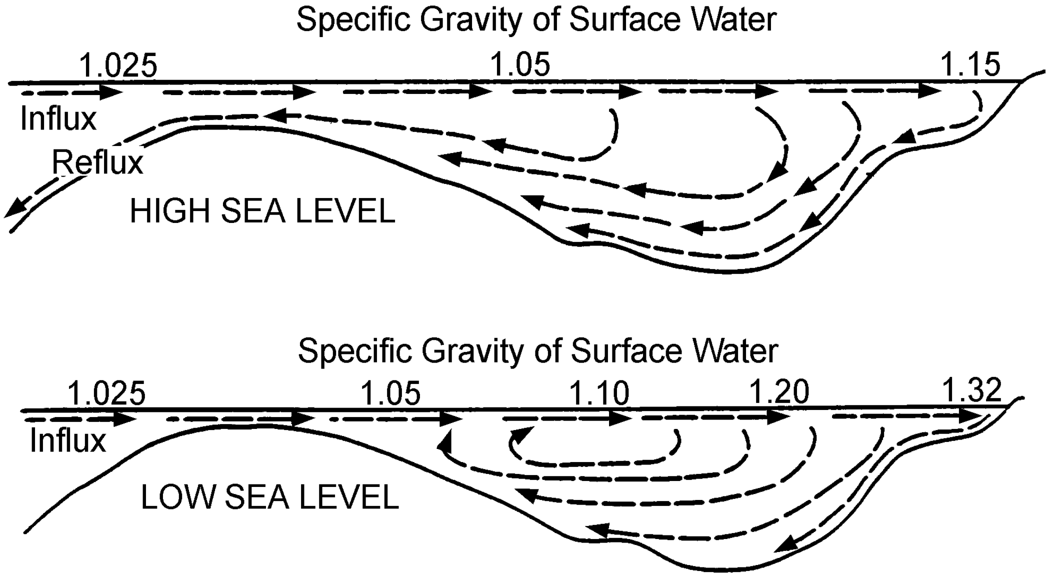


Figure 5.11. *Basin cross-sections showing the effect of sea level on circulation and salinity (adapted from Hite 1970). Numbers provided in the figure represent specific gravity (s.g.) of the aqueous solution in the basin.*

Sea water contains about 3.5% dissolved salts (35,000 mg L^{-1}). This sea water starts to concentrate due to high rates of evaporation. Concentrated brine, which is heavier than the sea water, sinks to the floor of the basin centre and at a certain concentration the concentrated brine starts to precipitate. The first minerals to precipitate are carbonates, commonly Ca-carbonates. When the water loss reaches 80% of the total, gypsum ($CaSO_4{\cdot}2H_2O$) will precipitate, and when it reaches 90% of the original, NaCl (halite) will precipitate. Complex Mg-K salts, polyhalites, start to precipitate when the volume is only 2-3% of the total. At this stage, the specific gravity of the brine is about 1.29 g cm^{-3}. Sylvite (KCl) and carnallite are the last minerals to precipitate. Potassium-bearing salts precipitate at the end of the evaporation cycle and occur only near the top of halite beds as thin layers of either Mg-sulphate rich K-salts (e.g. carnallite) or Mg-free minerals such as sylvite (Table 5.7). The resultant sediment sequence starts with carbonate, followed by sulphates, and ends with Na-salts and finally K-salts (Figure 5.12).

Table 5.7. *Mineral sequence from the evaporation of a seawater solution at 25ºC. Concentration factor is relative to average seawater.*

Mineral	Concentration Factor	Water Loss (%)	Brine Density (g cm^{-3})
K-Mg salts	63x	98.7	1.29
Halite	11x	90	1.214
Gypsum (anhydrite)	5x	80	1.126
$CaCO_3$	2-3x	50	1.10
Seawater	1x	0	1.04

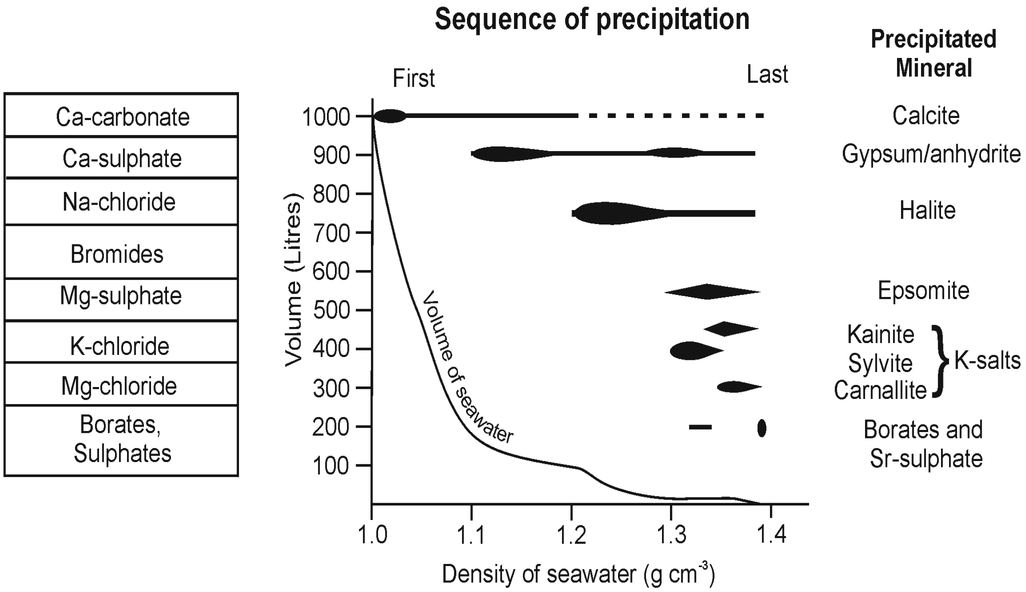


Figure 5.12. *Sequence of mineral precipitation from seawater upon evaporation (modified after Guilbert and Park 1986).*

Most evaporites have precipitated during specific times in geological history. While there are indications of evaporite precipitation in Precambrian times (now only seen as salt pseudomorphs), there were periods of widespread evaporite deposition, specifically during the Cambrian, the middle Paleozoic, the Permian as well as the Triassic and the Jurassic and the Miocene (Ronov *et al.* 1980). Several researchers have postulated that the large evaporite basins were formed during tectonically active times when tectonic forces generated rifts and induced basin restrictions (Warren 1989; Hay and Wold 1990).

Apart from variations in the abundance of evaporites in the Phanerozoic times (Ronov *et al*. 1980) there seem to be secular oscillations of the mineralogies of evaporites in the range of 150 – 200 million years (Hardie 1996). There are periods when potash deposits were precipitated that were richer in $MgSO_4$-salts (such as kieserite – $MgSO_4 \cdot H_2O$) than periods when K-deposits were characteristically rich in KCl and poor in Mg-salts (Hardie 1991). These were probably related to changing chemistries of the seawater (Hardie 1996).

Early models of the formation of K-salt deposits described direct evaporative precipitation in a single episode in a single basin. However, observed natural evaporative sequences point to a more complex process. Natural evaporite successions often consist of greater amounts of carbonates and gypsum than predicted. Commonly, the ratio of carbonates to sulphates to halites and K-salts is different from the expected ratio. Furthermore, simple evaporation models of sedimentary basins cannot explain the amount of halites in most deposits. Some salt deposits are more than 2000 m thick, which indicates that the sea would have had to be impossibly deep (Kendall 1984). Consequently, these early models have been replaced by more complex models (Eugster and Jones 1979, Kendall 1984).

Experimental geochemical work, phase equilibrium studies (Eugster *et al.* 1980), and computer modeling show that other factors have to be included to conform with the actual mineral sequence found in salt basins. Sedimentological evidence supports a model of a shallow, only partially isolated basin into which seawater is episodically added. Seawater becomes concentrated and trapped at the bottom of this basin and begins to precipitate. The rate of new influx of seawater and the rate of evaporation largely determine the concentration of the brine and the subsequent precipitation. Other processes that affect the complex successions of salts found in nature are convection and mixing of brines in the basin, re-solubilization, diagenesis and post-depositional reactions between precipitated salts and brines (Eugster and Jones 1979; Eugster *et al.* 1980).

Different types of K-salt deposits

Hardie (1990) divided potash-bearing deposits into two principal categories: Mg-sulphate rich K deposits with polyhalite, kieserite and epsomite as salts, and Mg-sulphate-poor K deposits. Other subdivisions of evaporites can be made based on geological depositional environments (Tucker 1981). These include:

- epicontinental basins,
- rift basins,
- salt-domes,
- coastal supra-taidal salt flats (sabkhas), or
- inland saline lakes.

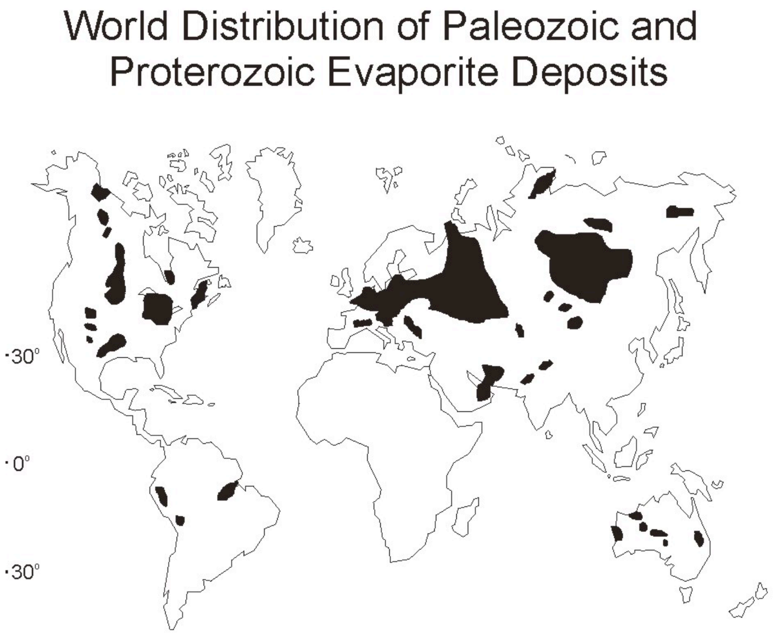


***Figure 5.13**. Distribution of Palaeozoic and Proterozoic evaporite deposits (source: Adams 1975).*

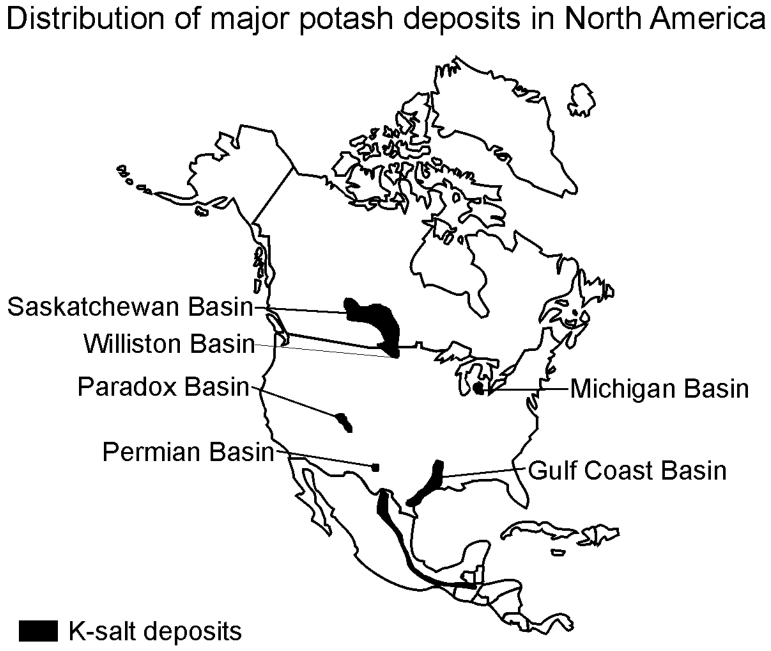


***Figure 5.14.** Distribution of major potash deposits in North America (modified after Kesler 1994, with permission).*

Epicontinental K-deposits

The largest K-salt deposits formed in epicontinental seas (shallow, intracratonic or near-continent seas) during the Devonian (in Canada) and the Permian (in Europe, the Urals of Russia and in the USA) (Figure 5.13). The formation of extensive K-deposits in Saskatchewan, Canada, is discussed in Holter (1969), Worsley and Fuzesy (1979), Zharkov (1984) and Kendall and Harwood (1996). The potash deposits of Saskatchewan extend into North Dakota and Montana, USA, into the Williston Basin (Anderson and Swinehart 1979). Other extensive North American K-deposits are located in New Brunswick, Canada (Anderle *et al.* 1979) and in the United States, in the Gulf Basin (Lowenstein 1982), in the Paradox Basin in Utah (Hite 1970; Adams 1975), and in Michigan (Harben and Bates 1984) (Figure 5.14). In Eastern Europe, the largest K-containing epicontinental evaporites are located on the western flanks of the Urals of Russia, in Belarus and the Ukraine (Harben and Bates 1984). In central Europe, large evaporite deposits of Permian age are located in the so-called ‘Zechstein Basin’ that stretches across central Europe, from England through the Netherlands, Germany and Denmark to Poland.

In Europe, potash ores are part of an extensive intracratonic evaporite basin, approximately 900 by 1500 km in size and occurring at the top of some of the five evaporite cycles (Z 1-5) of clastic sediments, carbonates, sulphates and halites. In Germany, K-rich salts are found in three of the evaporite cycles. A typical succession of salt sequences in the German potash-bearing evaporite basins of the ‘Zechstein’ Formation (the Zechstein Basin) is shown in Figure 5.15.

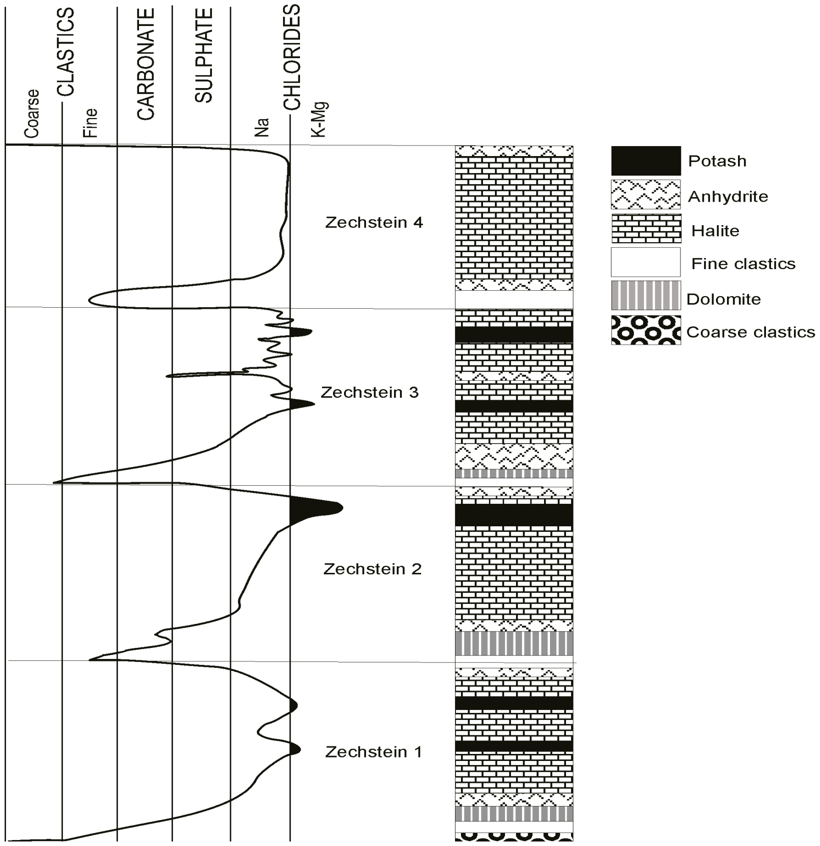


Figure 5.15. *Typical salt sequence in the Zechstein Formation of the German potash-bearing evaporite sequence (modified after Richter-Bernburg 1955).*

Rift-related deposits

Potassium deposition in continental rifts occurs in a similar way as in epicontinental basins. Sea water floods into continental rifts at the breaking up of continents, and then concentrates by evaporation. Evaporites finally precipitate from the dissolved load. Rift-related K-deposits can be recognized because they are usually underlain by typical continental rift sediments (for example red sandstones) or continental volcanics and capped by marine sediments. This succession indicates a gradual transition from a continental to a marine setting.

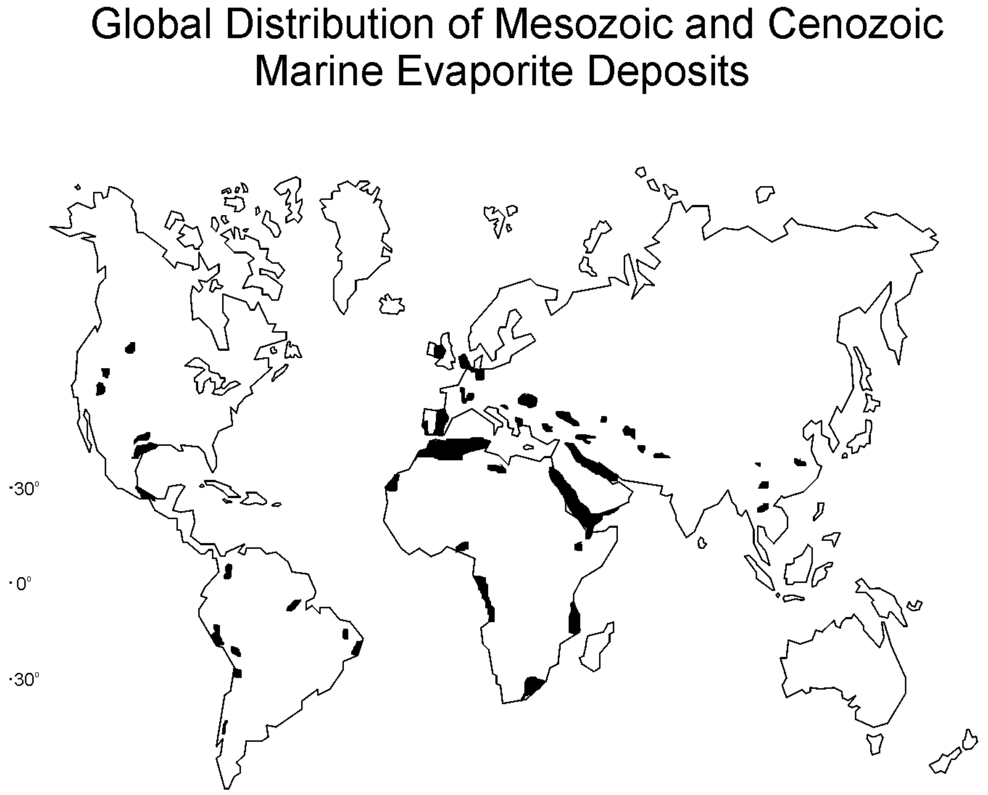

Global Distribution of Mesozoic and Cenozoic Marine Evaporite Deposits

Figure 5.16. *Global distribution of Mesozoic and Cenozoic marine evaporite deposits (source: Adams 1975).*

K-deposits of Mesozoic and Cenozoic age are mostly related to rift or paleo-rift environments (Figure 5.16). Some of the rift-related deposits of South America and of West Africa exhibit the same stratigraphical successions on both sides of the South Atlantic, indicating that they were deposited at the same time, when the two continents were just beginning to drift apart and seawater was invading the opening South Atlantic Rift (Figure 5.17; Rona 1982). Other rift-related deposits are found in the Red Sea area (Williams-Stroud *et al.* 1994), in the Rhine Graben of France and Germany, and on the eastern and western continental margins of the South Atlantic in Brazil (Szatmari *et al.* 1979), Angola, Gabon and Congo (de Ruiter 1979; Rona 1982). Potash deposits of Mesozoic and Cenozoic ages are mostly related to rift or paleo-rift environments (Figure 5.16).

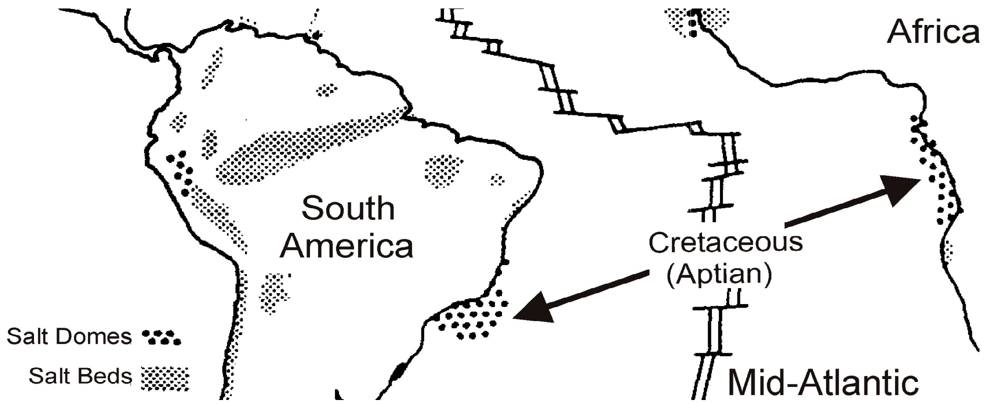


Figure 5.17. West African and Brazilian evaporite deposits. These salt deposits were formed in the early stages of development of the South Atlantic Rift (modified from Rona 1982).

K-deposits related to salt domes

Considerable amounts of K-bearing salts are also recovered from salt dome structures with deformed bedded salt deposits (Trusheim 1960). Salt domes form because salt has a lower specific gravity (<1.5 g cm^{-1}) than most other minerals, and also has a high plasticity and because salt 'flows' under high pressure. Consequently, when new layers of sediment are deposited over bedded salt deposits, the lighter salts try to find their way to the surface by migrating upward, piercing the overlying rock layers as they rise (Figure 5.18). Potassium salts are usually secondary targets of exploration since the more valuable resources associated with salt domes are oil and natural gas.

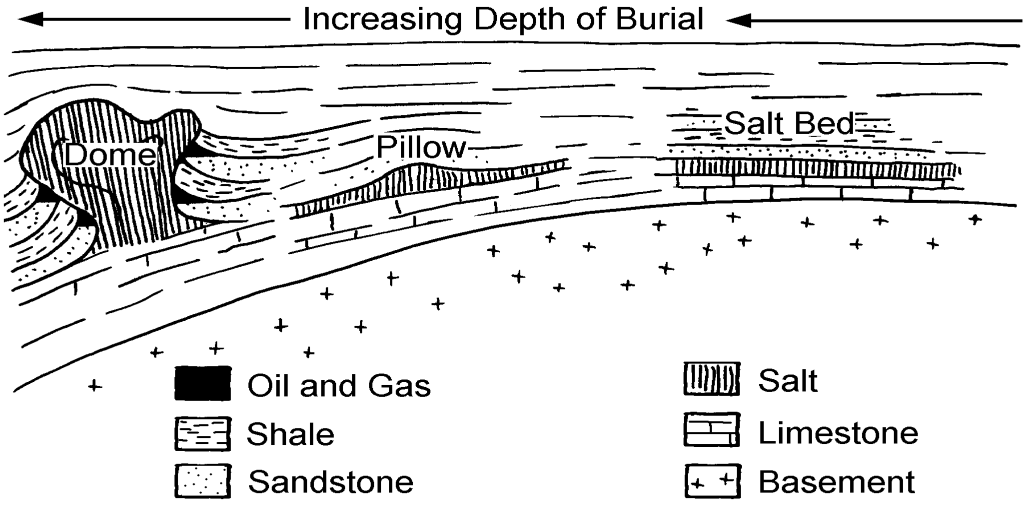


Figure 5.18. Formation of a salt dome (adapted from Trusheim 1960).

Sabkha- type deposits

Small amounts of K-salts are also found in shallow tidal flats, sabkhas. Sabkha is an arabic word for salt-flat. The deposition of gypsum-anhydrite and salts in sabkhas was discovered only in the 1960's along the coast of the Persian/Arabian Gulf (Shearman 1966). Sabkha-type potash salt deposits occur on desert coastal plains or tidal flats similar to those existing presently in the Persian/Arabian Gulf. The extremely high rate of evaporation on these tidal flats causes the drawing up of saline water from the oceans and subsequent crystallisation of salts, mainly at the level of the water table (Kendall and Hardwood 1996).

Salt Lakes

Relatively small amounts of K-salts are reported from salt lakes. These salt lakes are lakes without an outlet in an arid environment. Because there is not an outlet for the lake, the chemical load is trapped, and therefore becomes concentrated and eventually precipitates as salt deposits.

How to find K-salt accumulations

The discovery of K-salt deposits usually follows two exploration steps. The first step is target selection based on understanding the genesis of K-salt deposits. The second step is to utilize the best and most economic exploration tools to find and delineate deposits. Exploration tools for K-salt deposits are largely geophysical in nature. The combination of concept oriented surveys and detailed exploration is an important part of almost all mineral exploration.

Step 1 Target Selection

Evaporite deposits, including potash deposits, are not distributed equally in time and space. On a global scale, there have been certain periods when the climatic conditions were highly conducive to salt-formation, resulting in high rates of evaporite precipitation. Also, there are certain geographical-geological settings that are more prone to evaporite-deposition than others. Therefore, to target an area with a high probability of containing K-salts deposits, it is important to understand the optimal climatic conditions and geological settings that control the formation of evaporites.

Since there are no modern analogues to the main evaporite basins of the past, it is important to study the environmental conditions where evaporite precipitation has occurred. As described above, major evaporite deposits have generally been formed in restricted basins with saline, predominately marine conditions. These deposits occur in shallow sediments along continents, in large inland seaways, in passive margin areas, but also in back-arc areas and in rift situations. It is important to find areas where these geological conditions coincide with conducive climatic conditions, where evaporation exceeds rainfall. The main latitudinal distribution of modern evaporitic sediments is between 15 and 45 degrees north and south of the equator (Figure 5.20). In the past, periods of widespread evaporite deposition have occurred during the Cambrian, the middle Paleozoic, the Permian as well as the Triassic and the Jurassic and the Miocene (Ronov *et al.* 1980) (Figure 5.21).

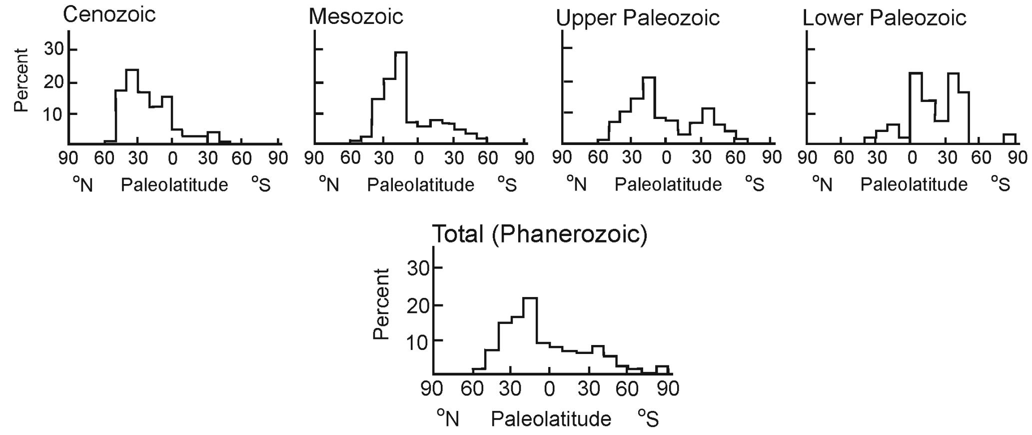


Figure 5.20. Latitudinal distribution of evaporite deposits during the Phanerozoic relative to paleo-equator (after Gordon 1975).

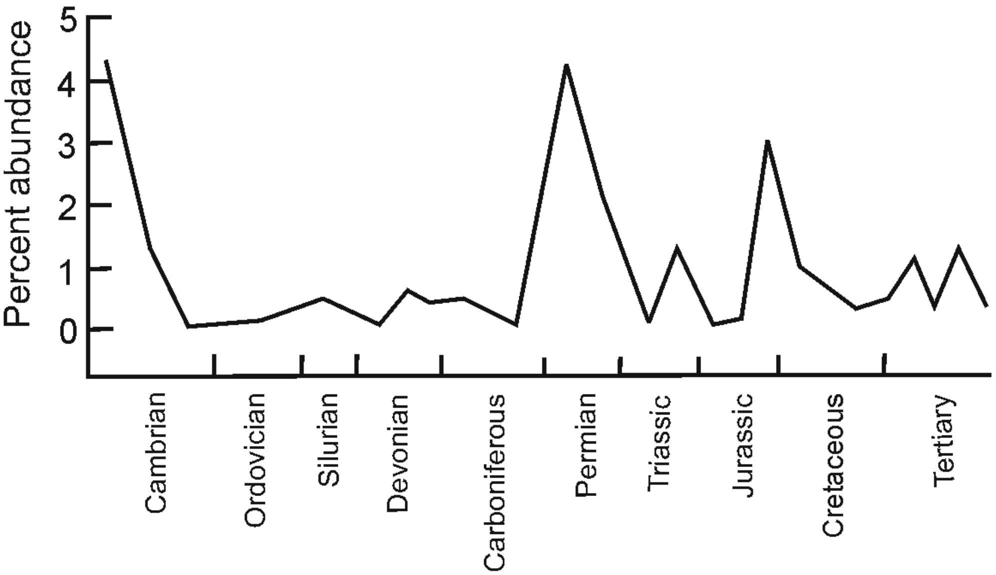


Figure 5.21. Temporal distribution of salt deposits in the Phanerozoic (modified after Ronov et al. 1980).

Step 2 Specific Surveys

Because of the soluble nature of salts there are only a few K deposits that are actually exposed at the surface, e.g. in the extreme arid Danakil depression of Ethiopia and Eritrea. However, at present all mined potash deposits are located below the earth's surface. Therefore once the target area is selected the next step is to employ methods to determine whether salt deposits are beneath the ground.

On a local scale, some indications of evaporite sequences can be deduced from surface indicators such as saline springs and wells, solution breccias, thick outcrops of gypsum or anhydrite, and domal or collapse structures, such as sink holes. However, to find K-salt deposits it is generally necessary to carry out detailed exploration work, mainly using geophysical exploration methods.

There are several types of geophysical exploration methods for K-salts including: gravity surveys, and geophysical and geochemical borehole measurements of various types.

Gravity surveys are survey types to identify materials by contrasting densities. Salt bodies with their low densities and salt structures (e.g. salt domes) can be identified and outlined with this kind of survey. However, the method does not discriminate between different types of salts and can be used only as a general tool to identify thick salt-bearing sedimentary sequences and salt structures.

Geophysical surveys, specifically radiometric borehole surveys, can be used to locate K-salts. This is largely based on the fact that a certain proportion of naturally occurring K is in the form of the radioisotope ^{40}K. Finding a spike in ^{40}K gamma rays in borehole measurements within salt structures usually indicates elevated concentrations of K salt (Figure 5.22). Geophysical and seismic surveys are also useful in the search for salt domes. These structures are most often targeted in the search for oil and natural gas.

Other exploration techniques for finding K-salts include geochemical borehole surveys for bromine (Br). This element is an indicator element in the search for K-salts because Br substitutes for Cl in the crystal structure of halite (NaCl). Figure 5.23 shows the typical regular increase in Br substitution in a sequence of halite samples from the bottom upward. A higher amount of substitution indicates that the concentration of NaCl in the remaining evaporite-rich seawater is increasing, and the deposition is nearing the end of NaCl precipitation and entering the phase of K-salt precipitation (Figure 5.23).

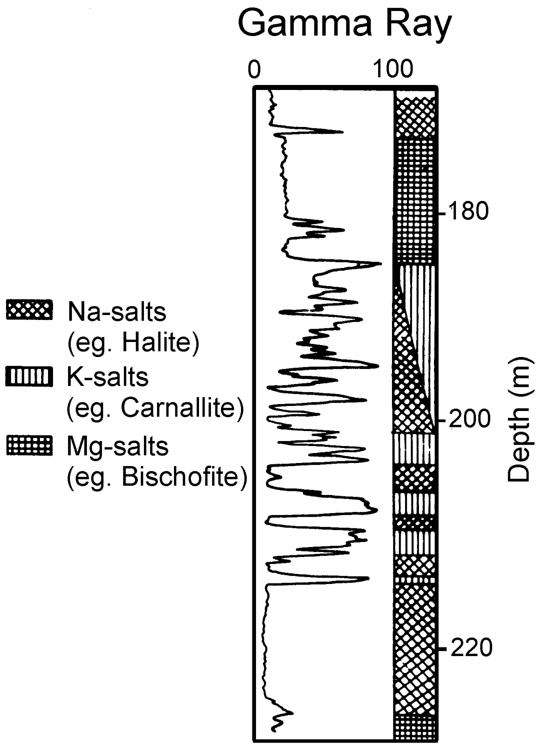


Figure 5.22. *A salt cycle with gamma ray log showing relationship between K-salts and gamma ray activity (modified after de Ruiter 1979).*

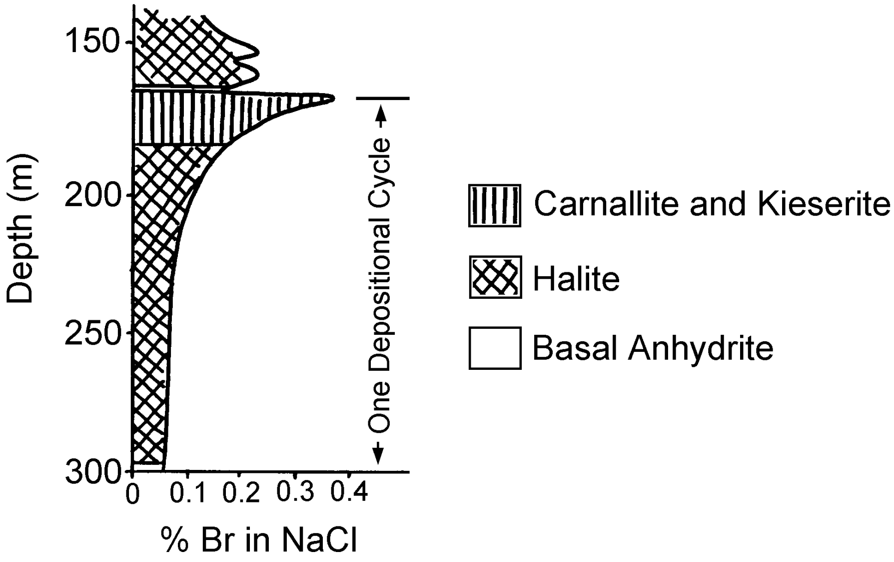


Figure 5.23. *Bromine profile from a German evaporite deposit showing the % Br, which substitutes for Cl in the mineral halite (adapted from Williams-Stroud et al. 1994).*

5.3.2 K-silicates

Most of the K in the earth's crust is incorporated in the silicate minerals feldspar, biotite, muscovite and the feldspathoids leucite and nepheline, as well as in sediments rich in clays, specifically illite, also called clay mica. Traditionally, only soluble K-sources (from salts) have been considered as K-resources for fertilization techniques. No major exploration efforts have been carried out to discover and delineate alternative K-silicate resources such as ultrapotassic volcanics or phlogopite/biotite resources. Nevertheless, it is well known that many of these resources exist either as unrecovered rock material in the ground or as unused 'waste' material in mining operations, for example from the igneous phosphate mining operations in Siilinjarvi, Finland, Phalaborwa, South Africa and Brazil as well as mica operations in Sri Lanka (Weerasuriya *et al.* 1993).

Feldspar, one of the most common K containing minerals, consists of an infinite network of SiO_4 and AlO_4 tetrahedra whereby the structural substitution of Al^{3+} for Si^{4+} generates a residual negative charge that is neutralized by cations such as K^+, Na^+ or Ca^{2+}. The K is tightly bound in the framework of this mineral and is released only very slowly and under certain conditions. In general, due to the strong structural bonding of K in the K-feldspars, K is released from feldspars only very slowly, much slower than K bound to micas and the clay mica illite. While K in feldspars occurs in weathering resistant framework lattices (Sanz Scovino and Rowell 1988) the minerals of the mica and micaceous clay group release K much more easily and faster as the K is less strongly bound in the mineral lattice (Tan 1980).

The structure of the micas is complex. Potassium occurs in phyllosilicates, consisting of silica tetrahedra sheets and alumina or magnesia octahedral sheets (Figure 5.24). The release of K from mica has been studied in fundamental mineral research in many laboratory studies (Rausell-Colom 1965; Schnitzer and Kodama 1976; Tan 1980; Feigenbaum *et al.* 1981; Kodama *et al.* 1983; Song and Huang 1988). The tightly packed muscovite mica weathers less rapidly than biotite or phlogopite. Consequently, K-release from muscovite is very low. Upon weathering, biotites and phlogopites commonly release Mg and Fe as well as K.

Leucite ($K(AlSi_2O_6)$), nepheline ($KNa_3(AlSiO_4)_4$) and kalsilite ($K(AlSiO_4)$) are feldspathoids found especially in silica undersaturated volcanic rocks and other alkaline rock suites. Among these, leucite has an especially high K_2O content (up to 21%) and a relatively high solubility (Evans, pers. com. 2004). Leucite bearing rocks are found in many parts of the world, in East Africa, China, Brazil, Indonesia, and the United States. So far, no agricultural utilization of nepheline- or leucite-rich rock materials has been reported. Mathers (1994) mentioned the high K-concentration of these K-rich rock types, and proposed that they be used as a potential K-source for use as direct application fertilizer.

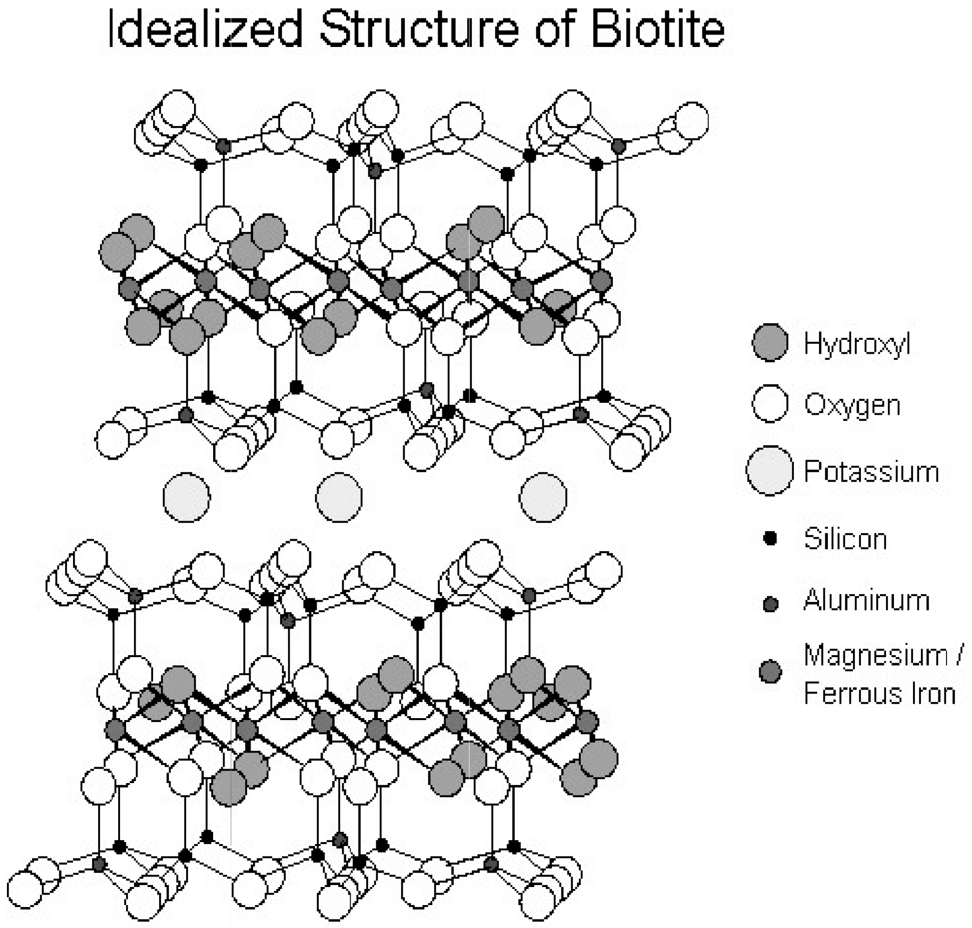


Figure 5.24. *Idealized mineral structure of biotite (courtesy of Dr. L. Evans, University of Guelph, 2004).*

Enhancing K-release from silicates

In Sri Lanka, Weerasuriya *et al.* (1993) conducted experiments with waste, 'scrap grade' phlogopite of a mica processing plant. They treated phlogopite with various acids and found that up to 65% of the K and Mg contained in the phlogopite could be recovered when acidulated with sulphuric acid. Greenhouse experiments showed that acidulated phlogopite chips (with application rates of 200 kg ha^{-1}) gave significantly higher yields of rice in comparison to control treatments with KCl (Weerasuriya *et al.* 1993).

Bioleaching experiments using leucite concentrate and the microorganisms *Penicillium expansum* and *Aspergillus niger* showed that between 21% and 27% of the K contained in the leucite mineral could be leached by microbial means (Rossi 1978).

5.4 Agricultural inputs of K

Potassium is removed from the soil through plant uptake and through leaching. A large amount of K can be lost from soil solution through leaching (Baligar and Bennett 1986), especially in sandy, acid soils with little negatively charged organic matter or clays, and in deeply weathered soils. Consequently, deeply leached soils in the tropics and subtropics along with sandy soils and soils developed on calcareous parent materials are prone to K-deficiencies.

The principle method to return K to the soil is through the application of fertilizers and organic residues. Plant residues can contain considerable amounts of plant available K. As K is concentrated in stems and leaves, plant residues left on the field can contribute significantly to K supplies in soils. Some plants, e.g. *Tithonia diversifolia*, contain up to 4% K in their dry matter (Palm *et al*. 1997). Tobacco stems contain up to 5% K_2O (Table 5.8). A good source of plant available K is urine and liquid manure.

Potassium-fertilizers are mainly obtained from sedimentary potash deposits containing sylvite (KCl) or complex K-Mg chlorides and sulphates. Sylvite, traditionally known as and marketed as 'muriate of potash' (MOP), requires no major processing past the beneficiation stage and is the fertilizer of choice for most crops. For high value crops, such as fruits, vegetables, coffee, ornamentals and tobacco, chloride free K-salt can be used instead, but these are generally twice as expensive as MOP. The principal non-chloride K-fertilizer, 'sulphate of potash (SOP), or K_2SO_4, is produced through the reaction of KCl with sulphuric acid. 'Niter' is another chloride-free K-fertilizer, produced through the reaction of $NaNO_3$ and KCl, and is used for speciality crops and in the horticultural industry.

Presently used K fertilizers are very soluble and easily available to plants, but they are also easily leachable, especially in sandy soils with little clay or organic matter. The efficiencies of these fertilizes are low. Baligar and Bennett (1986) calculated that approximately 40% of K applied to soils is utilized by the plants in first year of application. A large proportion is lost due to leaching losses to the environment. In addition, many of these soluble K-Mg sources are salts containing chlorine (in the form of chloride), which are unsuitable for salt sensitive crops such as potatoes and tobacco. Consequently, it is sensible to look for slow release alternatives.

While some common igneous rock types, e.g. granitic and rhyolitic rocks contain high total K concentrations, the availability of K in soils overlying these rock types is generally very low. There are some rock types, however, that contain high total and available K, including ultrapotassic volcanic rocks. And yet, in comparison to most soluble K fertilizers, the K concentration of available K from these slow release K-rich rocks are generally low.

Table 5.8. *Organic K resources.*

Resource	N (%)	P_2O_5 (%)	K_2O (%)
Cattle Manure (dry)	2	2.3	2.4
Cocoshell Meal	2.5	1	3
Cowpea Meal	3.1	0.6	1.3
Kelp Meal	1.5	0.5	1.5
Sheep Manure (dry)	4	1.4	3.5
Soybean Meal	7	0.5	2.3
Tobacco Stems	1.5	0.5	5
Wood Ashes (unleached)	0	1.5	8

Other K-sources include organic waste materials, (Table 5.8) as well as slow release K-bearing rocks. Fundamental research has shown that the release rate from mica, like biotite and phlogopite, is relatively slow and hence not generally practical for farmers' use. Consequently, silicate micas have not been used in agricultural practices and only a few research papers of applications of mica in agriculture have been published (Goldschmidt 1954; Borsch 1990; Weerasuriya *et al.* 1993).

Bakken *et al.* (1997, 2000) studied the fertilizing value of various K-bearing rocks and tailings on grassland field trials in Norway. They showed that considerable amounts of the K are plant available, some bound in biotite concentrate (from feldspar production in Lillesand, Norway), some from nepheline in alkaline complexes, as well as some from epidote schist. However, Bakken *et al.* (1997, 2000) concluded that the weathering rate of the rock and mineral products was too slow to replenish the native pool of plant-available K within a three-year period. While the micas released considerable amounts of K, the K released from K-feldspar was insignificant and unavailable to grass plants.

Glauconitic greensands have also been used as slow-release, low-grade (5-8%) K-containing soil amendments with CEC around 20 cmol (+) kg^{-1}. In the United States, the glauconitic sandstones of New Jersey were used in large amounts in the 19th century as soil amendments. In the 1860s, the annual production rates of glauconitic greensands were almost 1 million tonnes. Today, the glauconitic sandstones are no longer used as a soil amendment, but mostly for water purification purposes (Markewicz and Lodding 1983). For crops that require slow-release K-resources, such as oil palms, pineapples, coconuts and bananas, the use of rocks with >70-80% glauconite may offer a useful soil amendment.

In recent years, Berthelin *et al.* (1991), Hinsinger and Jaillard (1993), and Hinsinger *et al.* (1993) studied the release of K from phlogopite and biotite through the actions of microorganisms in the root environment. The researchers demonstrated that the roots of rape (*Brassica napus*) and ryegrass can transform phlogopite into vermiculite, releasing K and Mg from the micas to the plants. Roots and rhizospheres of these plants have shown to be active biological weathering agents that transform phlogopite and biotite into vermiculite, and subsequently result in the release of K and other cations.

5.5 Extraction, Beneficiation and Further Processing

There are four important requirements for an economic deposit of potash for conventional K fertilizer use. The deposit must have:

- a high analysis (high K_2O content, usually >14% K_2O),
- good solubility,
- high tonnage, and
- low costs for mining and beneficiation.

In 2004, the world's largest producers of K-salts (potash) were Canada (9.50 mill. t), Russia (5.40 mill. t), Belarus (4.65 mill. t) Germany (3.67 mill. t), Israel (1.94 mill. t) and the USA (1.20 mill. t) and Jordan (1.13 mill. t) (US Geol. Survey 2005) (Figure 5.7). Relatively low-grade K-resources are also exploited from the Dead Sea area in Israel and Jordan (Adams 1975; Williams-Stroud *et al.* 1994), where solar evaporation techniques are used to concentrate the brines and produce carnallite.

5.5.1 Extraction

Most potash is extracted (mined) by conventional underground mining 'room and pillar' methods. This type of mining is appropriate and relatively easy when the potash-salt deposits are flat lying and undeformed. Mining of strongly deformed potash deposits, for example in salt domes, is more complicated and costly.

A completely different mining approach is that of solution mining, extracting a mineral from below surface without physical access to the ore by injecting a solvent and pumping up a leach solution to the surface for further processing. In the case of potash, boreholes are drilled and injected with water. The water dissolves the potash, and the potash-rich solution is pumped to the surface for the recovery of K. There are already several solution mines in Saskatchewan, Canada, extracting K by this method.

Solution mining can extract potash from a much wider area, and causes much less surface disturbance and hence fewer environmental problems related to surface disturbance. If these methods were to be more widely operational in Saskatchewan, the volume of potash recovered could increase substantially (Figure 5.25). Solution mining, however, requires large volumes of water (3 m^3 $tonne^{-1}$ of salt), which are difficult to find in semi-arid inland areas of Canada. Solution mining can also create problems such as land subsidence over leached out areas.

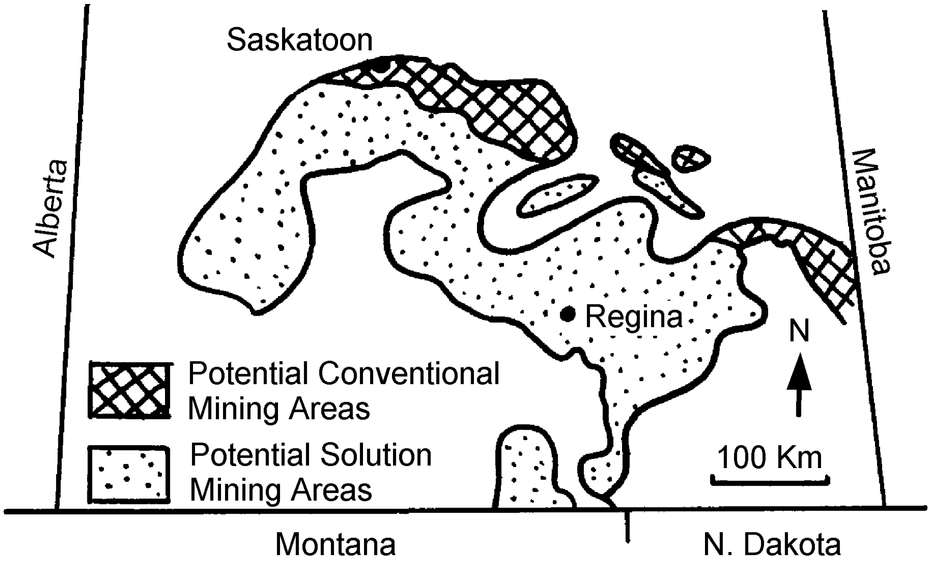


Figure 5.25. *Potential areas for expansion of potash extraction in Saskatchewan using solution mining techniques (modified after Holter 1969).*

5.5.2 Beneficiation

Beneficiation is the physical separation and upgrading of ore minerals whereby the ore minerals are liberated and separated from waste minerals, so-called gangue minerals. Various upgrading techniques are used to concentrate potassium salts for use as fertilizers, including solar evaporation, artificial crystallization and evaporation cycles, flotation and electrostatic separation techniques. The make-up of the gangue minerals largely determines the techniques used. For example, in Saskatchewan, Canada, the main impurities in the potash ore are NaCl and clays, together making up about 55% of the ore. Methods used to separate the ore from this gangue material include flotation, electrostatic separation and methods that utilize the solubility difference of K and Na-salts at different temperatures.

Flotation is one of the most common separation methods used in the potash industry (Williams-Stroud *et al.* 1994). In this method the ore is crushed and added to a liquid into which air bubbles are injected. These bubbles preferentially attach to KCl minerals, which are then carried to the surface and skimmed off. Sometimes a flotation agent must be added to enhance the attachment of the bubbles to the KCl minerals.

Some beneficiation processes use the solubility differences between KCl and NaCl at different temperatures (Williams-Stroud *et al.* 1994), or the electrostatic differences between the two minerals for separation (Singewald and Neitzel 1983). Evaporation, crystallization-evaporation and other techniques are used to separate KCl from NaCl in surface and subsurface brines (Williams-Stroud *et al.* 1994).

Production of K-fertilizers

Once removed from bedded deposits and separated from the gangue, the production of K fertilizers is relatively simple compared to the concentration and production of other fertilizers. Ninety-four percent of the K-fertilizers currently used are KCl (Muriate of Potash - MOP). Other common, naturally occurring K-salts include kainite ($KCl \cdot MgCl_2 \cdot 3H_2O$), carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) and langbeinite ($K_2SO_4 \cdot 2MgSO_4$). In fertilizer terms, langbeinite is called sul-po-mag (**Sul**phate of **Po**tash-**Mag**nesia). K_2SO_4 and KNO_3 are produced through the reaction of KCl with H_2SO_4 and KCl with $NaNO_3$ respectively.

5.6 Environmental effects of K-fertilizer production

Environmental effects of potash mining and processing fall into two principal categories: the effects associated with mining (extraction) and the effects associated with beneficiation and waste storage. The effects of mining are largely related to surface disturbance and land subsidence. While land disturbance is largely confined to the above ground structures of the mining and processing operation, conventional underground mining and solution mining of salts, including potash salts, can lead to damages due to land subsidence.

In common potash operations, large amounts of waste are produced, up to three times the weight of product extracted from the deposit. For example, in Canada the annual production of 10 x 10^6 tonnes of KCl gives rise to 28 x 10^6 tonnes of waste and 11 x 10^6 tonnes of brine (Anon. 1992). The disposal of waste in the semi-arid climate (350-450 mm annual precipitation) of Saskatchewan, where most of Canada's potash mining and beneficiation is carried out is challenging, especially the disposal waste brines. The area is far away from the sea, so the waste brines are hard to dispose of.

The liquid waste from other K-mining and processing operations is often dumped into the ocean (New Brunswick), into rivers (France, former East Germany) or injected into deep aquifers (Saskatchewan and Germany).

The most serious environmental concern related to the potash industry in Saskatchewan, Canada, is the possibility of salinization of groundwater by leaching from tailings. In 1992, tailings and brine ponds in Saskatchewan covered 35 square kilometres and tailings piles had a height of about 35 m. The current tailing disposal system involves piping the slurry to the pile and sloping the tailings pile 2-4 degrees (Figure 5.26), covering a wide area. It is anticipated that future tailings disposal systems will have steeper slopes to store more salt on a smaller area and will reduce seepage of the brine into the groundwater. To achieve this, cyclones (large centrifuges) will be installed to separate solids from the brine. This will result in drier tailings and will allow slopes of about 33 degrees rather than 2 degrees and create a smaller 'footprint' of the area where tailings are stored (Figure 5.26). Some technological questions as yet unanswered relate to the pore water pressure at the toe of the piles, especially tailings higher than 100 m, with steeper angles and what this means for the stability of the pile (Anon. 1992).

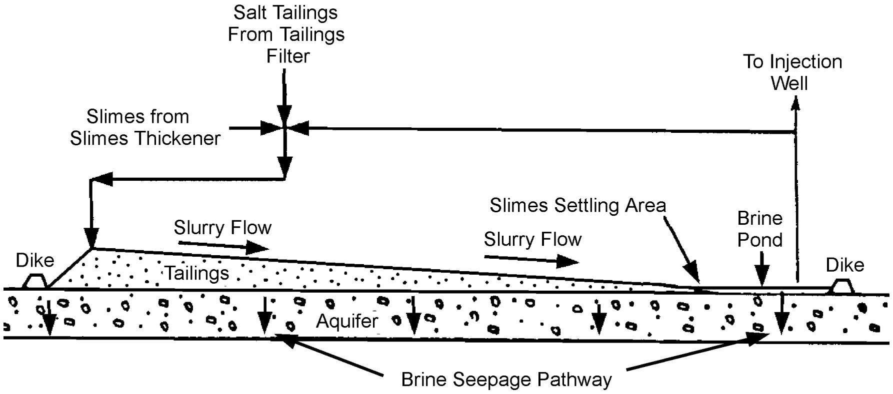


Figure 5.26. Conventionally spread out tailings piles in potash mining areas of Saskatchewan, Canada (Anon. 1992).

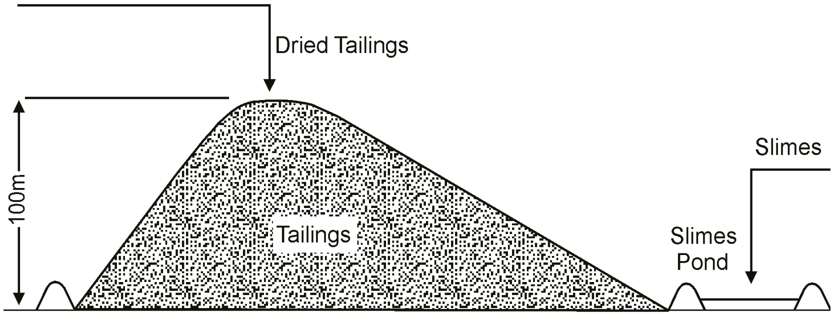


Figure 5.27. Dried tailings disposal of K-salt mining operation.

Even with advances in the storage containment of tailings and brines, some long-term decommissioning problems remain. The materials either require perpetual tailings maintenance in the form of capping or the tailings need to be utilized in some way, or transported to the sea and disposed of. All these options are very expensive.

The problem of disposal of tailings relates to their high volume, and the fact that there is only a very small market for the waste salts. In addition these tailings must be covered or liners must be installed to prevent excess leaching. In Germany, plastic covers and cemented hard covers are used and in Saskatchewan, sand mixed with polymerized bentonite is used to reduce infiltration. Backfilling of wastes into the mined-out areas is one of the methods considered as a measure to reduce the volume of wastes, currently stored in tailings above ground.

5.6.1 Environmental effects of K-fertilization

Although considerable K can be leached from soils if they lack both soil organic matter (SOM) and clays, contamination of groundwater through heavy use of K fertilizers is not common. However, another potential environmental concern for heavily K-fertilized soils is the concentration build-up of some other ions associated with K-salts, like Na^+, and SO_4^{2-}. Chloride is easily leached from soils and transported to ground and surface waters.

Chapter 6

Sulphur

Figure 6.1. *Oil well in front of rape-seed/canola crop, Alberta, Canada (left), by-product sulphur vat near natural gas operation, Waterton, Alberta, Canada (right).*

Sulphur (S) is an essential nutrient in two different ways, directly as a plant nutrient and indirectly for its importance in the production of sulphuric acid, which is used in the processing of phosphate rock (PR) into phosphate fertilizers. To a lesser extent, elemental S is used directly on soils or in a coated form as sulphur-coated urea. Sulphur occurs naturally in the elemental form (brimstone) as well as in sulphate and sulphide minerals.

Table 6.1. *Sulphur as a nutrient, its forms in plants and in common minerals.*

Nutrient	Uptake form	S in plants	Common mineral forms
Sulphur (S)	SO_4^{2-}	Amino acids, proteins and oils	Anhydrite (CaSO$_4$), Gypsum (CaSO$_4$•2H$_2$O), Pyrite and Marcasite (FeS$_2$), elemental S (S°)

Sulphur is important for the formation of amino acids and proteins. It is essential for the formation of vitamins and oils. Plants take up S from soil solution as the anion SO_4^{2-}, Like phosphate, this anion is easily adsorbed onto positively charged surfaces of iron and aluminium oxihydroxides and kaolinite edge positions. Table 6.1 outlines the form of S that is taken up by plants, the form of S within plants and some common S-bearing minerals.

Facts about S

Sulphur of sulfur? The spelling of this nonmetallic element varies depending on the industry, as well as geographic location. The spelling of sulphur used in this text is the English spelling, but the American spelling of sulfur, used in many industries, is also correct as per American Chemical Society and the American Geological Institute (Wessel 1994).

Sulphur occurs in four oxidation states (S^{VI}, S^{IV}, S°, S^{-II}). The S^{VI} form in sulphate (SO_4^{2-}) and the S^{-II} form in sulphide (S^{2-}) are the most common forms.

In the terrestrial environment, four stable sulphur isotopes occur: ^{32}S, ^{33}S, ^{34}S and ^{36}S, comprising 95.02%, 0.75%, 4.21% and 0.02% of the world's sulphur respectively. The isotopic composition of S is commonly expressed in the form of $\delta^{34}S$, denoting the ratio of the isotopes ^{34}S to ^{32}S. The fractionation and relative enrichments of S isotopes is important as it sheds light on the origin of the S in rocks and water.

Sulphur is used to vulcanize natural rubbers, as an insecticide, as a dying agent and in the manufacture of gunpowder.

Elemental S is extracted in small quantities from volcanic sources and from deposits in cap rocks over salt domes. Ca-sulphates, in the form of gypsum and anhydrite, are the most common geological S-sources, found in extensive layered sedimentary rock sequences in evaporite environments and in cap rocks over salt domes. Sulphur in the sulphate form is widely used as gypsum and is part of the fertilizer single superphosphate (SSP). Sulphides are common in many metallic sulphide deposits and are recovered as by-product or are discarded as waste.

Sulphur is also present in various forms in oil and gas, tar sands, bituminous oil shale as well as in coal. During the refining of oil and natural gas S-complexes are scrubbed and converted to elemental sulphur, so-called 'formed sulphur'. The recovery of these elemental S-resources is dictated by the production of the primary product, in this case natural gas. In coal S is often recovered as pyrite by-product.

In agriculture, S is best cycled in the form of organic matter (OM). In recent decades, S-deficiencies in soils have become more widespread due to reduced use of organic matter and sulphur-free fertilizers as well as increased crop yields. In S-deficient soils, S can be applied in the form of fast acting but strongly acidifying ammonium sulphates, or as elemental S, which is a slow acting and also strongly acidifying form. Slow reacting and non-acidifying S-sources include gypsum and SSP.

Based on environmental and economic considerations, interest in ammonium sulphate has decreased. In recent years the use of 'waste-gypsum' from phosphate processing and electric power generation has increased. Gypsum can be used both as an S-source and as a Ca-source, as well as an amendment to improve soil physical properties (especially sodic soils), and to reduce soil subsoil acidity. However, wider application of phospho-gypsum in crop production brings with it the risk of applying potentially harmful trace and radionuclide elements (see Chapter 4).

In this chapter, the role of S in agriculture will be discussed together with background geology and the use of the S-bearing agrominerals sulphur, sulphates and sulphides.

6.1 Sulphur in plants

Plants require sulphur (S) for the formation of amino acids, specifically the synthesis of the three amino acids: cystine, cysteine and methionine, the building blocks of proteins. Approximately 90% of the S in plants is found in proteins. Sulphur is also essential for the formation of vitamins (thiamine and biotin) and oils such as glucoside oils, which are found in onions, garlic and cruciferous plants (mustard, rape and oil radish). It is part of glutathione which is important for oxidation-reduction reactions. In addition, S promotes the growth of nitrogen fixing nodules in legumes and promotes the formation of seeds and chlorophyll as well as enabling the more efficient use of P in plants (Sinclair *et al*. 1996). Many crops contain as much S as P. Crops with seeds rich in protein commonly utilize large amounts of S. One example is cotton which takes up between 7 and 33 kg S ha^{-1} (Hearn 1981). Cotton leaves and stalks contain high concentrations of S.

Plants take up S predominantly in the form of the anion sulphate, SO_4^{2-}. Most of the sulphate from soil solution is supplied by the mechanism of mass flow, meaning that SO_4^{2-} is transported as anions along with the water that is taken up by the roots (Barber 1995). Sulphur in the form of sulphates taken up by plant roots have to be reduced to be incorporated in the main organic compounds including the amino acids cysteine, cystine and methionine as well as proteins that contain these amino acids.

Most plants require about one tenth as much sulphur as nitrogen. But, unlike nitrogen, sulphur is relatively immobile in plants. Sulphate taken up by the roots is distributed within plants via the xylem and the phloem, but predominantly in the xylem. The transport of S from older leaves to younger leaves in the phloem is relatively poor resulting frequently in S deficiencies in younger leaves.

Crops of the *Brassicaceae* family, such as cabbages, mustard, rapeseed, broccoli and turnip have elevated S concentrations in their grains and seeds (1-1.7% of dry matter) and consequently have high demands for S, more than 50 kg S ha^{-1} yr^{-1}. Crops that produce a high amount of organic matter, such as sugar cane, also require substantial amounts of S (Mengel and Kirkby 2001). Corn/maize (*Zea mays*) requires an average of 22-34 kg $ha^{-1}yr^{-1}$ of S. Legumes, tobacco, and cotton (0.24-0.32% of dry matter) generally have intermediate demands, and cereals generally have low S-demands. Competition for S between grasses and legumes is common (Nguyen and Goh 1994). Walker and Adams (1956) noted that in S-deficient soils sulphur was mainly taken up by grasses, and that N fixation by clover was reduced.

Plants that do not receive adequate S, experience reduced growth and extreme paleness of the younger (upper) leaves of the shoots. Symptoms of S-deficiency can easily be mistaken for N deficiencies. Sulphur deficiencies are not only seen in the youngest leaves but often affect the whole plant (general yellowing). Other symptoms of S-deficiencies include interveinal yellowing of young leaves, stunting and delayed maturity in corn and maize, as well as poor nodulation on the roots of S-deficient legumes (Mengel and Kirkby 2001; Scherer and Lange 1996).

Sulphur deficiencies in soils often result from low return of plant and animal residues to soils, and from poor crop management practices. A sufficient supply S to soils and crops can generally be supplied simply through organic matter (OM) cycling. However, when crops have high S demands, such as cabbage or rapeseed, it may be necessary to apply additional S to the soils for crop uptake. The additional S needed in these cases can be supplied by various mineral forms of S: elemental S, sulphates or sulphides. Even when the S demands of a crop are relatively low, deficiencies can arise when crop residues are burned, as is the case in many parts of sub-Saharan Africa.

6.2 Sulphur in soils

The mean concentration of S in soils is 433 mg kg^{-1}, in the same order of magnitude to the mean S-concentration in the upper continental crust, which is 621 mg kg^{-1} (Rudnick 2003). In a natural ecosystem, S in soils is derived either from rock weathering, from transforming S-containing biomass or from atmospheric inputs. Weathering inputs occur as rocks break down and S is released into the soil solution from S-bearing minerals (see Chapter 2). Organic matter in soils also releases sulphur in the soil solution as it breaks down. Atmospheric sulphur on the other hand, enters the soil solution mainly when it is washed from the air and deposited on the land through rain.

Atmospheric contributions come primarily from two sources, the ocean and industrial pollution. Only small contributions are introduced into the air through volcanic eruptions although most of the sulphur cycled on the earth's surface ultimately had its origin in the deep crust and mantle of the earth. On the surface, the earth's oceans represent an extremely large reservoir of sulphur, mainly in the form of sulphates. Consequently, in areas near to oceans sulphate contribution through sea spray may be significant. In heavily industrialized areas, soils may also receive anthropogenic S from the atmosphere, mainly in the form of acid rain. Anthropogenic S is emitted to the atmosphere through industrial pollution largely in the form of SO_2. This form is dissolved in the rain and finally oxidizes to SO_4^{2-}. As a general trend, anthropogenic S emissions have increased over the last few decades, and to a large extent contribute to the increasing global fluxes of S (Andreae and Jaeschke 1992). In the last few years however, the contributions to atmospheric S emissions have decreased again slightly in some parts of the world as a result of stricter environmental regulations.

In general, soils in temperate climates have higher S concentrations than soils in the humid tropics. This is due to the higher rate of leaching in tropical soils. In addition, soils far away from industrial areas and coastlines generally receive lower contributions from atmospheric S and sea spray depositions respectively.

Freney (1986) compiled soils data from various regions of the world, and showed that S in the surface of non-calcareous soils occurs predominantly as organic S. Most of the soil samples contained less than 10% inorganic S, and commonly more than 85% in the organic form. In regions with arid climates, the soil organic matter (SOM) content is low, making gypsum ($CaSO_4{\cdot}2H_2O$) the predominant form of S in the soils. Many soils that are low in OM reserves will develop S deficiencies in the long term, if S is not replenished through plant and animal residues or other S sources. For example, S-deficiency commonly exists in tropical areas with high rainfall levels and highly-leached soils where replenishment through returned OM or fertilizer management has not been practiced. There is a general relationship between the grain size of a soil, the SOM content and the concentration of available sulphates. In general, S-deficient soils tend to be coarse textured, with an organic matter content of < 2%.

However, it is not the total amount of S that is important for plant growth; it is the concentration of plant-available or potentially plant-available S in soil solution. Sulphur occurs in soils either in the inorganic form or the organic form, but is taken up by plants primarily in the inorganic form, SO_4^{2-}. The S cycle is complex with transformations from organic and inorganic mineral forms to plant available sulphate forms (Figure 6.2).

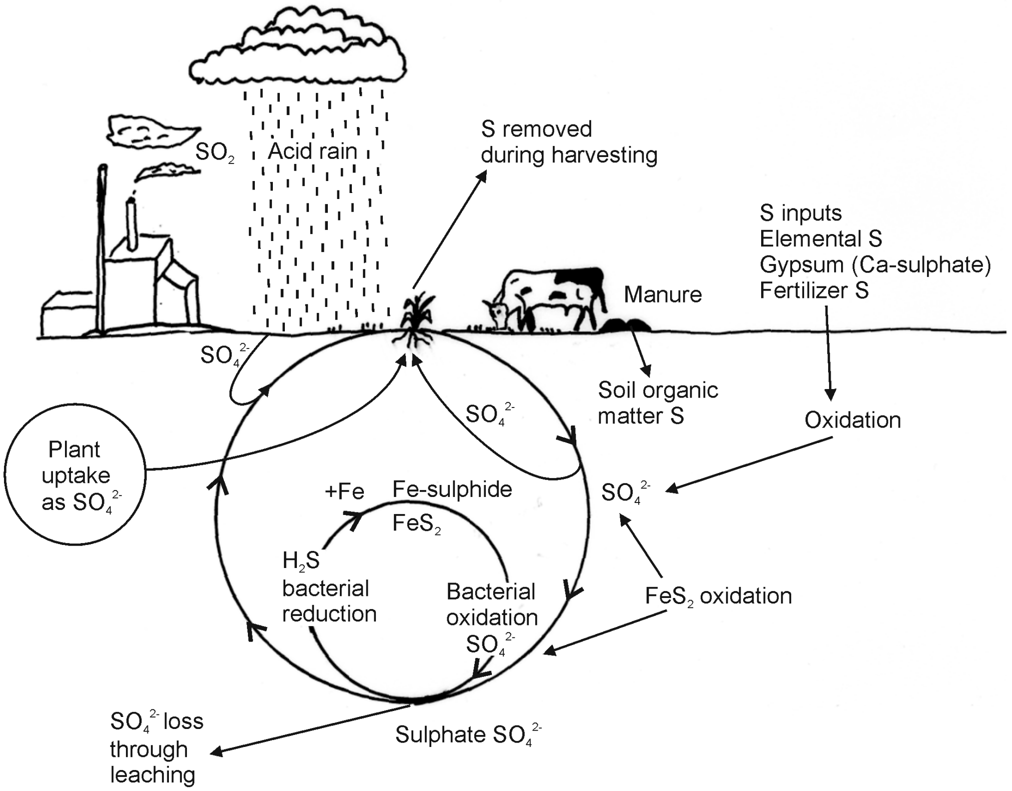


Figure 6.2. *The sulphur cycle.*

Sulphur occurs in the soil predominately in four forms:

- Soil solution S, predominantly as SO_4^{2-},
- Adsorbed S, on positively charged Fe and Al oxides and on positively charged kaolinite edges,
- Inorganic mineral S forms,
- Organic S forms.

6.2.1 Sulphur in soil solution

Plants take up S predominantly in the form of the anion sulphate, SO_4^{2-}. The relative concentration of this ion in soil solution is low. Healthy growing plants require concentrations of at least 5 mg SO_4^{2-} L^{-1} (Havlin *et al.* 1999). The supply of sulphates is influenced by redox conditions and by the presence and concentration of Fe and Al oxyhydroxides along with various other competing anions. Most of the sulphate used by plants is supplied to the roots by the mechanism of mass flow (Barber 1995). Since sulphates in soils are relatively soluble, losses of sulphates in drainage water in humid regions is high.

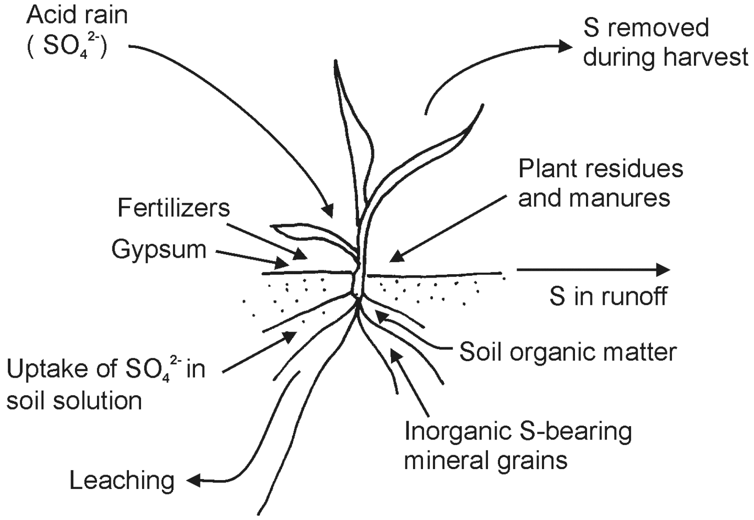


Figure 6.3. *Gains and losses of sulphur in the rock-soil-plant continuum.*

6.2.2 Adsorbed sulphates

Because of its negative charge, SO_4^{2-} is not chemically attracted to other negatively charged surfaces, such as most clay surfaces and OM particles. Instead, sulphates are easily adsorbed onto positively charged surfaces such as Fe and Al oxides and a particular position on clays, the positively charged clay edges. Kaolinite clays are well known for their positively charged edges. Sulphate can also adsorb to Al and Fe oxihydroxides through ligand exchange with surface hydroxyl groups. According to Turner and Kramer (1991), the relative strength of adsorbtion of sulphate on various surfaces is as follows:

Al_2O_3 > kaolinite > bauxite > peat > limonite > hematite > hydrated aluminum > goethite

In comparison to other ions, the binding strength of sulphate is not as strong as that of phosphate ions or organic polyanions such as citrate (Barrow 1970; Bowden *et al.* 1980). These ions compete for the same sites on Fe and Al oxides and hydroxides (Parfitt 1980). The order of binding strength is:

phosphate > citrate > sulphate

The competition between these ions yields some practical consequences. Increasing either the concentration of PO_4^{3-} in solution (through the addition of phosphate-fertilizer for example) or the concentration of citrate in solution leads to desorption of SO_4^{2-} from positively charged soil particle surfaces. Conversely, increasing the concentration of sulphate ions in soils, at a low pH, decreases the adsorption of phosphate ions on Fe oxyhydroxide goethite, leading to increased P-concentration, as well as enhanced P-uptake by plants (Geelhood *et al.* 1997).

6.2.3 Inorganic mineral sulphur

Microorganisms largely facilitate the conversion of inorganic mineral forms to plant available sulphate forms; for example, bacteria from the genus *Thiobacillus* enhance the oxidation of the mineral FeS_2 (pyrite) to SO_4^{2-} (equation 6.1).

$$\underset{\text{Pyrite}}{FeS_2} + 7^1/_2\,O_2 + 7H_2O \xrightarrow{\textit{Thiobacillus}} 4SO_4^{2-} + 2Fe(OH)_3 + 8H^+ \quad \text{(equation 6.1)}$$

Similarly, bacteria of the genus *Desulfovibro* mediate the reduction of sulphate ions under anaerobic conditions to sulphide ions, which are not available to plants. Redox conditions in the soil determine whether the reaction proceeds aerobically or anaerobically, and thus the form of S in soils. As such, sulphates are found under oxidizing conditions, whereas sulphides form under anoxic conditions. Some of the HS^- produced under anaerobic conditions is lost to the atmosphere in the gaseous form, as H_2S, or reacts with metals, for example Fe, to form insoluble precipitates such as pyrite (FeS_2).

6.2.4 Organic sulphur

In the soil, organic S-sources are found mostly in the organic matter (OM) pool as carbon bonded S, in the form of proteins and amino acids, and as ester sulphates. In most ecosystems, and for most crops, adequate S can be obtained through the cycling of OM, such as plant residues and manures. By and large, the organic pools provide a large percentage of nutrient sources for plants. If a soil is high in OM it is commonly high in N and also high in S. Commonly, organic matter has a N:S ratio of between 10:1 and 10:2. Across a variety of soils, the C:N:S ratio is on the order of 130:10:1.3. This ratio largely reflects the relative composition of N- and S-containing amino acids and other organic fractions (Turner *et al.* 1980).

The anaerobic decomposition of organic sulphur compounds into H_2S and the subsequent oxidation is generally acid producing (equation 6.2)

Step 1:

Organic sulphur compound → decay products
(proteins and amino acids) (incl. H_2S)

(equation 6.2)

Step 2:

Decay products + O_2 → $SO_4^{2-} + 2H^+$
(incl. H_2S)

The organic S-pool is made up of several fractions:

- Carbon-bonded S, mainly proteins and the amino acids cystine and methionine,
- Ester sulphate, a transitory S pool,
- Residual, recalcitrant S.

The organic forms of S make up a dynamic pool in which the transformation and rate of S-cycling from one pool to the other depends on factors like soil temperature, soil moisture content and microbial activities.

Carbon-bonded sulphur

Carbon-bonded S is a stable form of organic S in soils and is found predominantly in forest soils (David *et al.* 1982). The amino acids cystine and methionine along with other S-bearing complexes make up approximately 10-20% of the total S pool in soils. The conversion of organic S to inorganic S (mineralization of S) is controlled largely by the activity of microorganisms.

Sulphate esters

Sulphate esters such as alkylsulphates, as well as sulphated polysaccharids, and sulphated lipids make up a large portion of the S pool in soils. Although sulphate esters in their original form are unavailable to plants, they can be easily transformed into plant available sulphate forms through microbial action and the activity of sulphatase enzymes (Martens *et al.* 1992). Also, drying the soil can break up the ester-sulphur linkage (Barrow 1961). Since microbial processes largely influence the rate of conversion from organic to inorganic and plant available forms, environmental factors that influence the growth of microorganisms, such as favourable temperatures, soil moisture and availability of nutrients are important. All organic S fractions show temporal changes and seem to transform from one pool to the other (Castellano and Dick 1990).

Residual recalcitrant S

Residual S is the calculated net organic sulphur after substracting carbon bonded sulphur and sulphate esters. This form of S is largely undefined. It makes up approximately 30-40% of the soil's S pool.

6.3 Sulphur in rocks and minerals

There is a wide range of S-concentrations in different types of rocks and minerals. While the crustal average of S concentration is 500 mg S kg^{-1}, ultramafic rocks contain an average of 2850 mg S kg^{-1}, basalts 520 mg S kg^{-1}, and granites 300-400 mg S kg^{-1}. Much of the S in the crust of the earth is concentrated in sedimentary rocks. Pelitic sediments, like shales, contain up to 2400 mg S kg^{-1} (Wedepohl 1970). The three main solid natural S-containing mineral substances are elemental sulphur (S°), sulphides (S^{2-}) and sulphates (SO_4^{2-}) (Table 6.2).

Table 6.2. *Naturally occurring mineral forms of sulphur.*

Form	Formation	Chemical formula	Percent S (by mass)
Native sulphur (S^o) ('Brimstone')	Elemental S precipitates in volcanic areas; in cap rocks of salt domes; in evaporite sequences.	S°	Elemental S: 100% S
Sulphides	Formed under anaerobic conditions	S^{2-}	Pyrite (FeS_2): 53.3% S Pyrrhotite: 38.5% S Chalcopyrite: 35% S
Sulphates	Formed under aerobic conditions	SO_4^{2-}	Gypsum ($CaSO_4 \cdot 2H_2O$): 18.6% S Anhydrite ($CaSO_4$): 23.5% S

6.3.1 Elemental sulphur

Inorganic elemental sulphur (S^o) is also called 'native' sulphur or 'brimstone', 'the stone that burns'. Elemental S occurs in various geological environments. In the past, most elemental S was mined from active volcanoes. Even today, small amounts of S are still recovered from these resources, for example in volcanic areas of South East Asia and South and Central America. Also, extensive elemental S deposits have been discovered during exploration for oil and gas in evaporite sedimentary environments. They are commonly associated with gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$) deposits in salt domes, but also in layered gypsum and/or anhydrite deposits.

Today, large amounts of elemental S are recovered as a by-product from natural gas refining, so-called 'formed sulphur' (Harben 2000).

Volcanic sulphur deposits

Deposits of elemental sulphur are known from many parts of the world, especially in the volcanic 'Ring of Fire' in the Pacific Rim region, and in young volcanic areas in other parts of the world. Elemental S-deposits and occurrences are known in volcanic areas in North, Central and South America, in Japan, the Philippines, Indonesia, New Zealand as well as young volcanic areas in East Africa, in Italy (Dessau *et al.* 1962), Romania, Greece and Turkey. The majority of these deposits are only of small extent, and they are mined on a small scale.

Figure 6.4. *Elemental sulphur in the crater of the Papandayan volcano near Garut, Java, Indonesia.*

Volcanic S in the form of elemental S occurs in volcanic areas mainly as sublimation on the surface, as crusts, impregnations and void fillings in lavas and tuff deposits (Figure 6.4). The deposition of S by simple condensation of S-bearing gases is common near active volcanic centres and follows the reaction:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad \text{(equation 6.3)}$$

An interesting type of volcanic deposit is the S flow of the Siretoko Iosan volcano on Hokkaido Island in Japan. Here, the sublimated and disseminated S was heated by volcanic gases, which caused the S to melt, and eventually flow down the slope. Since the early 20th century, three S flows have been reported: one of the S flows was 5 m thick and filled a valley 20 m wide and 1400 m long (Harben and Kužvart 1996).

Volcanic S deposits are generally small and are mined on local scales. Commonly, the S-bearing ore is mined by relatively simple physical extraction techniques, melted in vats and concentrated to remove impurities.

Biogenic sulphur deposits

Ruckmick *et al*. (1979) proposed biological processes as being responsible for several elemental S deposits in the world including deposits of sulphur in cap rocks and in stratiform deposits. The crucial role of S-reducing bacteria in the formation of these elemental S deposits has been supported by isotopic studies of both S and carbon (Feely and Kulp 1957; Faure 1977). However, this mode of formation has been challenged by other researchers and alternate models for the formation of these deposits have been proposed by Orr (1974), Machel *et al.* (1995), and Nöth (1997).

The most economically important biogenic S deposits are cap rock S deposits and stratiform S deposits.

Biogenic sulphur in cap rock deposits

Elemental S occurs in association with gypsum and calcitic limestones in so-called cap rocks. These generally flat lying layers (cap rocks) immediately overlying salt domes are the result of dissolution of the upper portions of salt domes within approximately 2000 m of the surface. The S deposits in the cap rocks made up of gypsum, anhydrite and calcite were found rather accidentally during the search for oil and gas. Sulphur deposits occur in areas where a sulphate (e.g. anhydrite or gypsum) has been reduced by sulphate-reducing bacteria in the presence of a hydrocarbon source. Elemental S together with calcite is commonly found in the middle portion of the cap rocks overlying salt domes (Figure 6.5).

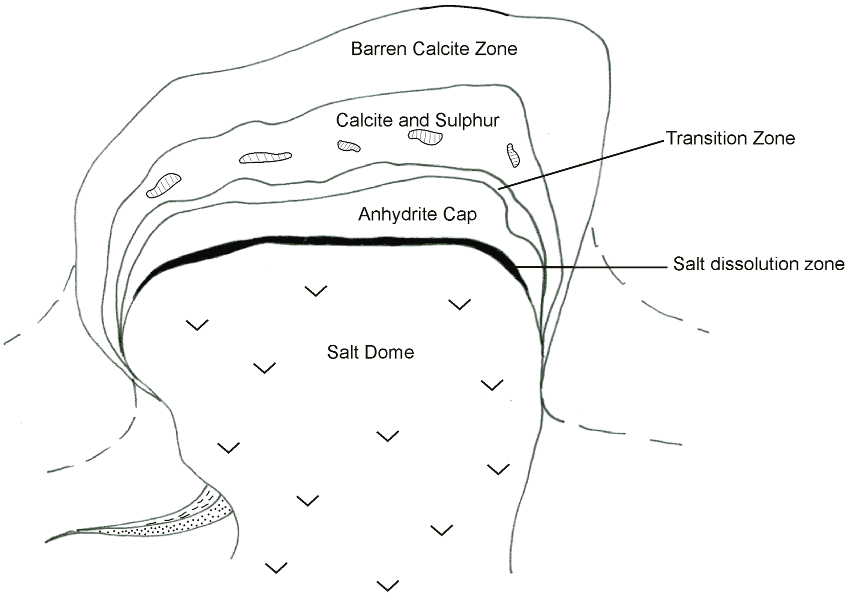


Figure 6.5. *Schematic profile of cap rocks and distribution sulphur and calcite on top of weathered salt dome.*

The microbial reduction of anhydrite or gypsum to S and calcite is thought to take place at relatively shallow depth (generally < 750 m) and at temperatures below 60°C (Ruckmick *et al.* 1979). It requires the presence of migrating meteoric water and the occurrence of sulphate reducing bacteria.

There are two steps for the formation of elemental S in cap rock environments: The first step is microbial sulphate reduction of gypsum/anhydrite to H_2S and calcite under anaerobic conditions with the aid of methane and sulphate reducing bacteria, for example *Desulfovibrio desulfuricans.* The simplified reaction is:

$CaSO_4 + CH_4 + \text{sulphate reducing bacteria} \rightarrow H_2S + CaCO_3 + H_2O$ (equation 6.4)

The second step is the oxidation of H_2S to elemental S. Hydrogen sulphide (H_2S) can be oxidized by various processes, including a microbial process that involves the presence of dissolved oxygen and the bacteria *Thiobacillus*. During this step, H_2S reacts with dissolved oxygen to form elemental 'native' S according to equation 6.5. Unfortunately this biochemical process is very slow and, as of yet, no industrial process has been economically successful to reduce sulphates such as gypsum to elemental S using microbial processes.

$2H_2S + O_2 \rightarrow 2S^o + 2H_2O$ (equation 6.5)

Major S deposits related to cap rocks over salt domes are located in the southern United States and Mexico, in the Gulf of Mexico (Davis and Kirkland 1979).

Biogenic sulphur in stratiform deposits.

Sulphur deposits in which the elemental S occurs parallel to the layering (stratiform) with gypsum and anhydrite has been recorded from many oil-producing evaporite basins in the world (Wessel 1994). However, only a few of these deposits are currently being extracted, for example the stratiform S deposits of Poland, Ukraine, the United States and Iraq (Barker *et al.* 1979; Pawlowski *et al.* 1979). The formation of these deposits is similar to that of cap rock S deposits over salt domes involving the presence and action of sulphate reducing bacteria (Davis and Kirkland 1979).

6.3.2 Sulphide deposits

Apart from elemental S, there are several other S-bearing geological resources, for example sulphides. The main sulphide mineral is pyrite (FeS_2), which is found in a number of different geological environments including volcanogenic, hydrothermal and sedimentary environments. Pyrite has been used for decades to produce sulphuric acid that can then be used in the production of phosphate fertilizers. In recent years, however, the use of pyrite for this purpose has declined in favour of using elemental S. Only a few pyrite deposits are mined for their pyrite content alone. Mostly, pyrite is obtained as a by-product from the extraction and processing of other earth resources. By-product pyrites are derived from processing (roasting) of metallic sulphide ores and pyrite (‘flotation pyrites’) as well as from upgrading of S-rich coals (‘coal pyrites’). The main pyrite producing countries in the world are China, Finland, Russia, South Africa and Spain/Portugal.

6.3.3 Sulphate deposits

Gypsum ($CaSO_4{\cdot}2H_2O$) is the hydrated form of anhydrite ($CaSO_4$), containing 27% water. Gypsum and its products have been known for their unique properties since historic times. Approximately five thousand years ago, the Egyptians made plaster from gypsum. Some of these smooth gypsum plasters are preserved in the interiors of the pyramids. The ancient Greeks coined the name gypsum from "Gypsos", which means plaster or chalk.

When ground gypsum is heated to 250°C for 2 hours and then at 300-350°C it loses 75% of its contained water to form hemihydrate ($CaSO_4{\cdot}{}^1/_2H_2O$), which is also called Plaster of Paris (POP), stucco or simply plaster. The equation for gypsum dehydration process is as follows:

$$CaSO_4{\cdot}2H_2O + \text{heat} \rightarrow CaSO_4{\cdot}{}^1/_2H_2O + {}^3/_2\,H_2O \qquad \text{(equation 6.6)}$$

After mixing with water the hemihydrate or plaster can be spread or molded and will then set to a hard structure. The formula for the re-hydration or setting process is the reverse to the reaction above.

$$CaSO_4{\cdot}{}^1/_2\,H_2O + {}^3/_2\,H_2O \rightarrow CaSO_4{\cdot}2H_2O + \text{heat} \qquad \text{(equation 6.7)}$$

Gypsum occurs in various forms: compact, granular, crystalline and fibrous**.** The most common form of gypsum is compact. One form of gypsum is ‘selenite’, which occurs as large, clear, and transparent gypsum crystals. The word selenite is derived from the Greek word ‘Selene’, the goddess of the moon. Another form of gypsum is ‘Satin spar’, which is a fibrous form of gypsum, found as secondary stress related mineral in fractures. Another form of gypsum is ‘alabaster’, which occurs in the form of very fine grained, compact gypsum and has been used for rock carving for centuries. Gypsum can also occur as gypsite, an impure mixture of gypsum with clay, sand and soil particles.

Gypsum is commonly associated with carbonates (limestones or dolostones) and shales. Natural gypsum occurs commonly as bedded primary deposits, but also as secondary deposits and as ‘cap rocks’ over salt domes. Bedded primary gypsum deposits occur in tabular bedded sedimentary successions in large shallow epicontinental evaporite basins or on supra-tidal salt flats under arid conditions (see Chapter 5) (Eugster and Jones 1979; Guilbert and Park 1986). Gypsum and anhydrite are part of the evaporite sequence in salt basins where evaporation exceed seawater inflow (see Chapter 5). This sequence of concentration commonly starts with carbonates, followed by sulphates, specifically gypsum, and concludes with the precipitation of salts, including K-bearing salts (see also Figure 5.12).

Gypsum, the hydrated form of Ca-sulphate ($CaSO_4{\cdot}2H_2O$), was likely deposited first in these evaporite basins under arid conditions and later dehydrated to anhydrite ($CaSO_4$). At a later time and at specific locations, close to basin margins and at shallow depths, the anhydrite was hydrated into gypsum again.

Figure 6.6. *Open pit gypsum mine near Ararapina, Pernambuco State, Brazil. Photo: courtesy Dr. Richard Heck.*

Secondary gypsum deposits occur also as surface concretions and crusts in arid environments, for example in the Sahara Desert in Egypt. In desert sands secondary gypsum in the form of crystal rosettes with sand, 'desert rose', is found. Other secondary gypsum deposits include the extensive gypsum dunes at 'White Sands'in New Mexico, USA, which were formed by wind action from reworked surface gypsum deposits. The dunes are made up of fine-grained selenite crystals (Harben and Kužvart 1996).

Gypsum is found in cap rocks of salt domes. These cap rocks of anhydrite or gypsum, together with porous limestones, rest with sharp contact on top of salt domes. The cap rock gypsum and anhydrite deposits make up only a small portion of commercial gypsum production (Harben and Kužvart 1996).

Apart from the naturally occurring gypsum there is also a large quantity of by-product gypsum formed from various manufacturing processes. In recent years, these by-products have become more and more abundant, specifically phosphogypsum, a by-product from the production of phosphoric acid for superphosphate fertilizers (see Chapter 4), and gypsum formed during the desulphurization of flue gas (Flue Gas Desulphurization – FGD) from the combustion of S-containing coal and sulphide ores. FGD processes are designed to reduce SO_2-emissions from coalfired and sulphide ore processing plants. During flue gas desulphurization, hot SO_2-rich gases are treated with lime-rich water ('scrubbed') to reduce SO_2 emissions with the secondary result of producing gypsum.

Other 'chemical gypsum' by-product sources are formed during chemical processing of titanium dioxide (titano-gypsum), citric acid (citro-gypsum) and the production of other acids (e.g. tartaric and lactic acids) (Harben 2002).

6.4 Gaseous forms of sulphur

The two most common forms of sulphur gas are 'sour gas' (H_2S) and sulphur dioxide (SO_2) (Table 6.3). Sour gas can be created from the reduction of sulphates (e.g. gypsum or anhydrite) and is present in natural gas. It is also reported as being a product of tidal marshes and mangrove swamps, in areas where sulphates are formed under anaerobic conditions.

Table 6.3. *Gaseous forms of sulphur.*

Form	Origin	Chemical Formula
Sour gas	Anaerobic breakdown of organic forms of S	H_2S
Volcanic emanations	During volcanic activity	SO_2, (H_2S)
Tidal marshes, mangrove swamps	Anaerobic breakdown of organic forms of S	H_2S
Pollution	Industrial activity	SO_2

SO_2 emanations are common in active volcanic areas, but their contribution to the global S cycle seems rather small (Andreae and Jaeschke 1992). SO_2 is also the main S-bearing gas derived from industrial activities including the combustion of oil, coal and oil.

Sulphur inputs from the atmosphere include wet and dry deposition, such as S-containing aerosols and various sulphides and disulphides derived from anthropogenic sources. Sulphur-containing dry and wet deposition of S can contribute considerable amounts of S compounds to soils, ranging from approximately 1 kg S ha^{-1} $year^{-1}$ in rural areas far away from industrial sites to greater than 100 kg S ha^{-1} $year^{-1}$ near urban and heavily industrialized areas (Paul and Clark 1996).

6.5 The use of sulphur in agriculture

Sulphate requirements for most crops can generally be met through the cycling of organic matter (OM), such as plant residues and manures. As such, without S-replenishment many soils that are low in OM reserves tend to develop S-deficiencies in the long term. Similarly, land that has been cropped for a prolonged period of time without S-replenishment tends to develop S deficiencies. For example, S-deficiencies commonly arise when crop residues are burned, as is the case in many parts of sub-Saharan Africa. The recent tendency to apply high concentration N and P fertilizers (such as urea or mono- and di-ammonium phosphates) instead of less concentrated S-containing N and P fertilizers (such as ammonium sulphate or single superphosphates) will, in the long term, contribute to S deficiencies in soils.

To replenish S in soils, it is necessary to add S either in liquid or solid forms. Sulphur in liquid forms is mainly added through irrigation water or as a consequence of acid rain precipitation in the form of sulphates (SO_4^{2-}). In agricultural systems, S can be supplied through the addition of natural, solid S-containing mineral phases, such as elemental sulphur, gypsum or pyrite, or through modified forms, such as manufactured fertilizers. Sulphur containing fertilizers include ammonium sulphate $(NH_4)_2(SO_4)$, single superphosphates (SSP), triple superphosphates (TSP) and sulphur coated urea (SCU). The main S-containing commercial fertilizer products are shown in Table 6.4.

Table 6.4. *Sulphur-containing fertilizer products*

Product	**S(%)**
Ammonium Sulphate	24
Single Superphosphate (SSP)	12
Triple Superphosphate (TSP)	1.4
Sulphur-coated Urea	10-20

Various trade-offs in the effectiveness of these options are greatly influenced by environmental conditions. While the sulphate bearing fertilizer ammonium sulphate provides both ammonium (NH_4^+) and SO_4^{2-} it strongly acidifies the soil. The application of this specific S-bearing fertilizer can be harmful to soils when applied on already acid soils. The application of elemental sulphur to alkaline soils proves to be a slow acidifying process. In contrast, sulphate bearing single superphosphate is a good source of both phosphates and sulphates. Gypsum provides sulphur in a slow acting not acidifying sulphate form.

While gypsum is sufficiently soluble in water to be plant available, it is easily removed from soils through leaching. On the other hand, elemental S has to be oxidized to produce sulphate, which usually takes some time. Furthermore, in alkaline soils, high amounts of elemental S are required to be effective for pH reduction. However, precisely because elemental S takes a longer time to be transformed into sulphate, it is actually favoured in soils that are subject to high levels of leaching. Under arid conditions gypsum tends to be more effective than elemental S as the low rainfall causes the sulphate in gypsum to be immediately available to plants (McLachlan 1975).

In addition to providing S to plants, the oxidation of elemental S into sulphuric acid can also have a positive effect on phosphate rock solubilization. A blend of S and phosphate rock has shown to increase in-situ phosphate solubilization and increase supplies of P and S to soils and plants (Swaby 1975; Rajan 1982, 1983, 1987; Loganathan *et al.* 1994). The oxidizing S forms sulphuric acid, which assists in the dissolution of phosphate rock. The amount of S used controls the actual rate of P release. A blend of elemental S and ground phosphate rocks, inoculated with the sulphur oxidizing bacteria *Thiobacillus ssp*, has proved to be an effective slow-release P and S fertilizer, like superphosphates (Logonathan *et al.* 1994). This blend, called 'Biosuper', is very effective in many tropical soils and is superior to single superphosphate in areas that receive more than 635 mm of rain (Swaby 1975). Biosuper can be used under these conditions as controlled P and S fertilizer, especially on pastures and long-term agricultural and horticultural crops.

6.5.1 The use of elemental sulphur in agriculture

Elemental S is applied in a 'wettable' form, directly to soils in order to lower the pH of alkaline soils. The principal action is S oxidation, which is moderated by microorganisms and is strongly dependent on soil conditions, including population density of S oxidizing microorganisms, soil moisture and temperature. Unfortunately, large amounts of wettable elemental S are needed to be effective, and in many cases this option is simply too expensive.

On crops like grapes and citrus fruits, and on various vegetables, finely ground wettable powder of elemental S is applied as a fungicide and an insecticide to protect them from various types of mildew and insects that cause plant diseases.

Sulphur coated urea (SCU) produced from preheated prills of urea, coated with molten S and a thin waxy sealant, is used to reduce the dissolution rate of urea and ensure slow release of N into the soil environment, as well as to provide S as a nutrient source. It has been applied with long term crops like sugar cane and pineapple, and with rice under delayed or intermittent flooding. Presently, it is used mainly in horticulture, turfgrass and landscape applications. SCU has excellent storage and handling characteristics but is a relatively expensive fertilizer.

6.5.2 The use of gypsum in agriculture

Gypsum ($CaSO_4 \cdot 2H_2O$) is used in agriculture for both its sulphate and Ca content and for physical and biological improvement of soils. Early in US history, gypsum, popularly referred to as 'land plaster', was imported to the southern States from Nova Scotia, Canada, for agricultural purposes.

The main applications of gypsum in agriculture are:

- as a nutrient source of Ca and S for plant growth,
- as a soil ameliorant for sodic and heavy clay soils,
- as an ameliorant for subsoil acidity and surface crusting, and
- as a method to reduce ammonia volatilization.

Gypsum is also used in a variety of applications specific to certain crops, for example as an alternative to fungicide for controlling root diseases of avocado seedlings caused by *Phytophthora cinnamoni* (Messenger *et al.* 2000a, 2000b). By-product gypsum in coal combustion ash has been used successfully to reduce weed growth, to improve the Ca-status of fruit trees (Korcak 1988) and to increase root growth (Ritchey *et al.* 1996). Specific applications for gypsum are summarized by Wallace (1994).

Calcium sulphates occur in nature in two principal forms as gypsum ($CaSO_4 \cdot 2H_2O$) and the unhydrated form anhydrite ($CaSO_4$). Although anhydrite is more abundant in natural mineral deposits anhydrite has higher hardness, higher specific gravity and higher solubility in soil. Gypsum's higher solubility in soils makes it the preferred mineral form for agriculture.

Gypsum supplies S in the form of sulphates, the form taken up by roots. The plant nutrient S is required in relatively high amounts by crops of the *Brassicaceae* family as well as fruit trees and crops that produce a high amount of organic matter, such as sugar cane.

The application of gypsum provides not only sulphates to plants but also Ca as nutrient. Gypsum contains easily available Ca and S-nutrients that are required in high concentrations by peanuts/groundnuts (*Arachis hypogaea*) (McNeil 1987; Alva *et al.* 1989; Caires and Rosolem 1991). For the production of peanuts/ groundnuts, it is imperative that a continuous supply of Ca is provided. Without sufficient Ca, pod development will be curtailed leading to empty pods or poorly formed seeds. Calcium is most critical for pod development between 15 and 35 days after the pegs reach the soil (Walker 1975). Gypsum is a valuable source of relatively available Ca and used in many countries for peanut/groundnut farming.

However, the main use of gypsum in agriculture is as a soil ameliorant for the reclamation of sodic soils as well as for the reduction of subsoil acidity and subsoil Al-toxicity (Shainberg *et al.* 1989; Wallace 1994).

Sodic soils, widespread in semi-arid and arid areas of the world, where there is not enough rainfall to rinse the soil of excess Na, commonly contain excessive quantities of Na adsorbed to clay minerals. These soils are characterized by surface crusting and commonly form physically impermeable, hard-setting soils.

Results from field trials in many parts of the world show that gypsum, applied at rates of several tonnes per hectare, decreases the sodium adsorption ratio, physically improves the infiltration rate and significantly increases yields (Shainberg *et al.* 1989). This occurs because the easily available Ca in gypsum replaces Na^+ from the exchange sites on the soil colloids, improving clay aggregation and soil structure and consequently enhancing water infiltration (Shainberg *et al.* 1989; Ju *et al.* 2003). Gypsum also reacts with soluble salts such as $NaHCO_3$ to form soluble Na-sulphates, which can be easily leached out after the application of gypsum.

Phospho-gypsum, an industrial by-product from the phosphate fertilizer industry has been shown to decrease the seal formation in soils even more than that of naturally occurring gypsum because of its relatively high rate of dissolution (Keren and Shainberg 1981). For highly sodic soils, gypsum is often used in combination with deep rooting plants in order to provide access and channels for Ca movement down the soil profile (Sumner 1993).

Gypsum is frequently used in agriculture to correct subsoil acidity, although the chemical action of gypsum is not the same as ‘liming’. Gypsum, applied at the surface or subsoil, is reported to reduce the phytotoxicity of acid soils (Alva and Sumner 1989; Sumner 1995). The mechanism for this reduction is the downward movement of soluble Ca ions and the subsequent reduction of toxic, exchangeable Al in the subsoil (McRay and Sumner 1990; Sumner 1993). $Ca(OH)_2$ reacts with available Al^{3+} ions in the soil solution to form insoluble $Al(OH)_3$, thus reducing the toxicity of Al in acid soils (Shainberg *et al.* 1989; Sumner 1993) according to equation 6.8.

$$2Al^{3+} + 3Ca(OH)_2 \rightarrow 2Al(OH)_3 + 3Ca^{2+} \qquad \text{(equation 6.8)}$$

Unlike lime, gypsum does not change the pH of soils but reduces Al toxicities. Gypsum is widely used on soils with subsoil acidity and Al toxicity problems, for example in the Cerrado soils of Brazil. Studies in Brazil, South Africa and the United States have found that gypsum significantly increases yields when applied at rates between 1 and 10 tonnes per hectare.

In many parts of North America and Europe, where large deposits of gypsum are found, there is little need for the use of gypsum as soil amendment because the levels of available Ca and S are generally adequate in most soils above a pH of 6.

Gypsum is also be used to reduce ammonia volatilization (Termeer and Warman 1993; Warman and Munro-Warman 1995). Experiments by Warman and Munro-Warman (1995) showed that the 1% and 3% application of gypsum to fresh animal manure significantly reduced ammonia (NH_3) volatilization in dairy manure but not in poultry manure. At a rate of 10%, however, the application of gypsum to poultry manure not only reduced ammonia volatilization, but also reduced odour strength and offensiveness. The use of gypsum to reduce ammonia losses from mushroom composts has been described by Gerrits (1977). All these results confirm historical experimental data by Salter and Schollenberg (1938), who demonstrated the effectiveness of gypsum as amendment to reduce ammonia volatilization from animal manures following the reaction in equation 6.9.

$$CaSO_4 \cdot 2H_2O + (NH_4)_2CO_3 \leftrightarrow CaCO_3 + (NH_4)_2SO_4 + 2H_2O \qquad \text{(equation 6.9)}$$

This reaction is thought to be reversible but the stability of the reaction products in manure over time has not been studied.

6.5.3 The use of sulphides in agriculture

There are many minerals that contain substantial amounts of S in the sulphide form. The most common sulphide mineral is pyrite (FeS_2). Pyrites can be used to amend alkaline soils. For example, sedimentary pyrites are used in some parts of India as soil amendments on alkaline soils. However, before applying pyrites to soils it is important to analyze the pyrite concentrates on heavy metals and arsenic (Tiwari *et al.* 1985). Pyrite is successfully applied on calcareous soils of northern Bihar State as an S and Fe fertilizer for production of chickpeas, peas and lentils (Tiwari *et al.* 1985).

Ground pyrite has also been tested as a soil amendment to reclaim sodic and calcareous soils. Not only does the oxidation of pyrite reduce the pH, but the soil structure is also improved (Banath and Holland 1976; Dubey and Mondal 1993). However, in many experiments, pyrite applied to alkaline sodic soils was outperformed by another sulphur-bearing mineral, gypsum.

Ground pyrites have also been used in composting systems, lowering the pH and providing Fe and SO_4^{2-}. In India, Gupta *et al.* (1988) incorporated pyrites and Mussoorie phosphate rock (MPR) in decomposing cattle manure and tested the effectiveness of the P- and S-enriched manure in pot trials. It was found that the concentrations of available P for mustard could be increased in cattle manures in the presence of acidifying pyrite.

In order to correct Fe deficiencies in calcareous soils, pyrites from mill tailings have been tested as an inexpensive material (Barrau and Berg 1977). Depending on the particle size of the pyrite and susceptibility to oxidation, pyrites have been suggested as slow release Fe sources on sodic and Fe-deficient soils (Vlek and Lindsay 1978).

Pyrite can also be used in the acidulation of phosphate rocks. Oxidizing pyrite produces sulphuric acid, which in turn can solubilize phosphate rock, creating a more plant-available form of P. Lowell and Weil (1995) tested pyrite as a means of enhancing P availability from phosphate rock in a laboratory study. They incubated pyrite with various African phosphate rocks in several ratios and measured the soluble P and pH in the leachates. Soluble P in the leachate was greatest in pyrite-phosphate rock mixtures with Togo PR and the Sukulu PR from Uganda. In contrast, the soluble P released from pyrites incubated with Tundulu PR (Malawi) and Minjingu PR (Tanzania) was virtually zero (Lowell and Weil 1995).

6.6 Extraction, Beneficiation and Further Processing

A diverse range of elemental S or S-bearing geological and by-product resources can be used for crop production purposes:

- Elemental sulphur recovered as by-product from natural gas processing (also called 'formed' sulphur),
- Elemental sulphur sources extracted by the Frasch Process from underground resources associated with oil and natural gas deposits,
- Calcium sulphate resources from naturally occurring gypsum deposits,
- Calcium sulphate as by-products from flue gas desulphurization in power plants and as 'waste' in the production of triple superphosphate (phosphogypsum),
- 'Waste sulphide' from various metal and coal resource development operations,
- Sulphate and S-bearing fertilizers.

Most sulphur is produced as a by-product of industrial processes (Figure 6.7). Waste sulphur compounds are produced by various processes and from various parent materials. The extraction of elemental S using the Frasch sulphur recovery technique requires non-entry in-situ mining methods, while most gypsum is produced from open pits.

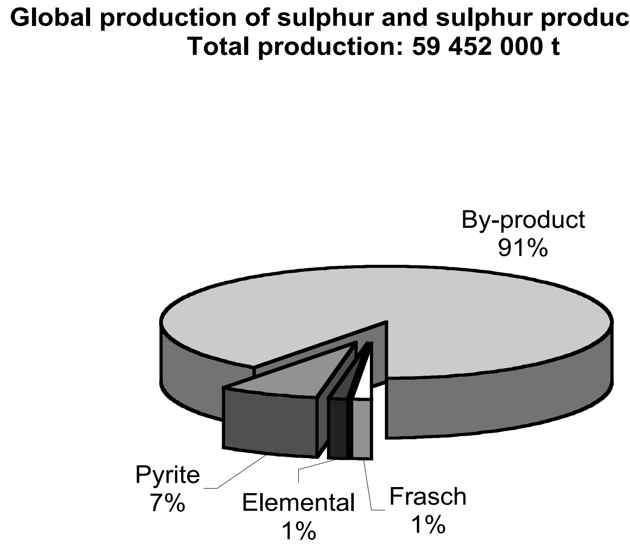


Figure 6.7. *Total world production of sulphur according to different types of sulphur in 2001 (source: US Geological Survey, Minerals Yearbook 2002).*

By-product sulphur

In recent years, increasingly large amounts of elemental S are recovered as by-product from petroleum refining, from natural gas processing and from coking plants. The so-called ‘sour gas’, H_2S, with its characteristic ‘rotten egg’ smell, is a by-product from the processing of natural gas. In order to sell natural gas to the consumers, even small amounts of this foul gas have to be removed. The gaseous S component in sour gas is converted to elemental S by the modified Claus Sulphur Converter Process, also called the Claus Process. This process involves the oxidation of H_2S under controlled conditions (equation 6.10). The elemental S produced by the Claus process is stored as ‘formed sulphur’ as slates, prills, and briquettes.

Step 1:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

(equation 6.10)

Step 2:

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$

The recovery process of elemental S from petroleum and gas processing was initially prompted largely by environmental concerns, but has turned into a viable business opportunity in its own right (Loughbrough 1991). According to statistics of the US Geological Survey, by-product elemental S accounts for approximately 91% of the total sulphur produced in 2001 (Figure 6.4). In 2001, the total tonnage of by-product S was 51,190,000 t, from which 35,000,000 t were derived from hydrocarbon processing, 11,600,000 t derived from metallurgy and 4,590,000 t derived from unspecified sources.

Sulphuric acid is a major by-product of the metal industry, specifically Cu-, Pb-, Mo- and Zn-roasters and smelters. These industries account for approximately 20% of the total production of S in all forms. Major sulphuric acid production as metallurgic by-product is reported from Canada, China, Japan and the United States.

Pyrite

Pyrite is rarely mined alone for its S content. Instead, pyrite is largely discarded as 'waste' in base metal and gold mining operations. It is also a common waste of coal mining and processing operations. Some pyrites can contain impurities with varying concentrations of heavy metals and arsenic. The main use of high-grade and 'clean' pyrite concentrates is for the production of sulphuric acid. Pyrite is crushed, screened and separated from other minerals, then oxidized at high temperatures ('roasted' – or 'burnt') to produce SO_2, which subsequently is converted to sulphuric acid (equation 6.11).

Step1:
$S + O_2 \rightarrow SO_2$

Step 2:
$2\,SO_2 + O_2 \rightarrow 2\,SO_3$ (equation 6.11)

Step 3:
$SO_3 + H_2O \rightarrow H_2SO_4$

In 1987, pyrites as source material contributed about 17% to the worldwide production of sulphuric acid (Russell 1989). In recent years, however, the production of sulphuric acid for the superphosphate industry has switched from pyrite roasting to the use of elemental S because the costs of cleaning up the pollution created by pyrite roasting are becoming more and more expensive.

Frasch-sulphur

The extraction of elemental S from salt domes requires a specific in-situ solution mining technique, the so-called Frasch 'mining' method, invented by Herman Frasch in Louisiana, USA in 1894. It involves drilling a borehole into S-bearing rocks below the surface, for example in cap rocks over salt domes, and injecting superheated hot water (approx. 150^{o}C) and air into the deposit. The superheated hot water melts the S in the porous rocks (melting point 115^{o}C) and the molten liquid S is air-lifted to the surface through the inner tube of the pipe.

Many of the native S deposits associated with cap rocks of salt domes in the United States have been extracted by this method. However, the recovery of elemental S by the Frasch extraction methods is declining. The last 'Frasch' mine in the United States, the Main Pass Mine, closed in the year 2000, and today the Frasch process is used only in Poland (Harben 2002).

Gypsum (Ca-sulphate)

Most of naturally occurring gypsum is mined in large open-pit operations. Only in a few countries is gypsum mined by underground methods (Harben 2000). In open pit operations gypsum is blasted, extracted by front-end loaders and then transported to primary crushers. Most of the gypsum is heated up (calcined) and converted into hemihydrate ($CaSO_4 \cdot {}^1/_2 H_2O$) for use in gypsum boards and other material for the building industry. For agricultural applications gypsum is used in the crude, unprocessed form.

Deposits of gypsum are reported from more than 90 countries. The main gypsum producing countries are USA, Iran, Spain, Canada, Thailand, Mexico, China, Japan and Australia (US Geological Survey 2005). In 2004, the total quantity of *natural* gypsum produced globally was 110.6 million tonnes. It is interesting to note that the 2004 production of *synthetic* gypsum (by-product gypsum) accounted for more than 200 million tonnes.

SSP and TSP

In the production of single superphosphate (SSP) the S is part of the gypsum, which makes up approximately 50% of SSP. During the production of TSP and ammoniated phosphates, the S does not become a value of the final product but is only an intermediary. In this process, the S-bearing mineral gypsum is finally discarded in waste piles. Most of the sulphur extracted and converted into sulphuric acid, thus ends up on large stockpiles. Phospho-gypsum piles in Florida, USA, for example have accumulated to a volume of 1 billion tonnes and pose a major environmental concern due to elevated concentrations of P, F, Ra and radionuclides in the phospho-gypsum piles.

Sulphur Coated Urea (SCU)

Sulphur coated urea is a slow release N-fertilizer consisting of a coating of elemental sulphur around urea particles. The sulphur coating is oxidized by microorganisms and acidifies the environment immediately around the urea particle before the urea is exposed to soil solutions. The N content varies between 36 and 38% and the S concentration can be adjusted to fine-tune the N release rate. SCU fertilizers are mainly used in horticultural applications, for turfgrass and use in landscaping.

6.7 Environmental concerns

The extraction of gypsum and anhydrite causes no serious environmental problems apart from common effects related to open-pit mining, such as dust, noise and traffic-related effects. However, major environmental concerns are related to the release of sulphide-bearing residues from the processing of S-bearing metal deposits and the release of SO_2 gases. The extraction of pyrite also causes major environmental concerns as the oxidizing pyrite produces highly acidifying aqueous environments (acid mine drainage, or acid rock drainage). Additionally, when uncleaned coals containing pyrites (high S coals) are burnt for electricity generation, the emissions are high in SO_2, which then convert into dilute sulphuric acid within the atmosphere, contributing to acid rain.

Other environmental concerns related to S-processing include the storage of elemental S. By-product S has accumulated over time in various locations near natural gas plants, especially when the price of elemental S was low. It is clear that the expected oversupply situation of elemental by-product sulphur will result in increasing accumulations of stockpiled S, which can cause environmental challenges with respect to potential acidification of their immediate surroundings.

Several companies in North America are investigating the possibilities of re-injecting excess S into sour gas reservoirs, or using the heat produced by burning elemental S and injecting the produced SO_2 into sour gas reservoirs. There are, however, major technical and operational challenges ahead to prevent gases to migrate into nearby aquifers.

Too much pyrite in soils produces another set of problems. The oxidation of pyrite commonly creates extreme acid conditions, a case that is particularly evident in the well-known acid sulphate soils of Asia. In a review paper, Dent and Pons (1995) claimed that “acid sulphate soils are the nastiest soils in the world”. When coastal lands with elevated sulphide concentrations are artificially drained and thus exposed to oxygen, the sulphides oxidize with the subsequent release of large amounts of acids. Land cultivated under rice and thus under submerged conditions can become so acidic that it can no longer support agricultural use and plant growth. Acid sulphate soils, with their acidity related fertility problems, have been subject to many studies and reviews, including Van Breemen (1982); Bronswijk *et al.* (1993); Howarth (1984); Luther and Church (1992); Dent and Pons (1995).

In recent years, the focus has moved towards finding local solutions to these acidity and Fe and Al related toxicity problems in acid sulphate soils. For example, Trân Van *et al.* (2000) and Nakabayashi *et al.* (2001) studied the use of acid tolerant species and the inoculation of rice with microorganisms (Trân Van *et al.* 2000) as well as the use of agroforestry systems to provide additional resource values for farming on these soils (Nakabayashi *et al.* 2001). There is evidence that some plants, such as the marshland grass *Spartina alterniflora,* can take up S in the sulphide form (Carlson and Forrest 1982).

While the use of gypsum-based fertilizers are not detrimental to most soil environment, the use of fertilizers containing elemental S as well as ammonium sulphate fertilizers have strongly acidifying effects on the soil environment.

Chapter 7

Calcium and Magnesium

Figure 7.1. *Plant with critical Ca requirement: groundnut/peanut (Arachis hypogea) typically grown on sandy soils (left); Mesozoic limestone succession, Sardinia, Italy (right) (courtesy Dr. I.P.Martini, University of Guelph).*

Calcium (Ca) and magnesium (Mg) are essential elements for plant growth, and animal and human nutrition. Calcium is the 5th most abundant element in the earth's crust and is part of many important mineral groups including carbonates, silicates, sulphates, fluorides and phosphates. Ca compounds have a very wide range of applications in industry (e.g. the manufacture of cement).

Magnesium is the seventh most abundant element in the earth's crust and one of the most prevalent elements in the mantle of the earth. Mg is a major element in seawater after Cl and Na. In minerals, it forms a major component in many silicates, carbonates, sulphates, chlorides and other compounds. Industrially, Mg compounds are widely used in the production processes of iron and steel, and in low weight alloys in the manufacturing sector.

In plant nutrition, Ca and Mg have specific roles in the growth of crops. While the main function of Ca is in the structural stabilization of cells, Mg is largely needed for photosynthesis and the formation of a number of enzymes. Both Ca and Mg are taken up from soil solution by plant roots in the ionic form, as the cations Ca^{2+} and Mg^{2+} respectively. Most of the Ca and Mg ions are supplied to roots via mass flow, the convective flow of nutrients in the stream of water that is taken up by the plant roots (Barber 1995).

Ca and Mg concentrations in soils are variable depending on the parent material. Relatively high Ca and Mg concentrations occur in soils overlying parent materials rich in Ca and Mg, such as mafic and ultramafic rocks of igneous origin or sedimentary and metamorphic Ca and Mg carbonate sediments and marbles.

Like most nutrient elements, Ca and Mg originate from geological sources. The most common minerals with high Ca and Mg concentrations are carbonates. Table 7.1 provides a summary of plant uptake forms, functions in plants, and common non-silicate Ca and Mg minerals.

Table 7.1. *The role of Ca and Mg in plants and commonly found non-silicate Ca and Mg minerals.*

Nutrient	Uptake form	Function in plant	Common Ca and Mg non-silicate mineral forms
Calcium (Ca)	Ca^{2+}	Cell wall stabilization, enzyme activation, controls root activity.	Calcium carbonate ($CaCO_3$) Dolomite ($CaMg(CO_3)_2$) Gypsum ($CaSO_4 \cdot 2H_2O$)
Magnesium (Mg)	Mg^{2+}	Chlorophyll, necessary for phosphorus metabolism, enzyme activity, protein synthesis.	Dolomite ($CaMg(CO_3)_2$) Magnesite ($MgCO_3$)

Calcium deficiencies in soils are best corrected with limestone (Ca-carbonate) and gypsum (Ca-sulphate). Magnesium-deficiencies can be corrected with dolostones, dolomitic limestones, magnesite as well as varies Mg-bearing salts, such as kieserite and Epsom salt.

Mafic rocks (e.g. basalts or mafic tuffs) contain cumulative concentrations of Ca and Mg in the range up to 10-15% and when finely ground, provide solutions with a high pH and considerable quantities of Ca and Mg. These finely ground Ca and Mg-silicate rocks can be considered slow-release alternatives when correcting Ca and Mg-deficiencies in soils.

In the following chapter we will discuss the role of calcium (Ca) and magnesium (Mg) minerals, including liming materials in agriculture. 'Liming material' is a loose term applied to a multitude of products including limestones and dolostones, as well as the calcined forms of limestone known as quicklime or calcium oxide (CaO) and its reaction product with water, slaked lime or calcium hydroxide ($Ca(OH_2)$). The role of the Ca and sulphate-bearing mineral gypsum ($CaSO_4 \cdot 2H_2O$) in agriculture has been discussed in Chapter 6.

7.1 Calcium and Magnesium in plants

7.1.1 Calcium in plants

In plants, Ca is essential for the stabilization of cells. Calcium is precipitated in cells, as Ca-pectate in the middle lamella of cells. Calcium in plants is more concentrated in leaves and stems than in the seeds. The bark of trees can also contain high concentrations of Ca. Calcium activates or inhibits certain enzymes and controls root activity and selectivity of uptake. Calcium is needed in areas with rapid cell division. It is essential for good seed germination and growth of seedlings. Calcium stimulates the development of root hairs and the entire root system. As such, it is involved in the production of new growing points, such as the root tips.

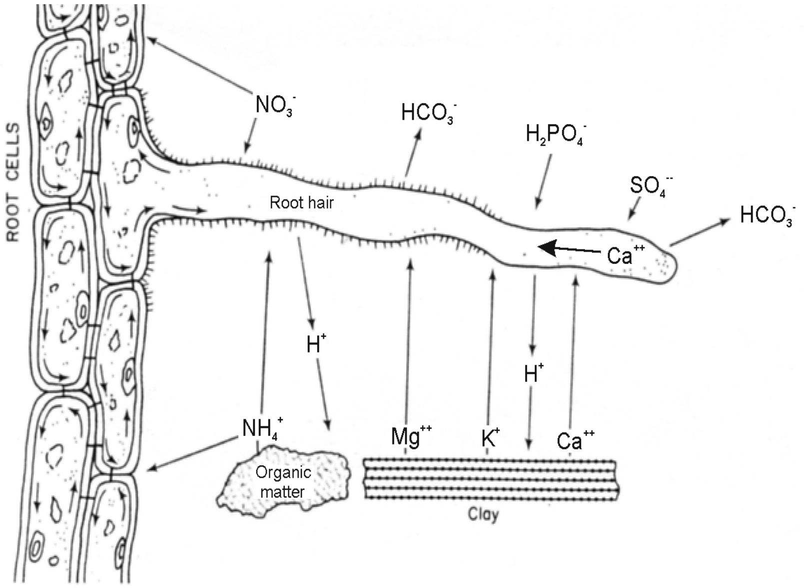


Figure 7.2. *Calcium uptake in the root system.*

Plant roots take up Ca as the cation Ca^{2+} from soil solution (Figure 7.2). However Ca^{2+} is relatively difficult for plants to absorb. Calcium ions exist in soils at concentrations roughly ten times higher than K ions (K^+), yet K^+ uptake is much higher as it is much easier for the roots to absorb (Mengel and Kirkby 2001).

Mass flow is the predominant mechanism for supplying Ca from the soil solution to the roots (Barber 1995). The rate of precipitation and soil moisture are thus crucial factors for Ca availability and transport. A generalized diagram of gains and losses of calcium in the rock-soil-plant continuum is shown in Figure 7.3.

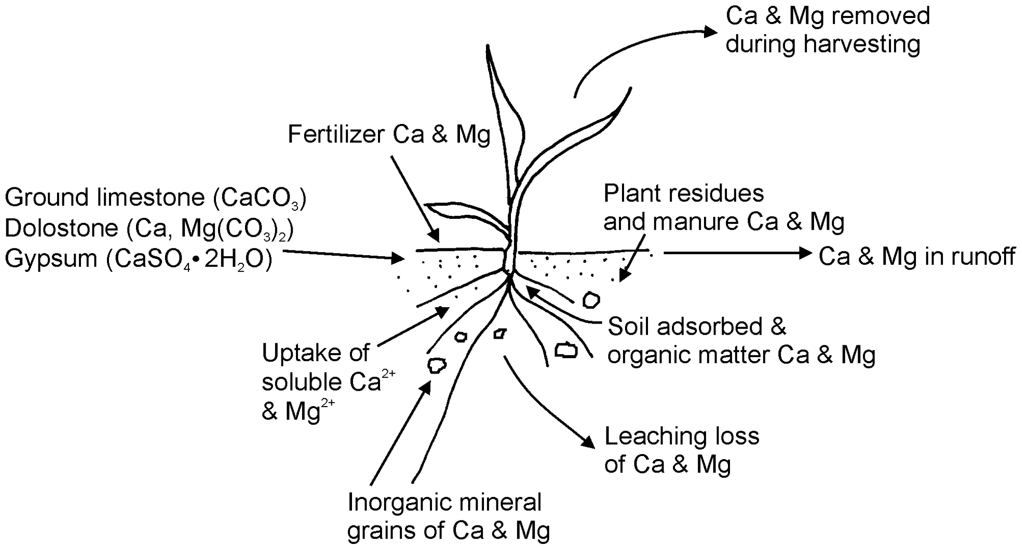


Figure 7.3. *Gains and losses of calcium and magnesium in the rock-soil-plant continuum.*

Within the plant, Ca is not very mobile, with Ca transport occurring mainly in the xylem. Once Ca has been deposited as part of cell structures, it cannot be remobilized. This means that the plant must have a steady supply of Ca throughout the growing season. Crop requirements differ considerably among plant species. Ca disorders such as Ca-undersupply in fruit and storage organs are manifested in apples, tomatoes and peanuts.

In general, dicots require relatively high concentrations of Ca to flourish, while monocot cereals like wheat and corn/maize have lower Ca requirements (Lonegaran and Snowball 1969; Hinsinger and Gilkes 1996; Mengel and Kirkby 2001). Peanuts/groundnuts, tomatoes and celery are known to have high Ca requirements. Other crops with high needs include fruit trees and crops like alfalfa, cabbage, potatoes and sugar beets (Havlin *et al.* 1999).

Many leguminous plants grow well in Ca-rich soils, partially because of their high Ca requirements. Legumes, such as soybeans, alfalfa and sweet clovers, grow best under near neutral or slightly alkaline soil conditions with high Ca availability (Table 7.2). Plants that prefer near neutral and Ca-rich soil conditions are sometimes called *calcicole*, 'Ca-loving plants' (Mengel and Kirkby 2001). These plants not only require Ca for their growth but also seem to cope well with low Fe concentrations in alkaline soils.

There is some debate over the range of tolerance that plants show for varying Ca-concentrations in the soil. Some have suggested that most crops grow poorly in acid soils, not because of the low pH, or low availability of Ca and/or Mg, but because of the toxic concentrations of Al.

Aluminum availability is inversely related to soil pH: the lower the pH, the higher the availability of Al-species. Soils with a pH of < 5.5 have a generally high Al availability and are thus toxic to many agricultural plants (Kamprath 1970; Sanchez 1976). Numerous studies have demonstrated that the exchangeable Al in soils, derived from strongly weathered alumino-silicate minerals, below a pH of 5.5 is toxic to plant roots causing yield reduction (Abruña *et al.* 1964; Coleman and Thomas 1967; Kamprath 1970; Foy 1974; Sanchez and Salinas 1981; Bennet and Breen 1991; Ding *et al.* 1993; Sale and Mokwunye 1993).

Several tropical leguminous plant species have adapted to Al-rich acid soils, for example tropical kudzu (*Pueraria phaseoloides*), as well as grain legumes such as cowpeas (*Vigna unguiculata*) and pigeon peas (*Cajanus cajan*) (Sanchez 1976). Wild blueberry (*Vaccinium angustifolium* Ait), also grows well in acid, Ca-deficient soils, particularly on igneous and metamorphic parent materials with well developed organic layers and peat rich soils (Sanderson *et al.* 1996).

In more tropical environments, the important plantation crops, pineapple and tea are well adapted to acid soils. Tea (*Camellia sinensis* L.) grows very well in highly weathered acid soil conditions and has adjusted to high exchangeable Al-concentrations (Sivasubramanian and Talibudeen 1972). Tea is commonly cultivated at high altitudes in the humid and sub-humid tropics where annual rainfall exceeds 1500 mm (Zoysa *et al.* 1999).

Table 7.2. *Selected plants with high Ca-Mg-S requirements.*

Crop type	**Ca (kg ha^{-1})**	**Mg (kg ha^{-1})**	**S (kg ha^{-1})**
Peanuts/groundnuts	118	31	24
Field beans	54	18	25
Alfalfa	280	59	57

Acid soils with a pH below 5.5 may restrict the growth of plants for several reasons related to plant nutrition including:

- Al-toxicity,
- Mn-toxicity,
- P-deficiency due to high P-fixation on Fe and Al oxihydoxides,
- Ca and Mg-deficiency, and
- Mo-deficiency, especially for legumes and plants of the cabbage family.

Plants such as blueberries, tea or peanuts/groundnuts are significantly different from other plants in their physiological responses to high concentrations of Al and Fe in acid soil solutions. The mechanisms to adapt to acid Al-rich soils are tolerance and exclusion Marschner (1991). Tea plants are acid tolerant plants that accumulate Al in their leaves.

Other plants adapted to acid high Al conditions by excluding Al through root induced changes in the rhizosphere (Marschner 1991). The physiological mechanisms for Al-tolerance and/or exclusion of Al vary with plant species and may be related to differences in root morphology, changes of pH in the rhizosphere, differences in translocation of Al to plant tops, or differences in uptake mechanisms of Ca and Mg (Foy 1974; Marschner 1991).

Calcium deficiencies in plants

Calcium is relatively immobile within the plant and Ca-deficiencies in plants are mainly manifested in the actively growing tissues. Ca-deficiencies cause the deformation and eventual death (necrosis) of apical growing points. Roots of Ca-deficient plants are usually short and stubby. When Ca-deficiency is less severe, only the youngest leaves of plants exhibit deformations and chlorosis at leaf margins. Calcium deficiencies consistently affect the development of fruit and storage tissue.

Apples lacking Ca have bitter pits, and small brown necrotic spots on the surface of the apple (Ferguson and Watkins 1989). Peanut/groundnut plants (*Arachis hypogea*) that lack Ca often form shells that do not contain pods (Skelton and Shear 1971; McNeil 1987; Alva *et al.* 1989; Caires and Rosolem 1991). Calcium is most critical for groundnut pod development between 15 and 35 days after the pegs reach the soil. Gypsum ($CaSO_4 \cdot 2H_2O$) is frequently used in peanut/groundnut production schemes as it provides both Ca and S (Walker 1975). However, groundnuts not only have high requirements for Ca but also for other nutrients, such as S and P, B as well as other trace elements.

Calcium deficiencies cause plant disorders such as ‘blossom end rots’ in tomatoes (*Lycopersicum esculentum*) and sweet pepper (*Capsicum annuum*) (Morley *et al.* 1993; Mengel and Kirkby 2001). Brussels sprouts (*Brassica oleracea*) growing with insufficient available Ca in soils will show internal browning (Mengel and Kikby 2001).

7.1.2 Magnesium in plants

Magnesium occupies the centre of the chlorophyll molecule and is thus required for photosynthesis. Magnesium is more concentrated in the seeds and grain than in leaves and stems. It is required by a number of enzymes. The cation Mg^{2+} activates enzymes associated with energy transfer and is essential for the synthesis of proteins. The Mg ion also builds a 'bridge' to phosphate groups especially adenosine triphosphate (ATP) and protein enzymes. As such, it has an important function in 'phosphorylation', a biochemical mechanism that enables the addition of a phosphate group into an existing organic molecule. The availability of sufficient Mg is often responsible for increased uptake and utilization of phosphorus (Mengel and Kirkby 2001; Marschner 2002). The function of Mg as P carrier is associated with the formation of lecithin and some proteins that are concentrated in seeds.

Roots take up Mg from the soil solution as the cation Mg^{2+}. As with Ca^{2+}, most Mg^{2+} ions are supplied from soil solution to roots via the mechanism of mass flow (Barber 1995). Plants find K much easier to absorb than Mg as they lack a special uptake mechanism to transfer Mg-cations across the plasma membrane of the roots walls. In addition, the presence of other ions in the soil can inhibit the uptake of Mg. High concentrations of K, NH_4^+ or Ca can inhibit Mg uptake and can induce Mg deficiencies, even if sufficient Mg cations are available in the soil solution. Especially common is the interference of K with Mg uptake. Within the plant, Mg is highly mobile, with transport occurring in both the phloem and xylem. Since Mg is easily translocated, it is used in plants over and over again.

Magnesium deficiencies in plants

Magnesium deficient soils can cause Mg-deficiencies in plants. Magnesium deficiencies result in the accumulation of carbohydrates in leaves and an undersupply to roots, thus impeding root development (Scott and Robson 1990). Symptoms of Mg deficiencies always start in the older leaves and later move to younger leaves. When dicots such as grapes, beans, potatoes and tomatoes, lack Mg, they exhibit intraveinal yellowing and leaves that fall prematurely.

When cereal crops such as wheat, oats and rye are deficient in Mg, they exhibit dark green spots of chlorophyll accumulation in pale green to yellow leaves. Chlorotic and necrotic symptoms also commonly occur at the tips of the leaves. The early stages of maize/corn growth show similar symptoms when Mg-deficient.

Some crops such as fruit crops, vines, sugar beets, potatoes and cauliflower are particularly susceptible to Mg deficiencies. Mg deficiencies in conifer trees growing on acid soils with low Mg concentrations frequently show discoloured needles with yellow tips. Application of sulphate of potash magnesia ($K_2SO_4 \cdot MgSO_4$) usually results in the re-greening of the affected needles (Mengel and Kirkby 2001).

7.2 Calcium and Magnesium in soils

Historically, farmers cultivated mainly on fertile, Ca, Mg and K-rich soils, such as soils found near volcanoes or in alluvial river flats. With increasing population pressure, farmers moved into areas with lower soil fertility and correspondingly low Ca, Mg and K-status. They had to increase soil productivity by adding organic and inorganic mineral materials that contributed to the increase in these nutrients and consequently in crop productivity. The practice of 'liming', that is adding liming materials such as $CaCO_3$ or $Ca(OH)_2$ to soils is very old and attests to the early understanding of farmers to correcting soil acidity.

7.2.1 Calcium in soils

The mean Ca-concentration of the earth's crust is 3.5% and the mean Ca concentration in soils is 1.96% (Ure and Berrow 1982). Calcium in soils occurs in various forms, the major being in the form of primary minerals. This fraction contains predominantly Ca-bearing silicates and the most prevalent form, Ca and Ca-Mg carbonates and gypsum. The carbonates are mainly present in calcareous soils and commonly occur as calcite ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$).

The concentration of total Ca in soils varies widely depending on the type of parent material and the degree of weathering. Most soils that developed on carbonate rocks and Ca-rich parent materials like basalt or dolerite or other mafic volcanic rocks are relatively rich in available Ca. As expected, the Ca-status of soils developed from Ca-poor parent material like quartzitic sandstones is low. Highly weathered and leached soils, for example lateritic and podsolic soils, are generally low in Ca. Surface layers of soils in humid regions, even when developed on calcareous parent materials, can have low Ca-status because of the removal of Ca and other cations through excessive leaching. Soils in arid and semi-arid environments are frequently characterized by relatively high Ca concentrations, occurring in the form of Ca-sulphate gypsum ($CaSO_4 \cdot 2H_2O$) or as calcite-rich crusts (calcrete).

Calcium has a great effect on soil properties, especially on soil structure. Soils with high Ca saturation on clay and organic complexes show a high degree of aggregation. They have a good porosity and a good tilth, meaning a good workability.

In humid climates the removal of Ca from the clay and organic complexes is often associated with replacement by H^+ ions. In contrast, in arid and semi-arid areas Ca is frequently replaced by Na, leading to poor physical soil conditions and the associated problems in the management of sodic soils. Theses sodic soils have high Na saturation on the exchange sites of clays and are sticky when wet and very hard when dry. To reverse this detrimental characteristic of sodic soils, Ca is added to replace Na thus improving soil properties of sodic soils (see Chapter 6.5.2, the use of gypsum in agriculture).

The critical exchangeable soil Ca-concentrations at which deficiencies occur in soils vary from crop to crop. Munson (1982) reports the critical exchangeable Ca-concentrations in tropical soils as below the range of 2-4 cmol (+) kg^{-1} or milli-equivalent per 100 g, which corresponds to 400-800 mg kg^{-1} (ppm). Ca in soil solution in temperate climates ranges from 30-300 mg kg^{-1} and a Ca-concentration in soil solution of 15 mg kg^{-1} has been reported as adequate for crops in these environments (Havlin *et al*. 1999).

7.2.2 Magnesium in soils

The mean total Mg concentration of the earth's crust is 2.33% and the mean Mg concentration in soils is 0.83% (Ure and Berrow 1982). Magnesium occurs in the soils in various forms. The main form is the non-exchangeable form, either as primary minerals (Mg-silicates or Mg-rich carbonates) or associated with secondary clay minerals. The concentration of total Mg in soils largely depends on the type of parent material from which the soil developed and the degree of weathering. In general, soils are well-supplied with Mg when they develop from mafic and ultra-mafic igneous rocks, such as basalts, pyroxenites and serpentinites, as well as dolomitic sediments. Most of these soils are also well supplied with Ca. But in some cases, for example over serpentinite, the concentration of Mg can be very high in comparison to Ca (low Ca/Mg ratio), which may lead to imbalances and even Ca deficiencies in soils (Brooks 1987). Highly leached soils may contain low concentrations of Mg, while Mg concentrations can be high in some soils formed in depression and zones of accumulation as in some marsh soils.

Draycott and Durrant (1971) determined a critical soil limit for exchangeable Mg as 35 mg kg^{-1} (ppm) equivalent to 0.28 cmol (+) kg^{-1}. Munson (1982) put the critical exchangeable Mg concentrations in tropical soils in the range between 24-121 mg kg^{-1} (0.2 and 1.0 cmol (+) kg^{-1}). Soils with lower concentrations of exchangeable Mg are considered to be Mg-deficient and may cause Mg deficiencies in plants growing on these soils.

7.2.3 Calcium and Magnesium deficiencies in soil

Many soils in the world show Ca and Mg deficiencies, mainly the highly weathered acid soils in the tropics and subtropics, and soils that are derived from Ca and Mg poor parent materials, e.g. from sandstones/quatzites and granitic rocks. These soils are characterized by a pH of less than 7 with high concentrations of protons (H^+) and associated high exchangeable concentrations of toxic Al and Mn.

Soil acidity

Acid soil conditions can be caused by various processes, some are natural and some are human induced. The main causes are:

- weathering of a parent material low in cations, for example quartzites (the acidity is inherent),
- extensive leaching or flushing out of the cations Ca, Mg, Na, and K, in areas of high rainfall, causing a relative accumulation of H^+,
- removal of cations through plant harvesting without replenishment of harvested cations,
- exudate from plant roots (more H^+-ions exuded than OH^- and HCO_3^- ions),
- decomposition of organic matter,
- deposition of *'acid rain'* caused by industrial pollution, and
- application of *acid forming nitrogen fertilizers* (e.g. ammonium sulphate).

Human induced acidification processes, such as the application of acidifying ammonium bearing fertilizers and atmospheric pollution, currently affect wide areas of Europe (Goulding and Blake 1998). The application of 100 kg ammonium sulphate fertilizer contributes to a loss of about 100 kg calcium carbonate equivalent (Cooke 1982). Liming materials are used to reverse this trend on agricultural land.

Availability of Al and Mn in acid soils

Several cations such as zinc (Zn^{2+}), aluminum (synonymous with aluminium) (Al^{3+}), iron (Fe^{2+}), copper (Cu^{2+}), cobalt (Co^{2+}), and manganese (Mn^{2+}) become soluble and available for uptake by plants in acid soils. The availability of these cations, especially Al^{3+} and Mn^{2+}, can become toxic in highly acidic conditions. Consequently, liming recommendations for acid soil with toxic Al-levels are often derived from the measurements of exchangeable Al and related Al-saturation. The aim of liming is thus not to increase the pH and neutralize the soil but to reduce the Al toxicity to an acceptable level. As such, these soils do not generally need to be limed to neutrality (pH 7) but only to a pH of 5.5 or 6 (Kamprath 1970). A similar relationship exists with Mn, which is soluble at pH conditions below 5.5 to 6. Liming these soils to levels above 5.5 to 6 is thus generally sufficient.

Calcium and magnesium for animal nutrition

Calcium plays a crucial role in nutrition for humans and animals as well as for plant growth. Milk and dairy products as well as leafy vegetables provide large parts of the Ca-requirements of human nutrition.

Calcium is required by animals for a number of important physiological and biochemical functions:

- For the formation of bone and teeth, predominantly as hydroxy-apatite [$Ca_{10}(PO_4)_6(OH)_2$]),
- For nerve functions and contraction of muscles,
- For blood clotting functions,
- As activators for various enzymes.

Growing cattle require considerable quantities of Ca for normal growth. Most of the Ca uptake by cattle is from the consumption of clovers and grasses. The Ca concentration in clover is generally higher than that of grasses. When pastures are too low in Ca, the farmers apply Ca either in the form of superphosphates or lime.

Magnesium is another important element for animal nutrition. Important biochemical functions of Mg are:

- Mg is a co-factor of enzymes involved in metabolism of carbohydrates and proteins,
- Mg is needed for nerve conduction and muscular contraction.

Lactating cows in New Zealand require 14–28 g of Mg per day; otherwise they may develop ‘hypomagnesia grass tetany’, a condition that can lead to convulsions and death (Grace 1983). Lactating dairy and beef cows are especially affected in the early phases of their pregnancy. Animals require considerable amounts of Mg in the spring, when a high proportion of forage is made up of grasses that are commonly low in Mg.

Methods used to prevent Mg-deficiencies in animals include the application of Epsom salts [$MgSO_4{\cdot}7H_2O$] or Mg pellets in feed, magnesium licks or the application of calcined magnesite on pastures (Grace 1983).

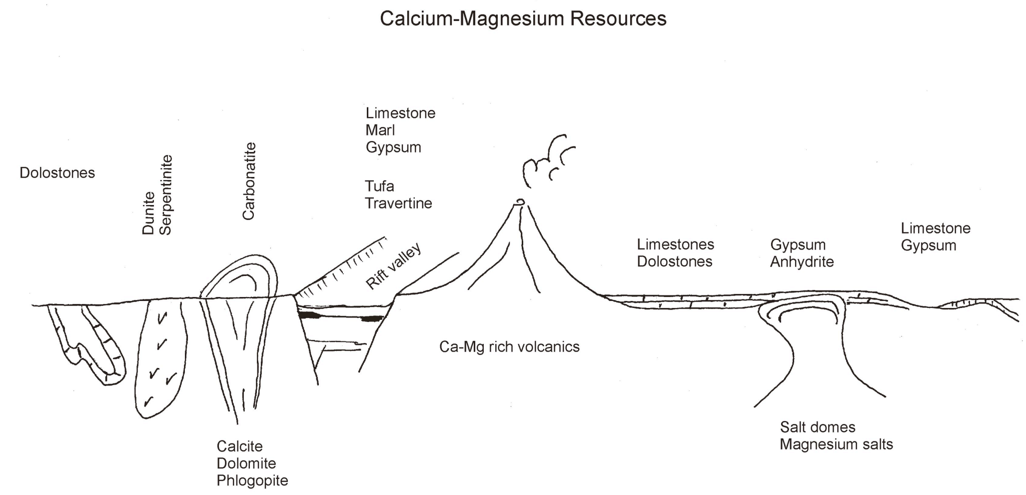


Figure 7.4. *Schematic section showing various geological Ca and Mg resources.*

Table 7.3. *Natural mineral forms of calcium, magnesium, and sulphur.*

Mineral	CaO (%)	MgO (%)	S (%)
Non-Silicates			
Calcite [$CaCO_3$]	56		
Dolomite [$CaMg(CO_3)_2$]	30.4	21.9	
Anhydrite [$CaSO_4$]	41.2		23.5
Gypsum [$CaSO_4 \cdot 2H_2O$]	32.6		18.6
Apatite [$Ca_{10}(PO_4)_6F_2$]	55.8		
Magnesite [$MgCO_3$]	48		
Kieserite [$MgSO_4 \cdot H_2O$]		29	23
Epsom Salt [$MgSO_4 \cdot 7H_2O$]		16	13
Silicates			
Diopside (clinopyroxene)	25.9	18.6	
Epidote	23.2		
Anorthite (Ca-rich plagioclase)	20.1		
Hornblende (amphibole)	14.9	13.0	
Tremolite (amphibole)	13.8	24.8	
Actinolite (amphibole)	13.3	19.1	
Forsterite (olivine)		57.3	
Serpentine		36-44	
Enstatite (Mg-rich pyroxene)		40	
Chlorite		20-36	
Talc		32	
Phlogopite		29	
Vermiculite		20-24	

7.3 The geology of Ca and Mg resources

Like most nutrient elements, Ca and Mg originate from geological sources. Table 7.3 shows many of the more common silicate and non-silicate rock forming minerals, containing Ca and Mg. A general diagram illustrating the main naturally occurring types of geological Ca and Mg resources is provided in Figure 7.4.

7.3.1 Carbonates

The most common highly available sources Ca and Mg are carbonates. Large volumes of sedimentary rocks deposited in geological times are made up of carbonates. The oldest carbonates reported are from the Paleoproterozoic, some 3.5 billion years ago. Todays carbonate rocks make up large volumes of whole mountain chains, such as the Himalayas, the Alps and the Rocky Mountains.

Carbonates are formed largely through chemical precipitation and/or biochemical processes either in situ or not far from their source of formation. According to Pettijohn (1975) there are five main groups of modern sedimentary carbonate deposits:

- Shallow water marine deposits, for example shelf carbonates or carbonates associated with reef complexes,
- Deep water marine carbonates, for example deep water carbonate oozes derived from the sedimentation of planktonic organisms and shells. These carbonates are found above a maximum depth of carbonate accumulations (4000 m), below which the carbonate shells would dissolve in the deep and cold water,
- Carbonates associated with evaporites in semi-arid areas, for example caliche and calcrete,
- Carbonates of freshwater lakes, for example marls underlying freshwater swamps,
- Eolian (wind transported) carbonate deposits, for example carbonate sands in dunes close to calcareous beach deposits.

The most common carbonate deposits are those of shallow marine environments, for example shelf environments and reef and reef related carbonate environments. Coralline limestones occur in clean and warm (25-30º) waters with depths of generally less than 30 m. The distribution of modern marine carbonate sediments near reefs is shown in a generalized cross section (Figure 7.5). In recent years, attention has also been drawn to the many cool water carbonates (Nelson 1988; James 1997; Sohlager 2003) that can be found in various oceanic environments.

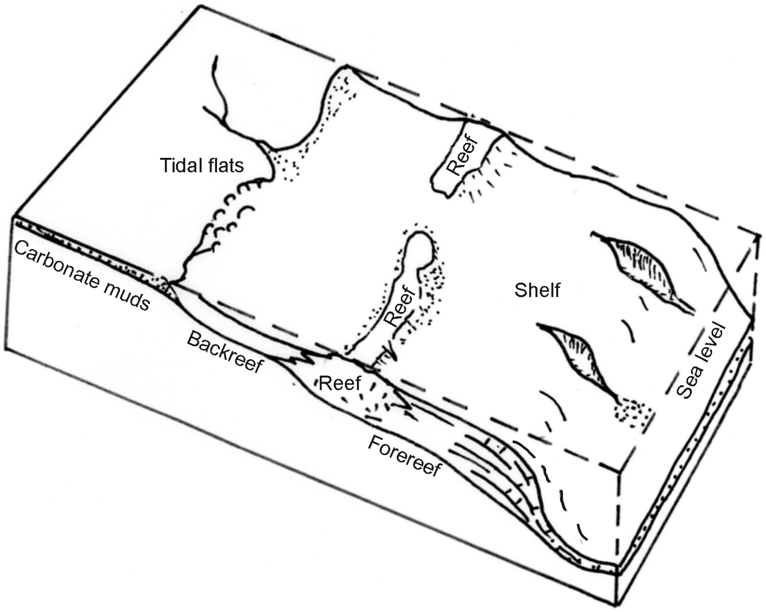


__Figure 7.5.__ Marine depositional environments of carbonate sediments near reefs.

Carbonate rocks are made up of varying amounts of the carbonate minerals calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). At one end of the spectrum is dolostone, containing more than 90% dolomite (Pettijohn 1975), and at the other end is limestone, containing more than 90% calcite. The percentage limits of limestone, dolomitic limestone, calcitic dolostone and dolostone respectively are shown in Table 7.4, and in Figure 7.6.

__Table 7.4.__ Nomenclature of sedimentary calcitic and dolomitic carbonates (modified after Pettijohn 1975).

Type	Dolomite (%)	Calcite (%)	MgO equivalent (%)
Limestone	0-10	100-90	0-4.4
Dolomitic limestone	10-50	90-50	4.4-22.7
Calcitic dolostone	50-90	50-10	22.7-41.0
Dolostone	90-100	10-0	41-45.4

Limestones and dolostones are found in differing quantities, in different geological environments and in different geological time periods. In times of warm water regimes worldwide, for example during the Cretaceous, much larger volumes of limestone were deposited than in times of colder climates, for example the Permo-Carboniferous Gondwana glaciation in the southern hemisphere (350-250 million years ago).

Over time, circulating fluids in the rock sequences altered many of these primarily calcitic limestones. One of the principal processes of alteration is the process of dolomitization, the replacement of Ca in limestones by Mg from circulating Mg-rich waters.

The resultant rocks of dolomitization are dolomite rocks, dolostones, with the principal mineral dolomite. In general, the older the carbonate rock the more dolomite-rich and hence the more Mg-rich it is. Precambrian carbonates are predominantly dolomitic in composition. The process of dolomitization has been studied by many authors and is summarized in Pettijohn (1975) and Tucker (1990). The classical documentation of the variation of the Ca/Mg ratio in carbonate rocks of North America and the Russian Platform have been presented by the Russian geologist Ronov (1972).

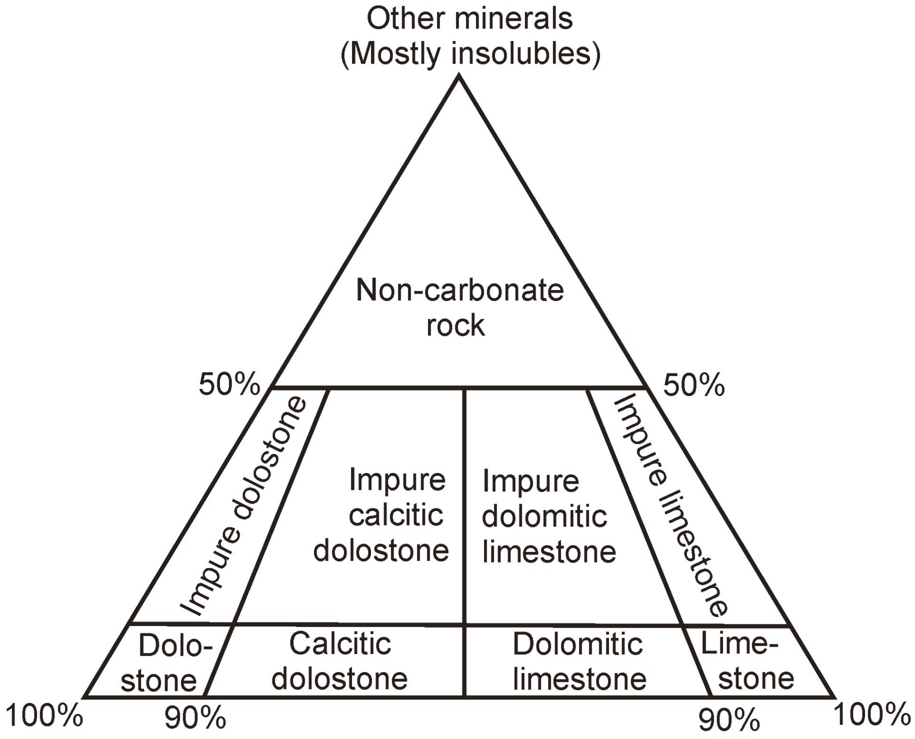


Figure 7.6. *The mineralogical classification of carbonate rocks (modified after Carr et al. 1994).*

The classification of carbonate rocks is complicated by the presence of varying amounts of impurities (Figure 7.6). The main impurities in limestones and dolostones are clays, quartz sand and silt grains, chert, organic matter, pyrite, and Fe-Al oxides. Some impurities found in carbonate rocks are a function of their precipiatation and geological environment during deposition.

Other impurities in carbonate rocks are connected to their porosity. While most sedimentary carbonates are relatively dense, some carbonates show considerable porosities, for example reef limestones. Young and unconsolidated reef limestones have high porosities with some of the carbonates still in the slightly more soluble aragonite form of $CaCO_3$ (Pettijohn 1975). Impurities can be introduced when pores are filled with fine material or other carbonates and quartz. Carbonates and quartz often recrystallize in voids and along cracks.

Limestones

Limestones make up approximately 15% of the world's sedimentary rocks (Carr and Rooney 1983). Geologically, the greatest volumes of limestones were formed in warm and clear marine shallow environments (Pettijohn 1975; Wilson 1975). But there are also considerable amounts of limestones formed under cold-water conditions. They consist mainly of discrete carbonate aggregates in a matrix of micro-crystalline calcitic 'ooze' or calcite mud (micrite). There are also pore fillings, made up of chemically precipitated coarse crystalline calcite (sparite). The aggregates in limestones are predominantly made of up of skeletal fragments of fossils or rounded and angular clastic fragments as well as precipitated spherical-subspherical grains, 0.5 to 1 mm in diameter, consisting of lamellae of aragonite or calcite, so called ooids (Tucker 1990).

There are several types of limestones: sedimentary bedded or massive limestone, dolomitic limestone, calcitic dolomite. Travertine is a special form of limestone, which is formed by rapid chemical precipitation from surface or groundwater, or by evaporation. Travertine can be hard and compact, layered and banded, or porous and spongy. 'Tufa' is the name for a soft, spongy and porous variety of travertine. Travertine and tufa deposits are commonly found in volcanic areas associated with hot springs.

Many limestones have organic origins, either containing large amounts of broken or intact shells, corals or other organic debris, to fine-grained lime mud and algal mats made up of carbonates. A special form of very pure fine-grained biologically derived limestone is chalk, made up of accumulations of very small marine planktonic algae, for example coccoliths. Famous examples of chalk are the 'White Cliffs of Dover' in southern England as well as chalk deposits in France, the USA and other countries.

Limestones are generally found as layered sedimentary rocks. Small amounts of limestones are also found in lake environments. Geologically speaking these are relatively rare and small occurrences. Similarly rare are the chemically precipitated calcite rich tufa and travertines that are found in areas of springs related to faulting.

Dolostones

Dolostones are sedimentary rocks consisting mainly of the mineral dolomite ($CaMg(CO_3)_2$). Dolostones have formed primarily as replacement of pre-existing carbonate minerals. The formation of dolomite as direct precipitate from seawater is strongly contested (Tucker 1981). In old Precambrian rocks more dolostones are found than limestones. The ratio of dolostones to limestones increases back in time. The older the carbonate sediments the more likely they are dolomitic. While some dolostones have been reported in geologically young sediments most carbonates of Cambrian age and older are dolomitic in nature. This can indicate that the carbonate rocks had more time to come in contact with Mg rich solutions or that seawater chemistry was different in the past (Tucker 1981).

Other carbonates

Other naturally occurring forms of Ca and Mg carbonates include, igneous carbonate, metamorphic carbonate (marble), marl, calcrete and magnesite.

Igneous carbonates are relatively rare with large accumulations occurring mainly in the core of carbonatite complexes. Intrusive (and rarely extrusive) carbonatites are commonly round to ellipsoidal in shape, 5-15 km in diameter and located along structurally weak zones of the earth crust. Carbonatites have been found in many countries, emplaced mainly in rejuvenated fault and shear zones outside stable granitic cratons. Due to their weathering characteristics carbonatites are not easy to detect under the cover of glacial sediments (in temperate climates) or in deeply weathered tropical terrains. The geology and structural setting of carbonatites in E. Africa was discussed by van Straaten (1989) and is described in detail in Chapter 4.

Marble is the term used for metamorphosed, usually coarse-grained limestone or dolostone.

Marl is soft calcite mixed with various amounts of clay and organic matter. This whitish to buff coloured, fine-grained material is found mainly in small freshwater lake environments, in swampy areas and in lacustrine sedimentary successions.

Calcretes or caliches are mainly Ca-carbonates formed by in-situ cementation of pre-existing Ca rich materials as secondarily precipitated $CaCO_3$ in near-surface environments. Calcretes can be earthy and soft, or form highly indurated hard crusts or nodular structures. They are generally found in semi-arid to arid regions of the world, for example in Australia, parts of India, Africa and the Americas (Milnes and Hutton 1983; Netterberg 1980). The genesis of calcretes or caliches is described by many scientists including Klappa (1983) and Phillips *et al.* (1987).

Magnesite is found in two principal geological environments: in the cryptocrystalline or 'amorphous' form in veins of serpentinites or in the crystalline (spary) form in sedimentary successions, associated with dolomites. The largest deposits are the sedimentary magnesites found in Eastern China, Australia and Canada (Harben and Bates 1984). Exceptionally large deposits of magnesite are reported from the Liaoning Province in eastern China (Schmid 1984; Zhang 1988). Here, the magnesite bodies show sedimentary features and have average thicknesses of 100 meters (Figure 7.8). The magnesite–bearing zone near Da Shi Chiao and Hai Chen in Liaoning Province is more than 30 km long and contains proven reserves of more than 2.5 billion tonnes of magnesite ore (Zhang 1988). Other major magnesite deposits in crystalline-spary and cryptocrystalline forms are reported from Australia, Canada, Brazil, Greece, North Korea, Russia, Spain and Turkey (Duncan and McCracken 1994).

Figure 7.8. *Massive magnesite deposit near Hai Chen City, Liaoning Province, China.*

7.3.2 Ca-phosphates, Ca-sulphates, and Ca-silicates

Apart from the typical 'liming materials' like limestone and dolostone there are many rocks and mineral sources that contain appreciable levels of Ca and Mg. Many of these rocks and minerals provide Ca and/or Mg but do not raise soil pH, so are not considered 'liming materials' in the strict sense. They include Ca-sulphates, Ca-phosphates and Ca-silicates.

The primary Ca-phosphate mineral apatite contains around 55% CaO with limited 'liming effects' (Hellums *et al.* 1989). Studies in New Zealand show that 1 tonne of reactive PR (13% P) was just as effective a liming material as 0.5 tonnes of agricultural lime that contained 80% $CaCO_3$ (Sinclair *et al.* 1993).

The agronomic effectiveness of phosphate rocks (PRs) follows their reactivity in acid soils. Reactive phosphate rocks (PR) such as Bahia Inglesa PR from Chile and Bayovar PR from Peru had the highest agronomic effectiveness and Ca uptake in comparison to PRs with low reactivity such as Hahotoe from Togo (Hellums *et al.* 1989).

Hellums *et al.* (1989) measured the agronomic effectiveness of various Ca-minerals in comparison to 100% calcite ($CaCO_3$). The relative agronomic effectiveness (RAE) of gypsum ranged from a 28% to 88% increase in dry matter yield of corn/ maize and an 8-58% increase in Ca uptake (Hellums *et al.* 1989).

Among the sulphates it is mainly anhydrite ($CaSO_4$) and the hydrated form of gypsum ($CaSO_4 \cdot 2H_2O$) that contain appreciable amounts of Ca. The use of gypsum in agriculture is reported in Chapter 6.

Some other useful Ca-containing agricultural products can be derived as by-products of other processes, such as the by-products of phosphate processing, phospho-gypsum, or gypsum from the processing of fossil fuel powered electricity generating facilities (flue-gas desulphurization gypsum - FGDG) or forms of processed limestones (quicklime and slaked lime).

The Mg-sulphate mineral kieserite contains appreciable amounts of Mg. Kieserite can be recovered from salt brines, produced as the by-product from salt and potash mining, or produced by leaching serpentinite or olivine with sulphuric acid or by reacting magnesia (MgO) with sulphuric acid (Duncan and McCracken 1994).

Many silicates also contain considerable concentrations of Ca and Mg, as can be seen in Table 7.3. The concentration of Mg is relatively high in olivines, pyroxenes, amphiboles and dark micas, while the concentration of Ca is highest in pyroxenes and amphibole minerals, and rocks containing large amounts of these minerals. The release of Ca and Mg from these silicates is generally slow, but depends on weathering conditions. In Uganda, the by-products of vermiculite mining have provided a useful source of Mg (+P) from the weathering of Mg-silicates (and small amounts of apatite). These by-products contain 9-12% MgO and approx. 2% P_2O_5 and have shown to be very effective Mg and P-sources in Mg and P-deficient soils in Uganda (Van Straaten, unpublished).

Ca-Mg rich silicates are located mainly in volcanic areas, in areas of converging plates, for example in volcanic regions around the Pacific Ocean or in diverging plate boundary zones, for example in rift environments. Massive outpouring of Ca and Ca-Mg rich silicate volcanics are found in many parts of the world, including India (the Deccan Traps), South America (Parana Basin) and parts of North America (Columbia River flood basalts) and the Siberian Plateau (Coffin and Eldholm 1993).

7.4 Agricultural use of Ca and Mg

There are several management options to overcome low crop productivity related to acid, Ca and Mg deficient soils. These include organic nutrient inputs (e.g. animal and/or green manures), inorganic nutrient inputs or the selection of crops adapted to acid soils and Ca and Mg deficiencies. The following section focuses on the option of using naturally occurring inorganic mineral inputs, specifically the use of Ca and Mg rock and mineral resources as liming materials and as Ca and Mg nutrient sources.

The addition of Ca (and Mg) rock to soils is done for several reasons:

- To adjust the soil pH to counteract acidity and reduce toxicities of exchangeable Al, Mn, as well as metals,
- To maintain adequate Ca (and Mg) concentrations in soils,
- To promote microbial activity in soils,
- To improve the structure of clay-rich, ‘heavy’ soils,
- To reclaim salt affected sodic soils.

Highly weathered and leached acid soils are often associated with exchangeable Al, which is toxic to plants. This toxicity can be overcome by raising the pH to 5.5 or 6. This is the pH at which Al is precipitated and no longer toxic.

Liming can also be used to reduce toxicities due to many other metals in the soil. An example of using liming materials to reduce Cu toxicities, induced by spraying Cu fungicides to vineyards, is given by Dias *et al.* (1993).

Many soils in the tropics are characteristically low in Ca and Mg and the addition of these two essential nutrients may be necessary for agricultural production. Sanchez (1976) provides some examples from South and Central America, where liming materials, mainly ground limestones and dolomitic limestones, are used not only to reduce acidity and related Al toxicity but also to provide nutrient sources for Ca and Mg deficient soils.

Liming can also promote specific microbial activities, for example by improving the environmental conditions for N-producing and fixing bacteria. In general, acid soils have higher populations of fungi than bacteria, as bacteria (including N-fixing bacteria) live better in neutral and slightly alkaline soils.

Calcium bearing minerals are also used to improve the structure of ‘heavy’ clay rich soils. The addition of Ca improves aggregate formation and stability and can thus improve the soil structure in soils that are either naturally rich in clay minerals with a lack of soil porosity or where the soil structure has been reduced by compaction (for example by heavy machinery).

Ca-minerals such as gypsum ($CaSO_4 \cdot 2H_2O$) are used in the reclamation of salt affected sodic soils. With the addition of Ca-sulphates Ca replaces Na from the exchange sites on clays and reacts with soluble salts like $NaHCO_3$ to form easily leachable soluble Na-sulphates. Practically, several tonnes of gypsum per hectare have to be mixed with the soil and later leached to achieve the removal of detrimental Na ions and improve the physical and chemical properties of salt affected sodic soils. More details on the use of gypsum to provide Ca and S as nutrients and on its soil-ameliorating effects are reported in Chapter 6.5.2.

7.4.1 Liming materials

Liming materials are materials that raise the pH of acid soils. The term liming material is commonly used very loosely. The term refers not only to materials that are lime *sensu stricto* (for example CaO quicklime, or $Ca(OH)_2$ hydrated lime) but also ground limestones, dolomitic limestones, dolostones, magnesite and other materials that raise the pH of acid soils. Although not commonly considered liming materials, many of the ground silicate rock fertilizers also provide liming functions, as their pH is mainly alkaline. Equation 7.1 shows a simplified chemical reaction of limestone (as calcite, $CaCO_3$) in an acid soil.

Step1:

$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$ (bicarbonate)

Step2:

$Ca(HCO_3)_2 + 2H^+ \rightarrow Ca^{2+} + 2CO_2 + 2H_2O$ (equation 7.1)

Net:

$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$

The quality of agricultural ‘liming materials’ is typically assessed by geologists who look for cement grade limestones. While more than 3-5% MgO is detrimental for the production of cement, Mg is beneficial for agricultural application. Experience has shown that sedimentary limestones and coral limestones are usually more effective for liming purposes than crystalline metamorphosed limestones and marbles. Unless the marbles are very finely ground the agronomic effectiveness of the much finer and more porous sedimentary limestones is usually higher than that of the crystalline limestones. Fine grinding increases the agricultural effectiveness of crystalline Ca-carbonates.

Most of the ground limestone or lime is applied in a powdery form and incorporated into the surface of the soils several days prior to planting. Moisture content and texture of the soils have to be optimal for high nutrient use efficiency and increase in pH. In order to reach deeper levels of the soil, deeper placement of the liming material should be made. This is difficult in most situations. The downward movement of Ca from the application of gypsum is higher than that of calcite, and therefore gypsum has been applied in acid, Ca deficient soils instead of lime or limestone (Ritchey *et al.* 1980; Shainberg *et al.* 1989; Wallace 1994).

Another method of making optimal use of agricultural lime is the application of lime in lime-seed-pellets. Small amounts of lime are coated together with *Rhizobia* species onto wet seeds to create evenly coated lime pellets. These pellets were field-tested and results showed early root development on legumes, as well as increased nodulation of various legume species (Pijnenborg and Lie 1990).

Liming materials should not be applied together with fertilizer containing NH_4^+ or animal manure, because a rise in pH results in the conversion of NH_4^+ to NH_3, as shown in equation 7.2. This newly formed ammonia gas can easily be lost through volatilization.

$$NH_4^+ + OH^- \rightarrow NH_{3\,(g)} + H_2O \qquad \text{(equation 7.2)}$$

Evaluation of liming materials

Traditionally, liming materials are evaluated on their potential agronomic effectiveness according to their neutralizing ability, fineness, and in some cases surface area. The neutralizing ability of liming materials is expressed as the weight percentage calcium carbonate equivalent (CCE) or neutralizing value (NV) and is measured by titration. The fineness is expressed as particle size distribution of ground and sized material. A mix of coarse and fine material is often advantageous to cover both short-term and long-term reactivity. In very finely ground materials, surface area and particle size show strong correlation. The finer the material is ground, the higher the surface area (Conyers *et al*. 1996). Soils laboratories apply standard laboratory procedures to determine the CCE or NV as well as grain size distributions of ground liming materials.

Table 7.5. *Liming materials and their calcium carbonate equivalent (CCE), or relative neutralizing values.*

Material	Common Name	CCE (%)
$CaCO_3$	Calcite (occurring in limestone)	100
$CaMg(CO_3)_2$	Dolomite (mainly occurring in dolostone)	109
CaO	Quicklime or unslaked lime	179
$Ca(OH)_2$	Slaked (hydrated) lime	137

In some countries the combined form of CCE (or NV) and fineness is expressed as 'agricultural index.' The CCE or NV of pure calcite is 100 as these values are defined as the ability of materials to neutralize acidity relative to the neutralizing ability of 100% pure calcite. The CCE-NV of dolomite is higher than that of calcite, at 109% (Table 7.5).

However, the CCE or NV only represents part of the picture. Calcite and dolomite neutralize soil acidity and reduce Al and Mn toxicities at different rates. Dolomite also has a lower solubility and is less reactive than calcite. Few limestones or dolostones are pure and other minerals may be present. Liming materials from coral limestone and young marine near-shore sediments often contain aragonite, which is another form of $CaCO_3$, slightly more soluble than calcite. Aragonite occurs only in relatively young rocks in carbonate muds as very fine aragonite needles, in small spherical forms (0.25 to 2 mm in diameter) in calcareous beach environments (oolites) and in various rock-building organisms, for example gastropod shells. Since aragonite is unstable under ambient conditions, it commonly changes into calcite in a matter of years (Pettijohn 1975). Generally the CCE or NV of liming resources has to be determined separately for each sample.

Another way of assessing the expected performance of liming materials is by measuring surface area (along with chemical composition and solubility). The surface area is expressed as the total surface area of the liming material and does not necessarily correlate with the particle size analysis as internal pores, cracks and irregular surfaces increase the surface area. Only in very finely ground materials do surface area and particle size show strong correlation.

Because liming materials are also used to provide essential nutrients to soils, consideration should be given to the nutrient-supplying power of liming materials with regards to Ca and Mg.

7.4.2 Determining liming requirements

An important preliminary step to determine optimal growing conditions for the proposed crop is to determine the optimal nutrient requirements and optimal pH conditions. In most cases it is not necessary to bring the soil pH up to neutral (pH = 7) to obtain optimal growing conditions. Most crops grow optimally at a soil pH between 5.5 and 7.0 and it is commonly not necessary to raise the pH to neutral.

It is advisable to test the soil characteristics by determining the soil pH, analyze the nutrient availability, and determine the effective cation exchange capacity (ECEC) of these soils. Highly weathered and leached acid soils are commonly associated with small concentrations of exchangeable Al, which is toxic to plants. This toxicity can be overcome by raising the pH to 5.5 or 6. This is the pH at which Al is precipitated and no longer toxic.

Most soils have a natural buffering capacity, which is the ability to resist changes of the pH. The buffer capacity of soils is largely related to the amount and type of clay minerals, organic matter content and the 'base saturation' of the cation exchange sites. Measuring the Al-saturation of the effective cation exchange capacity (ECEC) is crucial in determining the liming requirements (Sanchez 1976). Liming recommendations based on this concept (Kamprath 1970) are derived from the formulae shown in equations 7.3 and 7.4. The factor 1.5 (or 1.65 respectively) has to be raised to 2 or 3 in soils with organic matter contents of more than 7% (Kamprath 1970).

$$\text{Ca/100 g soil} = 1.5 \times \text{cmol (+) Al kg}^{-1} \quad \text{(equation 7.3)}$$

$$\text{Tonnes CaCO}_3 \text{ equivalent ha}^{-1} = 1.65 \times \text{cmol (+) Al kg}^{-1} \quad \text{(equation 7.4)}$$

In large parts of South America, where this concept has been adopted, the rates of liming materials have been considerably reduced without compromising yields, especially in highly weathered acid soils with low cation exchange capacities such as Oxisols and Ultisols (Sanchez 1976). Commonly applied agricultural limestone rates in South and Central America are in the range of 0.5 to 2.5 t ha^{-1} (Sanchez and Salinas 1981), but can reach up to 5 t ha^{-1} in very acid, Al-saturated soils. In Zambia, liming rates of 200 to 500 kg ha^{-1} have been calculated for some acid soils (see Case Study, this Chapter).

In temperate climates, the application of lime by broadcasting is commonly in the range of 2 to12 t ha^{-1} depending on soil type and crop requirements (Barber 1984). In the southern United States the application rates of lime range between 2.2 and 6.7 t ha^{-1} (Adams 1984).

Requirements for liming vary with the texture and CEC of soils. Sandy soils with low organic matter require less liming material than acid clay-rich ('heavy') soils. Soils with 1:1 require less liming materials than soils with 2:1 clays.

7.4.3 Over-liming

Excessive application of liming materials to soils can lead to chlorosis (loss of colour in the plant leaves), a physiological disorder caused by high concentrations of HCO_3^- (bicarbonate) (Mengel and Kirkby 2001). Chlorosis is worsened when the soil is wet and not well aerated because such soils can build-up carbon dioxide and bicarbonate. If this problem goes untreated, chlorosis can lead to the death of the plant. Lime-induced chlorosis is best treated by increasing the aeration of the soil, and by halting the addition of manures or other organic materials to the soils, as they are additional sources of carbon dioxide (Mengel and Kirkby 2001).

Overliming can also cause induced deficiencies of micronutrients, as their availability is largely pH dependent (see Chapter 8). A special case is that of Fe, the availability of which decreases with increasing pH. Sanchez (1976) cites examples of B, Mn, Fe and Zn deficiencies induced by overliming of tropical soils. He concludes that highly weathered tropical soils, high in Fe and Al oxides, should not be limed to pH values above 5.5. Again, texture, type of clay as well as ECEC are factors that must be considered when applying liming material.

7.4.4 Liming in temperate and tropical regions

The positive effects of applying agricultural limestones and other liming materials to acid soils have been known for a long time in temperate, tropical and subtropical countries. In temperate climates liming materials have been used for a long time and are generally applied on acid soils to raise the pH and to provide Ca for plants like alfalfa, clover and soybeans (Cooke 1982; Barber 1984). In Britain, it was calculated that soils lose between 100 to 1000 kg calcium carbonate equivalent each year (Cooke 1982). To replenish these losses and to keep the pH of the soils at optimal ranges for crops that are sensitive to acidity, it is necessary to apply heavy dressings of lime. Dressings between 4 and 20 t ha^{-1} have been reported from British farms (Cooke 1982).

***Figure 7.9**. Application of ground limestone on acid Zambian soils. The test trials depicted here were conducted in the framework of the project: 'FarmLime: Low cost lime for small-scale farming' (Mitchell et al. 2003), picture: courtesy Prof. S. Simukanga.*

In the tropics and subtropics volumes of lime used on soils is generally much lower. It is considered wasteful to lime soils to neutrality (pH 7) because many crops in the tropics are adapted to soil acidity and require only a pH of 5.5 to reduce Al-toxicity (Sanchez 1976). Success stories from the application of 0.5 to 5 t of liming materials on acid soils have been reported by many scientists, among them Sanchez and Salinas (1981), Friesen *et al.* (1982), Goedert (1983), Yamoah *et al.* (1992) and Mitchell *et al.* (2003) from South America, and Africa. Figure 7.9 shows the application of ground limestone in Zambia.

Locally available Ca and Mg-resources such as calcitic and dolomitic marbles, carbonatites, sedimentary marine and lacustrine limestones are relatively common in most countries and many are well suited for small-scale mining and processing.

7.4.5 Liming forests, plantations and pastures

Most research on the use of liming materials in crop production is carried out on annual crops like maize/corn, alfalfa, and soybeans as well as on vegetable crops. However, liming materials are also used for fruit trees, plantation crops, forests and pastures.

Soil nutrient stress has been implicated in the die-back in forests of the Pacific area (Mueller-Dombois 1991). Similarly, a decline of Ca in logged tropical forests in southeast Asia has been documented (Nykvist 1998). In response, liming forest soils has become a widely practiced form of correcting deficiencies in forests in temperate climates (Huettl and Zoettl 1993). In parts of North America, Europe and the Pacific Rim, forest ecosystems have been limed to counter declines in forest growth related to industrial and agricultural air pollution and subsequent nutrient losses (especially Ca and Mg) (Wilmot *et al.* 1996; Likens *et al.* 1996; Huntington 2000). In Central Europe's conifer forests, several other naturally occurring minerals have been tested as soil amendments as well, including kieserite ($MgSO_4 \cdot H_2O$), and/or dolomite (Huettl 1990). In New Zealand, Mg deficiencies have damaged large plantation forests of *Pinus radiata* (Mitchell *et al.* 1999). Here, the application of calcined magnesite (MgO) has resulted in a significant increase in soil exchangeable Mg. Blum *et al.* (2002) report that Ca in Ca-poor forestry systems is taken up from the Ca-phosphate mineral apatite by a tree that has ectomycorrhizal associations.

Magnesium sources are also used in plantations in some tropical and subtropical climates. The Mg-sulphate mineral kieserite as well as dolomite is used as materials to overcome Mg deficiencies in oil palm plantations (Zin *et al.* 2003) and calcined magnesite (MgO) has been used in rubber plantations of Southern China, to overcome widespread Mg deficiencies (Michalk and Zhi-Kai 1992).

Magnesium deficiencies have also been identified in pastures, for example in New Zealand and on infertile acid soils of subtropical China. In the latter case, correction with mineral Mg sources resulted in significant yield increases in subterranean clover (Michalk and Zhi-Kai 1992). In New Zealand, some of the Mg inputs for pasture come from the addition of the Mg-rich silicate rocks dunite and serpentinite, and from superphosphate fertilizers (Chittenden *et al.* 1967).

7.5 Extraction and processing of Ca and Mg

Liming materials have high place values, which means that their value diminishes as the distance from the source increases. Fuel for transport and the availability of transport media play a major role in determining the economic suitability of liming materials. In addition, processing beyond simple grinding can require a great deal of energy, either in the form of fossil fuel or wood.

7.5.1 Extraction

Like other industrial minerals, there are some important technical, economic and environmental considerations for the extraction of limestone/dolostone resources that have to be considered. They include location, form of deposit (bedded/layered or massive, inclined or horizontal), nature and thickness of the interbedded rock materials, as well as chemical and physical characteristics of the liming material. Important for economic recovery is the ‘ease of extraction’. Limestones and dolostones occur in different forms, hard and soft, massive and layered, consolidated and unconsolidated. These characteristics largely determine the mechanical methods of extraction, from blasting to simple excavation with pick and shovel.

For open pit mining it is not only important to understand parameters like volume, grade, intra-stratified layers of non-calcareous materials that has be removed and treated as ‘wastes’, but it is also important to determine the amount of overburden that has to be removed.

7.5.2 Processing of limestones and dolostones

In most countries the processing of the principal liming materials, limestones and dolostones, for agricultural purposes involves only crushing and grinding (Figure 7.10). Fine grinding of limestones, dolostones or magnesite is carried out by standard grinding mills. For agricultural liming materials to be reactive in soils, they need to be ground fine enough that 80-90% of the material can pass through a 100-mesh size 0.15mm sieve. Finely ground liming materials react more rapidly in soils than coarse-grained materials. However, fine grinding is energy intensive and the resultant fine and dusty materials are more difficult to handle by farmers. Furthermore, agricultural liming materials with a spectrum of fine and coarser grain size might be more suitable to ensure immediate and longer-term effectiveness of the material. Consequently, economic evaluations generally determine the optimal fineness (amount of energy used for grinding) *vis-a-vis* their agronomic effectiveness.

Figure 7.10. *Demonstration of the mobile locally produced modified hammer mill, used to grind local limestones in Zambia. (Photo, courtesy of Prof. S. Simukanga).*

In some countries, limestones and dolostones are heated before use. The heating process is called calcination and refers to a thermal reaction process, heating of calcite, dolomite and magnesite bearing rocks to temperatures below their melting point, commonly 900 to 1200^{o}C. During this process the carbonates are converted to oxides of Ca and Mg with the release of CO_2 to the atmosphere. This energy intensive process is used to upgrade the calcium carbonate equivalent (CCE) or neutralizing value (NV) of limestones and dolomites. The main products of these upgrading processes are quicklime and hydrated (slaked) lime (see below).

For the effective and efficient use of energy resources in the calcination process it is critical to find resources that minimize environmentally harm, and to determine low-cost, adapted beneficiation techniques (drying, crushing, grinding, physical concentration) suitable for the specific site. Energy consideration for grinding and calcining are of major environmental concern. More energy efficient kilns have been developed in the last few decades, which can reduce wood consumption. For example, Spiropoulous (1991) reported improved effectiveness of newly designed vertical-shaft kilns that are adapted to suit the specific conditions in Malawi.

Case study: low cost liming of acid soils in Zambia

A successful example of collaborative efforts between geologists, soil scientists and farmers is that of the collaboration between the British Geological Survey, the University of Zambia, the Geological Survey Department of Zambia and farmers from parts of Zambia in the project ‘FarmLime: Low cost lime for small-scale farming’ (Mitchell *et al.* 2003). This project focused on finding, processing and using affordable sources of agricultural limestone or dolomitic limestone to reverse crop yield decline on acids soils in parts of Zambia. The project developed an uncomplicated and robust grinding mill (a modified hammer mill) (Figure 7. 10) and carried out crop trials at demonstration sites to show the agronomic benefits of using agricultural limestone on acid soils. They also demonstrated the significant economic basis for successful small-scale agricultural lime production operations.

The application rates of ground limestone, based on Al-saturation and neutralizing values, were calculated as 200 kg and 500 kg ha^{-1} for two acid soils in Zambia. The actual costs for a tonne of agricultural limestone ranged from US$ 20 to 30. The value cost ratio (value of additional crop produced compared to the costs of agricultural limestone) ranged from 4.2 to 18 on very acid soils (pH< 4.5) to 2.5 to 11 for acid soils (pH <5). These economic benefits are well above the value to cost ratio (VCR) of 2, commonly considered to be met to make farmers believe of the benefits of a new agricultural technology. The project could show not only the increase in crop production for the smallholder farmers but also economic benefits (Mitchell *et al.* 2003).

Quicklime

Quicklime (CaO), also known as unslaked lime or burned lime, is produced by heating (calcining) calcite to 900-1200°C, resulting in CaO and CO_2. The carbon dioxide is released to the atmosphere, as shown in equation 7.5.

$$CaCO_3 \xrightarrow{900\text{-}1200^{o}C} CaO + CO_2 \qquad \text{(equation 7.5)}$$

This highly caustic powdery material is unpleasant and difficult to handle. It is irritating to both human skin and plant roots and reacts with the soil almost immediately. It is therefore not appropriate to place quicklime in the soil in direct contact with the plant's rooting system. Consequently, it is normally treated with water (to become slaked lime) before use. Caution should also be taken with the slaking process as the reaction from CaO to $Ca(OH)_2$ is exothermic (equation 7.6) and can easily 'burn' exposed skin. The calcium carbonate equivalent (CCE) or neutralizing value of quicklime is 179.

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{Energy} \qquad \text{(equation 7.6)}$$

Slaked lime ($Ca(OH)_2$)

Slaked lime (or hydrated lime) is much safer to use than quicklime. Although it also reacts in soils very quickly, its application in the rhizosphere is less harmful than quicklime. It has a CCE of neutralizing value of 136, higher than the CCE of calcite or dolomite but not as high a CCE as quicklime.

7.6 Alternative sources of calcium and magnesium

Phosphate rocks and single superphosphates (SSP) have been shown to be weak liming materials (Hellums *et al.* 1989; Sinclair *et al.* 1993). Both, phosphate rocks and single superphosphates reduce the Al toxicity in soils. Field studies in South America have shown that the application of SSP decreases the Al saturation in the soils. The calcium sulphate (gypsum) component in SSP readily moves down the soil profile and complexes the aluminum (Annual Reports 1978 and 1979 from the Cerrados Agricultural Research Center in Planaltina, Brazil, quoted in Munson 1982). Similar results were achieved by using phospho-gypsum, which is more soluble than naturally occurring gypsum (Keren and Shainberg 1981; Yu *et al.* 2003). Details of gypsum geology and the use of gypsum in agriculture are described in Chapter 6 (Sulphur).

Other alternative sources of Mg and Ca are quarry fines, particularly those of carbonate rocks, such as limestone or dolostone operations. Other Ca and Mg quarry fines can be found in mining operations of mafic-ultramafic rocks (e.g. dimension stones 'black granite'), kimberlites and serpentinites. Unfortunately kimberlite fines (from tailings) are difficult to obtain as they are the source rocks for the diamond mining industry, and most companies are not willing to give up their fines in case they still contain diamonds.

Voluminous K, Ca and Mg silicate resources as liming materils and muli-nutrient resources are found in the form of volcanic ultramafic rocks in rift valley environments in eastern and central Africa (Rogers *et al.* 1998), in volcanic fields in NE China (Zhang *et al.* 1995), and in the Cretaceous volcanic field of the Mata da Corda, SW of the Precambrian San Francisco craton, Brazil (Gibson *et al.* 1995).

Volcanic rock types like lamproites and kamafugites are not only rich in K (and sometimes P), but also rich in Ca and Mg. These SiO_2 undersaturated, ultrapotassic and ultramafic rocks can occur as large eruptive volcanic tuff layers, like in Brazil. Here, the volcanic tuffs and flows of the Mata da Corda cover an area of 4,500 km^2 (Gibson *et al.* 1995). The easily mineable, friable tuffs of ultrapotassic and ultramafic materials contain large amounts of relatively easily weathereable Mg and Ca sources (for example from olivine and leucite/calsilite).

The pH of this material is commonly above 8. The concentration of total Al is low and the available Al concentration at the pH of >5.5 is negligible. Although these rock materials are comparatively low in immediately available Ca and Mg, their nutrient content is largely associated with minerals that break down fast under atmospheric conditions, e.g. olivine. Their agronomic potential should be tested on K, Ca and Mg responsive crops and tree species, e.g. plantation crops, in areas close to the existing geological resources. Experiences from Brazil indicate that this is an effective whole rock 'fertilizer' suitable for applications on depleted laterite soils (Leonardos *et al.* 1987; Theodoro and Leonardos 2006), see Chapter 9.

Serpentinite and asbestos-bearing rocks contain high concentrations of Ca and Mg, but they can also contain elevated concentrations of Ni and Cr, and can therefore only be used in a diluted form. Serpentinite fines are used in New Zealand as a source of Mg for crops and as additives to superphosphates (Chittenden *et al.* 1967).

Lime kiln dust and under-calcined waste rocks in lime operations can be good sources of Ca and Mg. Another waste material, discarded refractory bricks can contain up to 50-58% MgO. The sugar industry produces residues rich in Mg and Ca. Sugar cane companies use lime to clean impurities out of their raw juice, and this mixture is generally discarded, although it is high in both minerals and organic residues.

Dust and fines from cement stacks contain a mixture of Ca and K rich compounds with a very alkaline pH in the range of 11-12. This very fine material with a high surface area is highly reactive. Due to its fineness and caustic characteristics the material is difficult to handle. Blast furnace slags and fly ash are also rich in Ca but require proper screening for heavy metals, B and Se before being applied on acid soils. Wood ash also has not only excellent liming properties but can also provide other nutrients, for example, modest amounts of P and K (Ohno and Erich 1990).

Another Ca-resource is Ca-silicate slag, a by-product from the iron industry. This 'basic slag' has been used for a long period of time as P-fertilizer and liming material for grassland on acid soils in many countries, including New Zealand (Lynch and Davies 1964), Germany (Fleischel 1972) and Brazil (Sanchez and Uehara 1980). Basic slag has proved effective in forest soils as a liming material and fertilizer, providing P, Ca and Mg (Vandre *et al.* 1991; Belkacem *et al.* 1992). The application of Ca-Si rich slags has resulted in increased yields of sugarcane (Ayres 1966; Anderson *et al.* 1991).

Termite mounds, known for their naturally enhanced soil fertility, are also used as liming material. They are used in some tropical countries as soil amendments to increase the pH, as well as provide additional organic matter (Watson 1977; Moormann and Kang 1978; Nyamapfene 1986).

Chapter 8

Micronutrients

The eight essential plant micronutrients are boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn). These eight elements are essential for the growth and reproduction of plants and many of them are required in animal and human nutrition as well. In addition to the eight 'essential' micronutrients, five 'beneficial' micronutrients (cobalt, selenium, silicon, sodium and vanadium) act as plant nutrients for some plants but not all, or are beneficial in the sense of adding mainly physical strength to plants (silicon).

The term micronutrients is used mainly by soil scientists and plant nutritionists. With the exception of iron (Fe) this term is largely synonymous with the term trace elements used by geochemists. Micronutrients are so-called because they are used by plants, animals and humans in much smaller amounts than macronutrients. Micronutrients are taken up by plants in 'trace' amounts, commonly in the parts per million range and it is the relatively small plant requirement and uptake of these elements that characterize them as trace or 'micro'-nutrients and not their concentration in soils.

Except for borates, most micronutrients are extracted from metallic minerals and ores. The supply of micronutrient resources is characterized by huge resource capacities, generally in the range of millions of tonnes, against very small soil requirements, in kg ha^{-1}, and relatively small and specialized markets. Only a few micronutrient sources are mined for the sole purpose of extracting a specific element. Most of the micronutrients are by-products from mining operations and metallurgical processing for other minerals for other purposes, especially metals.

The study of micronutrients brings together the interests of professionals from many different disciplines: exploration geologists, geochemists, medical scientists, epidemiologists, plant and animal nutritionist, soil scientists, and agrogeologists. Exploration geologists and geochemists tend to see both plants and element concentrations in certain plants as tools to find mineral deposits (Hawkes and Webb 1962; Levinson 1974). Certain 'indicator species' and high concentrations of trace elements in soils serve as indicators of possible ore deposits below the soil surface. Epidemiologists, medical scientists and 'medical geologists' (Bowie and Webb 1980; Appleton *et al.* 1996; Skinner and Berger 2003; Selinus *et al.* 2005) study soils to better understand the relationship between human health and soils, and specifically the influence of trace elements on human health (Oliver 1997). Plant nutritionists and plant scientists see plants as beneficiaries or recipients of micronutrients and are interested in providing ‘sufficient’ concentrations of available micronutrients to support plant growth and reproduction. Concentrations should neither be insufficient (deficient) nor over-supplied (toxic) (Figure 8.1).

8.1 The role of micronutrients in plants

Research conducted over the last few decades has provided us with an increased understanding of the role of micronutrients for plant and animal health (Donald and Prescott 1975; Mortvedt *et al.* 1991; Bennett 1993; Mengel and Kirkby 2001; Kabata-Pendias 2001; Marschner 2002; McDowell 2003). Many nutrients are directly involved in some areas of plant metabolism and reproduction. Plants need specific elements for nutrition and will not complete their life cycle without them. The function of these essential nutrients cannot be replaced by another nutrient. Research has determined that B, Cl, Cu, Fe, Mn, Mo, Ni and Zn are essential to plant growth and reproduction. Other elements, like Co, Si, Se, Na and V improve the growth of certain plants but not of all plants. Other elements are not essential to plants, but are important for animal growth, for example small amounts of Cr, F, I and Sn.

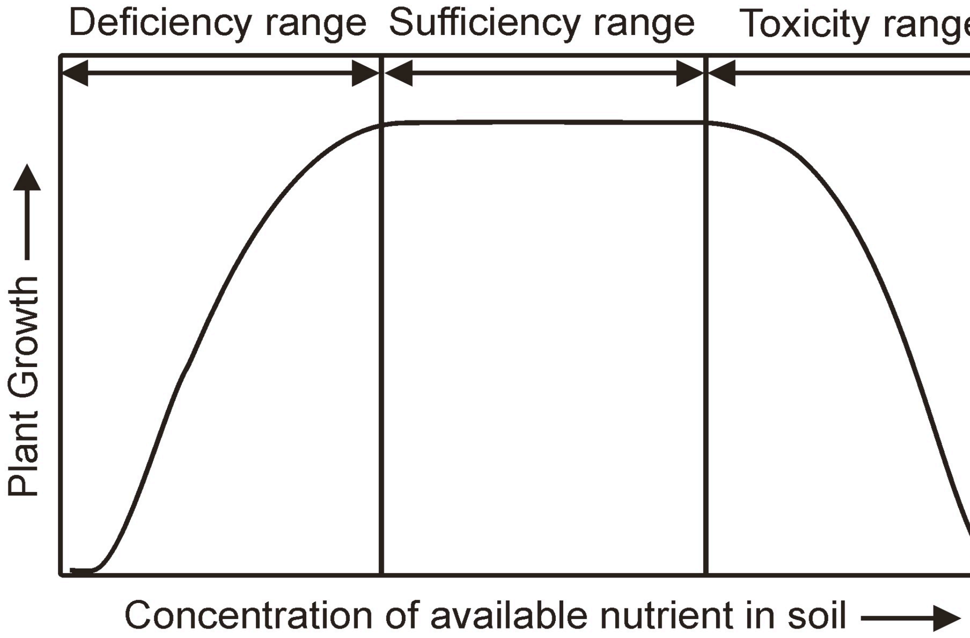


Figure 8.1*. Relationship between micronutrient availability and plant growth: Range of deficiency, sufficiency and toxicity.*

Micronutrients play key roles in a number of enzyme systems, acting as catalysts to promote organic-organic and organic-inorganic reactions. The efficiency of many enzymes is dependent on the availability of certain trace elements and on environmental conditions such as suitable pH, temperature, moisture and other factors. Micronutrients also play an important role in the symbiotic fixation of nitrogen. In addition to the availability of an inoculum, for example a bacterium from the *Rhizobium* family, leguminous plants require the nutrients P, K, Ca and S, as well as small amounts of Co, Mo and Fe in order to 'fix' nitrogen. In addition, N_2-fixing efficiency of leguminous plants is dependent on specific environmental conditions, for example, suitable soil pH, adequate O_2 concentrations and optimum soil temperatures.

Plants require sufficient nutrients to grow and they show characteristic deficiency symptoms when major nutrients and micronutrients are undersupplied. But while the liberal application of the major nutrients such as N, P, K, S, Ca and Mg rarely causes oversupply and toxicity for plants, micronutrients can become toxic when available above certain threshold concentrations. It is thus important to determine the 'window' of concentrations between deficiencies and toxicities, the sufficiency concentration of nutrients. While this window of sufficiency can be wide for some elements it is rather narrow for others (Table 8.1).

Under natural conditions micronutrients are supplied to plants from soil solution. Plants take up micronutrients from the soil solution in different forms, most of them as cations but some, for example Mo and Cl, as anions. Boron is largely taken up by plants in the undissociated form of boric acid. Table 8.2 shows the form in which micronutrients are taken up by plants, their functions, and some common minerals with high concentrations of trace elements. Micronutrients can also be taken up in the form of chelates. The term chelates is derived from a Greek word meaning 'claw'. Chelates are soluble organic compounds that form complexes with various metals, such as Fe, Zn, Cu and Mn, and increase their solubility and uptake by the plant roots.

Trace uptake occurs despite the abundance of these nutrients in the soil. Iron in particular can be quite abundant in soil environments, often occurring in the percent range. Availability is complicated by the fact that the solubility of many micronutrients is controlled by pH, and only their soluble form is available for uptake by plants. Iron becomes insoluble in soils with high pH and iron chlorosis often occurs, even in soils with abundant iron. Furthermore, overabundance of these nutrients in the soil can be toxic to plants. Plants vary in their sensitivity to micronutrient availability. Some plants have low sensitivities (are tolerant) to under-supply (deficiencies) of micronutrients, while others do not. Table 8.3 outlines sensitivities of various plants to micronutrient deficiencies. In order to prevent problems related to deficiencies or toxicities in plant growth it is important to test soils for availability of micronutrients.

Table 8.1. *Generalized micronutrient concentrations in plants, and symptoms of deficiencies and toxicities, in alphabetical order (after Bennett 1993).*

Micro-nutrient	Critical conc. (mg kg^{-1})	Sufficiency range (mg kg^{-1})	Toxicity conc. (mg kg^{-1})	Deficiency symptoms
Boron (B)	< 10	10-100	> 100	Interveinal chlorosis, often reddish; short internodes; leaf resetting; deformation of flowers; cork-like tissue; heart-rot in beets.
Copper (Cu)	< 6	8-20	>20	Whitening of leaf tips and twisting of leaves; shortening of internode intervals; bluish-green tint; white tips of onions.
Chlorine (Cl) (%)	<0.2%	0.2-2.0%	> 2.0%	Stubby roots; plant wilt; chlorosis of new leaves.
Iron (Fe)	< 50	50-250	Generally non-toxic to plants; in rice: > 300	Interveinal chlorosis. Young leaves turn yellow and later virtually white, old leaves remain green.
Manganese (Mn)	10-20	20-300	> 300	Interveinal chlorosis - beginning at leaf margin.
Molybdenum (Mo)	< 0.5	> 0.5- 5	Generally non-toxic to plants	Early symptoms of Mo deficiencies resemble N and S deficiencies; yellow spot of citrus halves; whiptail of cauliflower.
Nickel (Ni)	Not available	Not available	Not available	Germination of seeds depressed; intraveinal chlorosis in wheat, barley, and oats.
Zinc (Zn)	15-20	20-100	> 400	Interveinal chlorosis; shortened internodes of stems; reduced size (little leaf) and rosetting of leaves.

Table 8.2. *Micronutrient uptake, functional role and natural mineral form of occurrences.*

Micro-nutrient	Uptake form	Functional role in plants	Main nutrient supplying mineral
Boron (B)	$B(OH)_3$	Cell division, pollination, cell wall formation, sugar translocation.	Borax, Colemanite, Ulexite, Kernite, Tourmaline; marine clays.
Chlorine (Cl)	Cl^-	Activates enzyme system for production of O_2 in photosynthesis.	Halite, Sylvite.
Copper (Cu)	Cu^{2+}	Enzyme formation, metabolism and N-fixation.	Chalcopyrite, Chalcocite, Bornite, Malachite, Azurite, Cuprite.
Iron (Fe)	Fe^{2+}	Constituent of chloroplasts essential for photosynthesis, constituent of leghaemoglobin for N-fixation.	Magnetite, Hematite, Goethite, Siderite, Pyrite.
Manganese (Mn)	Mn^{2+}	Controls various oxidation-reduction systems, formation of O_2 in photosynthesis.	Pyrolusite, Psilomelan.
Molybdenum (Mo)	MoO_4^{2-}	Nitrogen fixation, toxicity antidote.	Molybdenite.
Nickel (Ni)	Ni^{2+}	Essential for enzyme urease activation; needed for germination of seeds	In olivine and serpentine, Ni-sulphides (e.g. pentlandite).
Zinc (Zn)	Zn^{2+}	Enzymes, growth hormones, starch and seed formation.	Sphalerite

Table 8.3. *Sensitivity of plants to micronutrient deficiencies (from various sources).*

Micro-nutrient	High sensitivity	Medium sensitivity	Low sensitivity
Boron	Asparagus, beet, *Brassica* plants, celery, spinach, sunflower, alfalfa, clover, sweet clover, oats, apple, grapes, pear.	Carrot, lettuce, onion, sweet potato, cotton, cherry, olive, peach, pear, raspberry, strawberry.	Beans, maize/corn, cucumber, peas, white potato, buckwheat, cereals, grasses, sorghum, soybean, citrus, blueberry.
Copper	Beet carrot, maize/corn, rice, carrots, lettuce, onion, spinach, alfalfa, most grains and grasses (including oats and wheat), sunflower, most large fruits, and citrus.	*Brassica* plants, celery, cucumber, parsnip, maize/corn, clover, cotton, sorghum, blueberry, strawberry.	Beans, potato, rye, soybean, rapeseed.
Iron	Fruit trees, citrus, grapes, pineapple.	Asparagus, cabbage, maize/corn, alfalfa, oat.	Wheat.
Manganese	Beet, bean, cucumber, lettuce, onion, pea, potato, spinach, radish, oats, sorghum, soybean, Sudan grass, wheat, apple, cherry, citrus, grapes, peach, raspberry, strawberry.	Broccoli, cabbage, carrot, cauliflower, celery, maize/corn, cucumber, tomato, turnip, alfalfa, barley, clover, rice.	Asparagus, parsnip, field maize/corn, most grasses, rye, blueberry.
Molybdenum	*Brassica* plants (cabbage and relatives), beet, lettuce, onion, spinach, tomato, sweet clover, citrus.	Bean, pea, alfalfa, oat, soybean.	Carrot, celery, maize/corn, potato, cotton, wheat and most grains and grasses, sorghum, most fruit.
Nickel	Oats, soybeans, redbeet, Swiss chard	Spring wheat, barley, maize/corn	Serpentinophytes, Ni-hyper-accumulator plants, like *Alyssum*.
Zinc	Bean, maize/corn, onion, tomato, cotton, flax, hops, sorghum, Sudan grass, soybean, most large fruits, incl. citrus.	Beet, potato, alfalfa, barley, clover, rice.	Asparagus, carrot, pea, most grasses, oat, rye, wheat.

8.2 Micronutrients in soil

The primary sources of micronutrients in soils are minerals and rocks. Chemical, physical and biological weathering processes are the principal routes of nutrient liberation from rocks and minerals. The desired sink and recipient of the micronutrients are roots of plants. But before the nutrients released from the mineral sources arrive at the root sink, the nutrients have to compete with other sinks. The availability of micronutrients to plants is thus a function of complex interactions of liberation from minerals and rocks, the nutrient form and mobility of the micronutrient in solution and the competing soil constituent sinks on which the nutrient can be retained. The forms and interactions of the liberated nutrient with competing sinks in the soil largely determine the availability of the nutrients in the soil solution. When analyzing micronutrients in soils it is less important to analyze the total concentration of micronutrients than it is to analyze the 'residual' nutrient concentrations in the soil solution that are available for plant uptake.

The factors that influence the availability and mobility of micronutrients in soil solution are:

- Soil type, soil pH,
- Form of liberated nutrient element in solution (speciation),
- Type, duration, and intensity of weathering activity,
- Oxidation state of trace element (e.g. Fe, Mn),
- Form and concentration of complexing ligands, such as various anions and low and high molecular weight humic substances in the soil organic matter,
- Distribution of adsorption sinks, like organic matter, hydrous Fe and Al oxides and clay minerals,
- Environmental conditions such as soil temperature and soil moisture.

Most forms of trace elements are more available under low pH conditions (e.g. Zn, Cu, Mn, and Fe), other micronutrient ions, such as the anion MoO_4^{2-}, are more available under high soil pH conditions.

Micronutrient sources are predominantly derived from minerals from igneous, metamorphic or sedimentary rocks, all of which have differing chemical and mineralogical characteristics, and hence micronutrient concentrations. Commonly, the geochemical make-up of rocks provides a good geochemical signature. This geochemical fingerprint can often be seen in young soils that developed directly from rocks and minerals. Thus, from analyses of soil trace element distribution it is often possible to gain some information of the chemistry and composition of concealed bedrocks. This is obviously an important tool for exploration geochemists.

Besides the origin and mineralogical make-up of rocks, the stability of minerals in these rocks in the weathering environment, principally in low pressure – low temperature environments, influences the release of micronutrients from rocks and minerals. The simplified sequence of changing chemical and mineralogical composition of igneous rocks (Bowen's reaction series) and the related Goldich sequence (Goldich 1938) both provide a general outline of the stability of minerals and rocks.

The element behaviour in the weathering environment is strongly related to mineralogical and chemical characteristics like ionic radius, ionic charge, bond strength and 'affinity of elements' for particular environments, such as siderophile, chalcophile, lithophile and atmophile, as has been described by one of the eminent founders of modern geochemisty, Victor Moritz Goldschmidt (1954). In many minerals, ions are substituted by related ions and many of the substituting ions are micronutrient ions.

The two parameters ionic radius and ionic charge play a major role in ion substitution into common rock-forming minerals. Micronutrients incorporate preferentially into the lattice of the common rock-forming minerals when the ionic radius is similar and the ionic charge is the same or varies by no more than one. For example, the ionic size of the divalent micronutrients Cu (0.77 Å) and Zn (0.74 Å) are similar to that of the divalent Mg (0.78 Å) and Fe^{2+} (0.83 Å). During the crystallization of minerals at elevated temperatures some elements, such as Cu or Zn have been accommodated in these sites in proxy of Mg or Fe. Consequently, ferromagnesian rich minerals and rocks can contain higher concentrations of these elements in their lattice than Fe and Mg poor minerals and rocks.

Examples of enhanced concentrations of Cu are mafic rocks, such as basalts. In contrast, igneous rocks that contain only small amounts of ferromagnesian minerals and high amounts of silica, for example rhyolites and pumice contain only low concentrations of Cu, and consequently, soils developed on these rock types are known to be very low or deficient in this element. Generally, soils developed over basaltic parent materials contain higher concentrations of Ca, Mg, Fe, Cu and Zn than soils developed from granitic parent materials. In contrast, soils over felsic Si-rich parent materials, for example granite or rhyolites, are commonly low in Cu and Co.

Soils over sediments have differing trace element signatures, depending on the type of sediments (e.g. limestone, shale, sandstone), texture (e.g. coarse sandstones versus fine-grained shales), differing pH (e.g. alkaline limestones versus acidic quartz-sandstones), and differing cation exchange capacities. Sediments that normally contain large pools of trace elements include shales, especially black shales or bituminous shales. The concentrations of Cu, Zn and Mo in soils found overlying or developed from black shales are commonly more than two to three times the average crustal concentration.

Soil-forming processes such as leaching-precipitation, pH changes, reduction-oxidation, as well as biologically mediated processes and sorption processes on charged surfaces of clays, hydrous Fe and Al oxides and organic matter can severely influence the availability of micronutrients. The micronutrient concentration in soils, inherited from the bedrocks, therefore depends largely upon the kind, duration and intensity of weathering and other processes related to soil profile development.

In regions of the world where weathering activities are not very intensive, for example in areas with less than 600–700 mm precipitation per year, a close relationship can be found between composition of bedrock and overlying non-transported soils. The concentrations of trace elements in soils are reflections of the chemical composition, especially the trace element concentrations of the bedrocks beneath them. An example for the strong correlation between soils and bedrock is illustrated in Zimbabwe. Nyamapfene (1991) describes the dominating role of the parent material on the development of Zimbabwean soils: “In Zimbabwe, it is generally accepted that parent material influences the development of soils and their properties more than any other factors”. Nyamapfene (1991) illustrates with maps and descriptions the relationship between soils and underlying rock formations.

Table 8.4. *Rock types with elevated potentially beneficial or detrimental trace element/ micronutrient concentrations (Levinson 1974, and other sources).*

Rock Type	**Trace Elements/micronutrients**
Ultramafic igneous rocks	Cr, Co, Ni, Fe, Mn
Basalt (mafic)	Cu, Zn, Mn, Fe, Co, Ni, V
Granite (felsic)	Ba, Li, W, Rb, Mo, Cu, Zn, Cl
Carbonatite	Rare earth elements (REE), Nb, P, F, V
Black shale	Cu, Pb, Zn, Cd, U, Au, Se, Ni, Mo, V,Fe, B, and others
Red shale/Sandstone	U, V, Se, As, Mo, Pb, Cu

However, even in regions of the world that are subjected to intensive and long lasting chemical weathering, some trace elements can be found that reflect the chemistry of the original parent materials underneath. Trace elements in thick tropical soils in Nigeria for example have shown to be good ‘bedrock reflectors’

(Matheis 1983). This geochemical 'fingerprinting', even through a thick soil cover, demonstrates the importance of trace elements/micronutrients as exploration guides for underlying rock types. Rock types with commonly elevated trace element/ micronutrient concentrations are shown in Table 8.4.

In recent years, inputs from industrial and farming operations have added more micronutrients to soils. In conventional farming operations, heavy manure application, irrigation water, and spraying with herbicides and fungicides can increase the availability of micronutrients to a stage that care must be taken not to induce micronutrient toxicities. For example, Cu concentrations in soils have increased due to the application of fungicides, which contain Cu. Copper-rich fungicides are commonly applied in orchards, vineyards and fruit-growing operations and are used to control algal growth. The surface soils of certain French vineyards, where the Cu-sulphate rich fungicide 'Bordeaux mixture' was applied on grapes for several decades, show Cu concentrations between 100 and 1500 mg kg^{-1} (Besnard *et al*. 1999) against a soil average of 20 mg kg^{-1} (Ure and Berrow 1982).

Many pig-feeds are Cu-enriched, because Cu stimulates weight gain in pigs. As a result, the manure from pigs that are fed Cu-enriched diets is enriched in Cu. Repeated applications of this pig manure on land can cause toxic build-up of Cu in the soil and it is not a recommended treatment over an extended period of time unless the crops cultivated on these soils have high Cu requirements. Soils treated with certain sewage sludges can also get enriched in Cu. Copper accumulations in soil up to 1170 mg kg^{-1} have been reported after the application of sewage sludge (Crompton 1998).

8.2.1 Geographical distribution of micronutrients

The distribution of micronutrients in soils, as a reflection of rocks and minerals, has been described on various scales. Chesworth (1991) compiled the distribution of six micronutrients in rocks on a global scale using the plate tectonic model. He describes the order-of-magnitude distribution of micronutrients in crustal and mantle segments, such as mantle, continental interior, continental rift, ocean basin, ocean ridges and active continental margins.

On a regional scale, Kubota (1980), Shacklette and Boerngen (1984), provide generalized maps of nutrient deficiencies in soils of the United States. Donald and Prescott (1975) provided one of the first modern accounts of micronutrients in Australian soils. The Geological Survey of Uganda (1973) published geochemical maps that outlined the distribution of trace elements in stream sediments and some soils. In the UK, geochemical maps on a scale of 1:250,000 have been published by the Institute of Geological Sciences of Great Britain (Plant and Moore 1979; McGrath and Loveland 1992).

Similar maps and atlases have been produced and published by the German Geological Survey – BGS (Fauth *et al.* 1985) and also by the Government of Japan (http://www.aist.go.jp/RIODB/geochemmap/zenkoku/zenkoku.htm).

A large pool of potentially useful information has been collected and analyzed for their 'trace element' contents by exploration geologists and geochemists for the purpose of finding and delineating metal deposits. Thousands, if not tens of thousands of trace element data, compiled by exploration geochemists, are stored and largely available at national geological surveys. However, these data are rarely shared between the geochemists and the soil scientists. Soil scientists have yet to integrate much of this information into soil maps.

8.3 Essential micronutrients

The next section will focus on the main micronutrients essential for plant growth, in alphabetical order, B, Cl, Cu, Fe, Mn, Mo, the newly identified essential micronutrient, Ni, and Zn as well as two micronutrients, Co and Se, not directly essential for plants but important in symbiotic N fixation and for nutrition of animals. The role of micronutrients in plants, deficiencies and toxicities and their symptoms in plants, as well as their distribution in rocks and soils and sources for plant and animal nutrition will be discussed in the following sections. An account on the essential micronutrients will be followed by brief summaries of the 'beneficial' nutrients Co, Na, Se, Si, and V.

Boron

The role of boron in plants

Boron (B) is not essential to animals but is essential to plant life. Boron is an important component of cell division, and it is strongly bound in cell wall constituents. It is also crucial in phenol metabolism, and thus lignification. Boron plays a significant role in translocation of sugars. It also plays a part in the differentiation of vascular elements and the coordination of the growth process. Boron is essential for the development and growth of pollen.

Boron is unique among the essential elements as it is taken up from soil solution mainly as undissociated boric acid, H_3BO_3. It is relatively immobile within the plants. In general, dicots require more B than monocots (Hu and Brown 1997). Also, it seems that mycorrhizal plants have higher requirements for B than non-mycorrhizal plants (Lambert *et al.* 1980).

Crops that respond well to higher concentrations of B in the soil are alfalfa, rutabaga (*Brassica rutabaga*), sugar beet, celery, cauliflower, broccoli and apples. Typical B deficiency symptoms in brassica crops, e.g. cauliflower, are 'brown heart' and 'hollow stem'. B deficiencies in alfalafa manifests itself as 'bronzing' of leaves, while the lower, older leaves stay green. Boron deficiencies produce abnormally thick stems and cause the growing points to die. Grain legume crops such as chickpea (*Cicer arietum*) and mustard (*Brassica campestris*), commonly farmed in South Asia are particularly sensitive to B deficiencies. Deficiency symptoms in chickpeas are tip yellowing and 'little leaf', a progressive reduction of sizes of younger leaves and the dying of terminal buds. The above mentioned grain legumes show significant yield increases with the addition of as little as 0.5 kg B ha^{-1} (Srivastara *et al.* 2005).

In legumes, there is severe restriction of nodule development with B deficiencies (Bonilla *et al.* 2002). Symptoms of B deficiency are different from crop to crop, the most common ones are: dieback of growing tips, malformation of leaves and heart rot (sugar beet, eucalyptus and pine), cracking of stems (celery and Chinese cabbage), reduced seed set (sunflower, coffee, oilseed, rape, olive and clover), fruit fall (cotton and apple) and deformed fruits (apple, grape and olives) (Gupta 1979).

Crops that are sensitive to high levels of B (toxicity) in the soil are beans, oats, barley and wheat. Planting beans after a rutabaga crop can cause problems for the beans because rutabaga requires additional B fertilization, whereas beans do not grow well in high-B soils. Typical B requirements by various crops are shown in Table 8.5.

Table 8.5. *Typical B requirements of selected crops (from various sources).*

Wheat	Clover	Carrots	Sugar beets	Sunflowers and vines
5-10 mg kg^{-1}	25-60 mg kg^{-1}	30-80 mg kg^{-1}	40-100 mg kg^{-1}	HIGH

Boron in soils

Boron deficiencies in soils are quite widespread. Soils inherently low in B concentrations are sandy dry soils derived from acid igneous rocks, such as granites, and metamorphic rocks, e.g. gneisses. Figure 8.2 shows the area extent of B deficiency in global soils.

The availability of B is largely controlled by the B concentration in soil solution, which is a function of parent material, as well as soil texture, moisture and temperature, pH and the presence of organic matter. The average concentration of B in the earth's crust is 11 mg kg^{-1}. The B concentration in soils varies strongly, ranging from 1 to 1000 mg kg^{-1}. The mean overall B concentration in soils is 38.3 mg kg^{-1} (Ure and Berrow 1982). However, the B concentrations in soils developed from weathering rocks vary largely. Soils on sedimentary rocks with high marine clay and mica (phyllosilicate) contents as well as rocks of mafic compositions such as basalts generally have higher B concentrations than soils developed from felsic rocks like granite or from sandstones. Studies of the geographic distribution of B in

Zheng *et al.* (1983) showed that soils in China derived from granite or from gneisses were particularly low in B, while soils developed on marine sediments, for example in the Himalayan region, contain high concentrations of B. Boron is strongly adsorbed to organic matter and consequently, soils rich in organic matter contain relatively high concentrations of B. Boron concentrations in coal ashes commonly reach concentrations of 100 to 200 mg kg^{-1}.

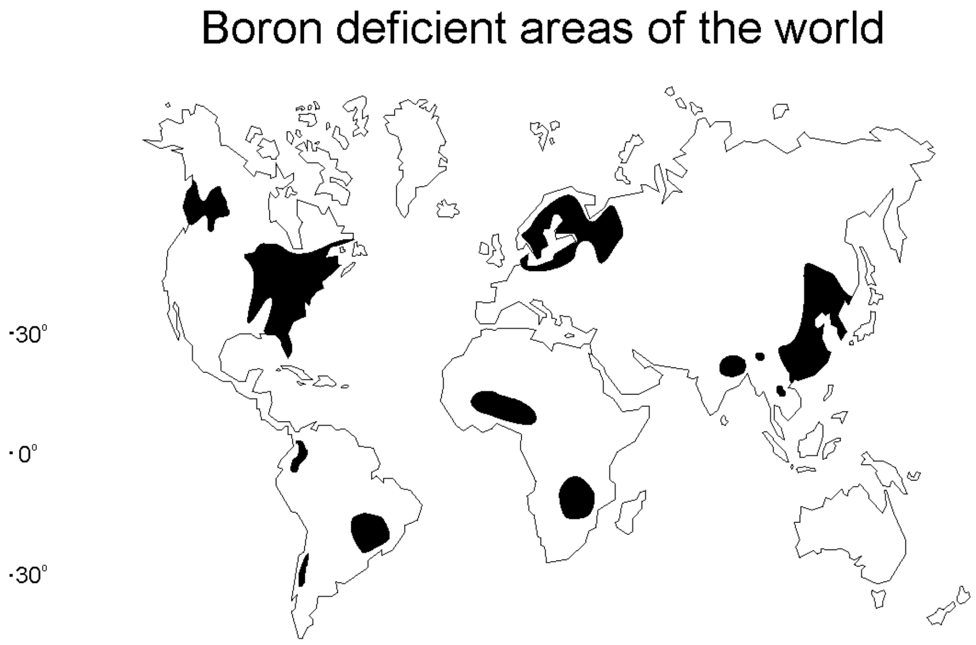


Figure 8.2. *Areas of boron deficiency in the world (modified after Shorrocks 1997).*

Boron concentrations in soils are commonly low in highly weathered environments due to heavy leaching of B-containing clays and organic matter. Sandy soils are particularly low with 2-6 mg B kg^{-1} (Adriano 1986). Other B deficient soils are highly weathered soils and podzols (Shorrocks 1997). Highest concentrations of B occur in areas with arid and semi-arid climates.

Hot water extraction of B from soil is the most common soil test. Deficiency can be expected when the critical hot water extractable B concentration in soils is < 0.5 mg L^{-1} (Havlin *et al.* 1999). B toxicity can be expected when hot water extractable B is above 4-5 mg L^{-1}. The availability of B decreases with increasing soil solution pH. In soils with a pH above 6.5, adsorption increases (Keren and Bingham 1985) and B is precipitated as relatively insoluble Ca-borate (McBride 1994). Boron is strongly retained by hydrous Fe and Al oxides. Boron adsorption on Al oxides and Fe oxides peaks at a pH around 7 and 8 respectively (Goldberg 1993). As B uptake is reduced in alkaline soils, liming of acid soils can induce B deficiency. Boron toxicities in plants are commonly found in alkaline soils of semi-arid areas, for example in South Australia (Cartwright *et al.* 1984).

Boron deficiencies have been reported from most parts of the world, with deficiencies mainly reported from various legumes, as well as sugar beet (*Beta vulgaris*), crops of the *Brassica* family (oilseed rape, cauliflower, cabbage, turnips, swedes), as well as carrots, sunflowers, apples and grapes (*Vitis vinifera*), coffee and fruit trees (Shorrocks 1997). Monocots are less able to take up B than dicots. Among the mocots, most *Gramminae* have low B requirements except onion, and coconut (*Cocos nucifera*) and oil palm (*Elaieis guineensis*).

Boron toxicities are predominantly reported from soils developed from marine argillaceous sediments and from anthropogenically contaminated soils. The most sensitive crops to B toxicities are peach, grapes, kidney beans and figs (Mengel and Kirkby 2001). Sources of B contamination of soils include sewage waste water, some of which contain large amounts of B from detergent sources. Other sources are sewage sludges and fly ash. Reduction of B toxicities in soils is difficult. Amelioration with gypsum has been proposed for B-rich sodic soils in India (Bhumbla and Chhabra 1982, cited in Kabata-Pendias 2001). Also phytoremediation with plants of the *Brassica* family seems a potentially powerful method to reduce B toxicities in soils (McGrath 1998).

Geology of boron

Natural abundances of B in common rocks are generally low. The highest B concentrations occur in marine sedimentary rocks, especially those rich in clays, e.g. shales, and in organic matter (Table 8.6). Silica-rich igneous rocks, like granites, and most metamorphic rocks along with sandstones contain low concentrations of B. Marine sediments containing clays, specifically illite where some of the B is substituting for Al^{3+} and/or Si^{4+} in the lattice, as well as glauconite-bearing sediments contain the largest amounts of B.

The average concentration of B in fresh water is 0.1 mg L^{-1} and in sea water 4.6 mg L^{-1}.

Table 8.6. *Average abundance of total boron (mg kg^{-1}) in various rock types (Levinson 1976, Ure and Berrow 1982; Rudnick 2003).*

Earth's crust	Ultra -mafics	Basalt	Grano -diorite	Granite	Shale	Lime -stone	Organic matter	Soil
11	5	5	20	15	100	10	700	38

The relatively insoluble complex borosilicate minerals from the tourmaline group with 3-4% B are formed in high temperature igneous rocks, for example in contact zones around granite intrusions ('greisen' zones), in pegmatites and in skarn deposits. A typical tourmaline mineral in coarse grained pegmatites is the black tourmaline 'schoerl', with the formula $NaFe_3B_3Al_3(Al_3Si_6O_{27})(OH)_4$. The distribution of major B deposits in the world is illustrated in Figure 8.3

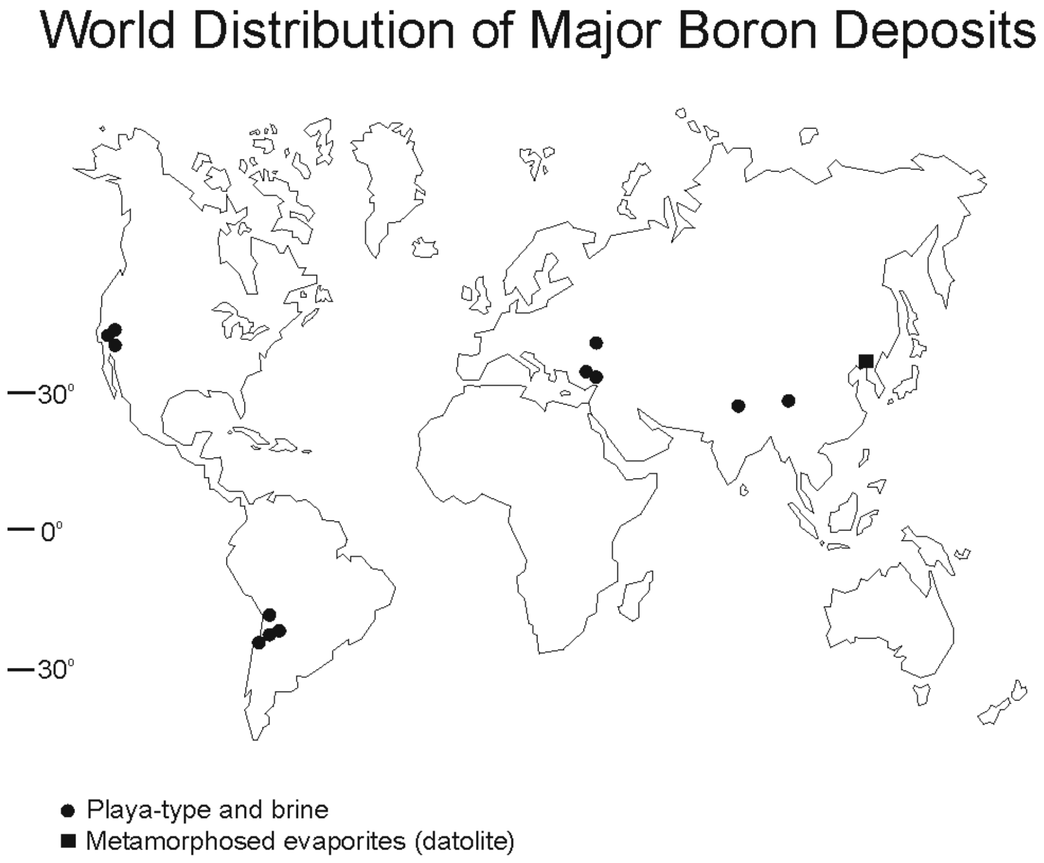


Figure 8.3. *Distribution of major B-deposits in the world.*

Economically extracted natural B minerals can be grouped into three categories:

- Playa-type B deposits: chemical precipitates of B-rich springs in playa-type basins and B-brines (examples: California, Peru-Bolivia-Argentine-Chile, Turkey, Tibet and Tsaidam in China, Inder in Khazakstan),
- Skarn-type B deposits: contact metamorphic deposits in areas with granites intruding carbonate rocks (example: datolite deposit Dalnegorsk, Russia),
- Boron deposits associated with metamorphosed evaporites in a volcano-sedimentary environment, for example in Liaoning Province, China (Peng *et al.* 1998).

It should be noted that most of the playa-type and borate deposits are associated with continental sediments and Neogene volcanics in areas of active volcanism associated with converging plate margins. These deposits are, preserved in areas with arid climates. Boron concentrations in gases and hydrothermal solutions in mid-ocean ridges and continental rifts, such as the East African Rift, are very low (Ozol 1977).

The B-deposits associated with playa-basins and brines in areas of volcanism above subduction zones constitute by far the most important deposits for the B-mining industry. Major accumulations of B as hydrated Na and Ca borates are found in relatively young, closed, non-marine sedimentary basins in arid environments of Turkey, California, USA and the western side of South America. The hydrated borate minerals of these major deposits were formed as a result of high evaporation rates in closed terrestrial basins close to volcanic areas. The relatively soluble Na and Ca borates are the results of concentration of B-rich brines from plate margin related volcanic activities in arid, shallow lake environments with interior drainage, in playas. High evaporation rates increased the concentration of these brines and finally led to the precipitation of hydrated borates together with other salts. Accounts of these type of deposits are summarized in Kistler and Smith (1975), Kistler and Helvaci (1994) and Harben and Kužvart (1996).

Apart from the very insoluble boro-aluminosilciates tourmaline there are relatively soluble hydrated Na and Ca borate minerals such as borax ($Na_2B_4O_7 \cdot 10H_2O$), kernite ($Na_2B_4O_7 \cdot 4H_2O$), ulexite ($NaCaB_5O_9 \cdot 8H_2O$) and colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$). Economically extracted B-minerals also include the B-silicate datolite ($CaBSiO_4(OH)$). The rare borate minerals suanite and ludwigite are found in 2.2 billion year old metavolcanic and metasedimentary successions in northeastern China, interpreted as metamorphosed playa sediments (Peng *et al.* 1998).

The most favourable geological environments for B-salt preservation are those where impervious clay layers overlie the B-salt accumulations. In general, hydrated borate accumulations form under the following conditions and in the following areas:

- In close proximity to volcanic areas, specifically volcanism related to converging plate margins,
- In lake environments where B-salts could be dissolved,
- In areas close to volcanic sources, with high evaporation rates,
- Rapid burial conditions under impermeable cover sediments to preserve the dissolution of the highly soluble borate minerals.

By far, skarn-type B deposits, contact metamorphic B deposits of granites with carbonate rocks, and the vein-type B deposits are the less economic B deposits. When granitic magmas rich in B crystallize, the boron is not incorporated in the common rock forming minerals but enriched in the remaining fluids. When these fluidal phases react with carbonate-rich rocks they can form so-called skarn deposits and B-rich minerals, usually B-containing Ca and/or Mg silicates are concentrated in these types of skarn deposits. An example of this type of deposit is the datolite deposit at Dalnegorsk near the Sea of Japan and other parts of the Former Soviet Union (Harben and Kužvart 1996).

Boron-containing minerals are also found in marine evaporite beds of Permian age. For example, Mg-borate minerals were recovered as by-products during potash mining in Germany (Kistler and Smith 1975).

Extraction of borates

Borates are mined by different techniques, but mainly by open pit methods, as extensive near-surface B deposits make this method possible. Thin layers of borates in dried saline lakes are mechanically extracted or in special cases are hand picked. In-situ leaching is another borate extraction technique by which underground B accumulations are accessed via drilling, follwed by in-situ leaching and subsequent pumping of the pregnant brine to the surface. The B-rich brine is subsequently blended with lake water to increase the pH to precipitate B mineral phases.

Table 8.7 shows the 2005 world production of borates. Borates are mined and processed into many products, including B fertilizers. The average price of granulated pentahydrate borax in 2003 was $400-425 per ton (US Geol. Survey 2004).

Table 8.7. *World production of borates (in million tonnes) in 2005. (Source: US Geological Survey, 2006).*

Country	Borate produced (millions of tonnes)
Turkey	1.7
USA	1.23
Argentina	0.55
Chile	0.60
Russia	0.50
China	0.14
Total	**4.86**

Agriculture represents only a very small fraction (approximately 6%) of the total usage of borates. The main markets of borates are fibreglass, fire retardants, textile grade fibreglass, borosilicate glass, soaps and detergents (Harben and Kužvart 1996). Table 8.8 shows the principle B fertilizers. Another source of B, albeit much less concentrated, can be wood ash. Because B is adsorbed on OM, high concentrations of B (100-200 mg kg^{-1}) can be found in plant and wood ash, as well as in fly ash.

In the past, farmers relied predominantly on borax and other solid B-sources as B-fertilizer (Table 8.8), but recently foliar sprays, including “Solubor” have become the most popular form of B fertilizers.

Table 8.8. *Main B fertilizers, their formulae and B-contents.*

Fertilizer	Formula	B (%)
Borax	$Na_2B_4O_7 \cdot 10H_20$	11
Boric acid	H_3BO_3	17
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$	10-16
Sodium pentaborate	$Na_2B_{10}O_{16} \cdot 10\ H_2O$	18
Sodium tetraborate: Fertilizer Borate-48 (Agribor, Tronabor)	$Na_2B_4O_7 \cdot 5H_20$	14-15
Sodium tetraborate: Fertilizer Borate-68 (Agribor, Tronabor)	$Na_2B_4O_7$	21
Solubor	$Na_2B_4O_7 \cdot 5H_20$ + $Na_2B_{10}O_{16} \cdot 10H_20$	20-21
Ulexite	$NaCaB_5O_9 \cdot 8H_20$	9-10
Boron Frits	Complex borosilicates	Varies

Boron can be applied either as refined B fertilizer products, completely soluble and to be applied either as solid fertilizer or in solution, such as borax and boric acid, or in the form of crushed B-ores, especially ulexite and colemanite. The latter form is a form of slow-release fertilizer that can be applied in forestry operations (Shorrocks 1997). Another form of B-application, boronated fused magnesium phosphate, is used in Brazil and Japan. Boron-frits, a fused form of B fertilizer with varying concentrations of B, is also used (Shorrocks 1997). Foliar B sources, applied at certain growth stages of a plant or as quick acting remedy for B deficiency are widely used. Solubor application rates vary from 0.17–8% B, with an application rate of 0.3–4.8 kg B ha^{-1}. Foliar Solubor suspensions have been applied from the air to sunflower plantations in South Africa and Spain (Shorrocks 1997).

Boric acid and Na-borates are active ingredients in insecticides (as poisons for ants, cockroaches and termites), in herbicides (causing desiccation or disruption of photosynthesis in plants) and in fungicides (controlling fungi in timber) (Harben 2002), and reach the soils via precipitation and leaching.

Chlorine/Chloride

The role of chlorine/chloride in plants

Chlorine does not occur in its elemental form in rocks, soils and plants. Chlorine occurs predominantly in the anionic form of chloride (Cl^-), which is involved in several important photosynthetic and water regulatory activities. The uptake of Cl^- is not pH dependent and is accomplished by the roots and from aerial sources through their leaves. Chloride is very mobile within plants. It is involved in the transport of several cations, specifically K, Ca and Mg, and plays a major role in stomatal regulation and water flow in plants. Chloride also seems to be involved in stimulating enzyme activities (Mengel and Kirkby 2001). The anion Cl^- can also substitute for NO_3^- and SO_4^{2-}. The application of Cl^- is known for the suppression of fungal root diseases, certain leaf rusts and stalk rot in maize/corn.

Plants differ in their demand for chloride, the average concentration of Cl in plants is 1-20 g kg^{-1} (Römheld and Marschner 1991). However, there are plants that can accumulate up to 4% Cl (Smith *et al*. 1987). There are few reported incidences of chloride deficiencies in plants. In Kiwifruit, which have high requirements of chloride (Smith *et al*. 1987), observed deficiencies develop first in older leaves, with discrete pale green leaves near the tip of the leaf.

Excess of Cl is more of a problem than Cl deficiency. Excess of Cl increases the osmotic pressure of soil water and thus lowers the availability of water to plants. Toxicities of Cl are found mainly in soils of arid and semi-arid climates, or in soils with excessive Cl loadings with chloride bearing fertilizers, sludges or irrigation with highly mineralized waters.

While some crops are very tolerant to high Cl concentrations, others are very sensitive. Barley, maize/corn, spinach and tomatoes are very tolerant to high Cl levels, whereas tobacco, cotton, beans, lettuce, potatoes, citrus and some legumes are prone to toxicities. Also, some trees are sensitive to Cl, for example conifers. Damage to these trees can often be observed in temperate northern countries along roadsides that have been salted during the winter. Chloride toxicity symptoms on fruit trees and crops sensitive to salinity are burning of leaf margins, bronzing and premature yellowing.

Inorganic Cl sources, such as ammonium chloride (NH_4Cl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$) or potassium chloride (KCl) and sodium chloride (NaCl) are applied when Cl uptake by plants is reduced due to high concentrations of NO_3^- or SO_4^{2-} or as a means of suppressing root diseases, for example in winter wheat (Havlin *et al.* 1999). The Cl requirements for most crops in temperate climates are 4-10 kg ha^{-1}.

Chlorine in soils

The mean global Cl concentration in soils is 485 mg kg $^{-1}$ (Ure and Berrow 1982). The sources of Cl differ strongly, the main sources being rock weathering and atmospheric inputs. Chloride concentration in soils decreases with increasing distance from the oceans as Cl is largely supplied by precipitation from the atmosphere.

Chloride is not adsorbed to minerals and is thus very mobile in soils. Soils with elevated concentrations of Cl are commonly those that are close to the oceans, those affected by irrigation with Cl rich waters, or soils in areas with high evaporation rates, for example in arid and semiarid climates. In humid environments, Cl is largely leached out of the soil. However, chloride ions form strong complexes with metals. For example, high levels of cadmium (Cd) have been observed in potato crops in Australia, in land irrigated with Cl-rich water. The cadmium is derived from phosphatic fertilizers (McLaughlin *et al.* 1997).

Geology of chlorine

The average Cl concentration in the upper continental crust is 244 mg kg^{-1} (Rudnick 2003). Since Cl^- is the major anion in seawater, sedimentary rock types formed in marine environments can have relatively high concentrations of Cl. The lowest concentrations of Cl are reported from sandstones. The highest Cl concentrations in rocks are found in evaporite sequences with NaCl and other salts, including K-salts being concentrated in evaporitic basins and in coastal areas. Igneous rocks contain between 50 and 400 mg Cl kg^{-1}. In some minerals chloride is substituting for OH groups, for example in micas, amphiboles and apatite. Chloride is very mobile during hydrothermal processes and in some cases precipitate as metal chlorides (e.g. AgCl, $PbCl_2$) (Kabata-Pendias 2001).

Table 8.9. *Average abundance of total chlorine (mg kg^{-1}) in various rock types (Levinson 1974; Ure and Berrow 1982; Rudnick 2003).*

Earth's crust	Ultra-mafics	Basalt	Granite	Shale	Lime-stone	Sand-stone	Soil
244	85	60	165	180	150	10	485

The natural chloride resources for agriculture are mainly derived from chloride-bearing rocks but large contributions of Cl inputs into soils are via precipitation. While the Cl inputs into soils close to the sea may be in the range of 100 kg Cl ha^{-1}, at a distance of 200 km from the coast it may be only 20 kg Cl ha^{-1} or less (Fixen 1993). Most naturally occurring agricultural inputs of Cl are in the form of K fertilizers such as the naturally occurring sylvite (KCl), carnallite ($KCl \cdot MgCl \cdot 6H_2O$) and kainite ($4KCl \cdot 4MgSO_4 \cdot 11H_2O$). These K-salts are mined by conventional underground methods and solution mining (see Chapter 5). The global reserves of Cl sources are extremely large, with seawater and rock salts contributing to this large reservoir.

Copper

The role of copper in plants

Copper (Cu) is an essential nutrient for plants. Typical concentrations of Cu range from 3-15 mg kg^{-1} dry weight in ryegrass and 5-12 mg kg^{-1} dry weight in white clover (Whitehead 2000). Deficiencies are reported when Cu concentrations in plants fall below 4 mg kg^{-1} dry weight (Havlin *et al*. 1999). Copper is important in the function of a number of enzyme systems involved in oxidation-reduction reactions (Marschner 2002). Copper is taken up in the roots mainly as the cation, Cu^{2+}. It is not very mobile in plants, but can be translocated from older to younger leaves (Mengel and Kirkby 2001).

The availability of Cu influences carbohydrate and N metabolism. It is suspected that Cu plays a role in symbiotic N-fixation, although this connection has not yet been proven (Mengel and Kirkby 2001). There are indications that high N applications increase the requirements of plants for Cu. That means, if only N but not additional Cu is supplied, Cu deficiency symptoms might be the result, especially in the younger leaves. Plant species differ in their sensitivity to Cu deficiencies. Crops that are sensitive to under-supply (deficiency) of available Cu are wheat, oats, onions, carrots, spinach, alfalfa, citrus, and lettuce. Oats are extremely sensitive to Cu deficiencies. Sensitivities to Cu deficiencies of other plants are shown in Table 8.3.

Plants contain usually 8–20 mg Cu kg^{-1}. Deficiency symptoms appear commonly when the Cu concentration in plant tissue is below 6 mg Cu kg^{-1}. Plants with Cu deficiencies commonly exhibit visible foliar symptoms of chlorosis in the young leaves, stunted growth and excessive production of laterals. Citrus crops react to Cu deficiencies in soils with dieback and gum pockets under the green bark of young wood (Wutscher and Smith 1993). In cereal crops like wheat, signs of deficiencies include: whitening of leaf tips and twisting of leaves, as well as shortening of internode intervals. Deficiency symptoms also include ‘dieback’ of young growing tips. A typical visual symptom in onions on Cu deficient soils is the dieback of the leaf tips and spiral growth (Bennett 1993). In other plants the dieback may be followed by the development of additional buds below the dead tips resulting in bushy growth also known as ‘rosetting’.

Plants as indicators of mineralization have been known for decades (Brooks 1972). Indicator plants for Cu-mineralization include *Papaver commutatum*, the ‘copper poppy’ a plant of the mint family, which has been used successfully in Zambia for

Cu exploration purposes. This indicator plant is found in soil with Cu concentrations higher than 100 mg kg^{-1} (Brooks 1972). High concentrations of Cu in soils cause morphological changes in the plant, for example specific changes in colour and form of petals, depending on the Cu concentration in soils. Changes in colour and shape of the petals of the 'copper poppy' (Figure. 8.4) have been used in Armenia to outline Cu-Mo mineralizations (Brooks 1972). Other 'copper plants' are *Becium homblei* and the hyper-accumulator plant *Haumania katangensis* (Brooks 1998).

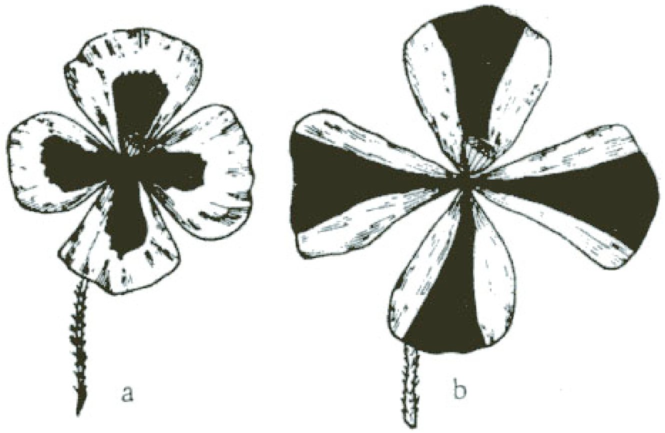


Figure 8.4. *Colour changes and shading differences in Papaver commutatum a) normal appearance b) modified colouring due to growth on copper-molybdenum rich substrates (source: Brooks 1972).*

Copper in soils

The overall average Cu concentration of soils is 20 mg kg^{-1} (Ure and Berrow 1982). Total Cu concentrations in soils range from 2–100 mg kg^{-1}, but are usually between 25 and 60 mg kg^{-1} depending on the composition of the underlying bedrock and the intensity of weathering. Cu in soils occurs mainly as divalent Cu^{2+}. It is strongly adsorbed by organic matter, and hydrous oxides of Al, Fe and Mn (McBride 1994). More than any other micronutrients, Cu is very strongly complexed by organic matter. In waterlogged soils, Cu is partially reduced to Cu^{+} and occurs commonly as insoluble CuS. The solubility of Cu^{2+} is strongly pH dependent. It increases by a factor of hundred for each unit decrease in pH. Copper as Cu^{2+} is most available in acid soils below a pH of 6. Cu^{2+} deficiencies are prevalent on soils with a pH above 7.0.

Copper concentrations in soils below 1-2 mg kg^{-1} are considered deficient (Havlin *et al*. 1999). Deficient, marginal and sufficient Cu concentrations in soils, as determined by extraction with DTPA (diethylenetriaminepentaacetic acid) are 0-0.4 mg kg^{-1}, 0.4-0.6 and > 0.6 mg Cu kg^{-1} soil respectively (Havlin *et al.*1999). Cu deficiencies in plants are prevalent on soils with inherently low total Cu concentrations as a reflection of the low Cu concentrations in the parent material and on organic soils. Kubota (1983) describes the geographic distribution of Cu in legumes in the United States. Very low concentrations of Cu are reported from the central wheat belt and Atlantic coastal areas where soils overly unconsolidated sandy sediments. Forbes (1978) outlined areas in New Zealand with low Cu concentrations in alfalfa. These low Cu soils occur over yellow-brown Si-rich and nutrient poor pumice rock.

When crop sensitivity to Cu availability is high and Cu^{2+} availability in soils is low, plant growth can be substantially reduced. An example of Cu deficiencies caused by low inherent Cu concentration on volcanic soils over pumice is reported from SW Tanzania (Kamasho and Singh 1982). While the soil Cu concentration in soils overlying basalts is 'normal', the soil concentration of total Cu in soils on Si-rich pumice are below 10 mg kg^{-1}, which is in the deficiency range. In addition, the farmers were growing wheat, a crop with a high sensitivity to Cu deficiencies. As a result the farmers produced only very low yields. Dramatic yield increases were experienced when the farmer added small amounts of Cu to the soils. In recent years, the deficiency of Cu in intensively cultivated soils is less common because of the extensive use of Cu rich fungicidal sprays.

Although the requirements of plants for Cu are relatively small, Cu deficiencies are known from a number of soil types and crops. Soil Cu deficiencies are reported mainly from soils rich in Mn-oxides, iron oxides and organic matter as well as clays because of their strong complexation. Cu deficiencies are prevalent in soils with high organic matter content, e.g. peat soils. Although peat soils commonly contain sufficient total Cu, the copper is strongly complexed by the organic matter and hence not available. Leached sandy soils (with little Cu retention) also show Cu deficiencies.

Soils with toxic concentrations of Cu are commonly found over tailings from mining operations and soils receiving repeated high dosage of Cu containing sludge. Soils of tropical plantations of citrus, coffee, tea, olives as well as vineyards and orchards often contain elevated levels of Cu resulting from repeated applications of Cu-fungicides (Kabata-Pendias 2001). The accumulation in soils due to the use of Cu-fungicides has particular importance for grassland agriculture and aquaculture systems. Both sheep and fish are sensitive to Cu toxicities. For example, sheep should not graze on lands heavily fertilized with pig manure, especially when the Cu-rich pig manure is spread on acid soils, and is therefore likely in an available form. Also, erosion from Cu-rich soils can cause health problems for fish in rivers, lakes and aquacultural operations.

Geology of copper

Copper availability in soils is largely related to the inherent Cu content in parent materials, on the weathering status of the soils and on soil environmental conditions such as pH, drainage, soil organic matter and clay contents. The average Cu concentration of the earth's crust is 55 mg kg^{-1} and 20 mg kg^{-1} in soils respectively (Levinson 1974; Ure and Berrow 1982). Table 8.10 shows the average abundance of copper in various rock types and in soil. It is obvious that the rocks of afic compositions such as basalts contain higher amounts of Cu than Si-rich igneous rocks, such as granite and rhyolite, or pumice-rich volcani-clastic rocks.

Table 8.10. *Average total Cu abundance (mg kg^{-1}) in various rock types (Levinson 1974; Rudnick 2003) and soil (Ure and Berrow 1982).*

Earth's crust	Ultra-mafics	Basalt	Grano-diorite	Granite	Shale	Lime-stone	Sand-stone	Soil
55	10	100	30	10	50	15*	8-10	20

* Because the soils on limestone bedrocks are often alkaline, Cu is not readily available.

Exploration geologists make use of the fact that various rocks have inherently different Cu concentrations. Differences in Cu concentrations in soils and vegetation can outline different rock types below the soil cover. High Cu concentrations in soils may be 'fingerprints' of underlying ferromagnesian bearing mafic rocks but high Cu concentrations in soils could also be an indicator of Cu deposits for mining purposes.

Copper sources for agricultural use are primarily derived from geological resources. Commercial Cu ores are mined from different ore types in the primary and secondary environment. The main naturally occurring Cu mineral is chalcopyrite ($CuFeS_2$), formed in so-called hydrothermal (hot-water-derived) deposits, but also in magmatic deposits. The most important hydrothermal deposits are the porphyry copper deposits, which are made up of small intersecting veinlets of quartz, chalcopyrite and other metalliferous minerals associated with silica-rich magmatic intrusions. They formed when Cu-rich hydrothermal solutions flowed through highly permeable zones that surround granodioritic intrusions. These intrusions are found mainly along specific structural zones where plates collided, at convergent plate margins, for example in Chile, Peru and the USA (Figure 8.5) (Mitchell and Garson 1981).

Other Cu deposits are associated with mafic volcanics, in the form of volcanogenic massive sulphide deposits, and sediment hosted Cu deposits. The latter are mined in Zambia and the Democratic Republic of Congo (Fleischer *et al.* 1976).

Copper ore is mined from all these deposits by open cast or underground mining operations. After mining the ore, Cu is physically enriched and chemically processed into metallic Cu of high purity. The production of Cu metal in 2003 was 13.9 million metric tons (US Geol. Survey 2004). The main Cu producing countries are Chile (4.86 mill. t), Indonesia (1.17 mill. t), USA (1.12 mill. t), Australia (870,000 t), and Peru (850,000 t). The land-based resources of Cu are estimated to be 1.6 billion tons with additional reserves in deep-sea nodules of 700 million t (US Geol. Survey 2004). The price for Cu in 2003 ranged from US $0.78 – 0.82 per pound (US Geol. Survey 2004) and reached a high of US $ 3.32 per pound in June 2006, according to the London Metal Exchange.

Copper used for agricultural purposes forms only a minute fraction of the total global Cu consumption. Copper for fertilizing purposes is processed into Cu-sulphates, Cu-ammonium phosphates and Cu-chelates (CuEDTA). These products can be used in granular or foliar form. An application rate of 1-20 kg Cu ha^{-1} is usually adequate, but higher application rates might be necessary for crops growing on organic soils. Foliar applications of Cu chelates should be applied only as emergency treatment, when deficiencies have been identified after planting. Foliar applications are commonly more expensive than granular applications.

A common fungicide is the ‘Bordeaux mixture’, a blend of Cu-sulphate ($CuSO_4 \cdot 5H_2O$), lime and water.

Other suggested sources for use in soil amendment include natural Cu minerals such as malachite and azurite, $Cu_2CO_3(OH)_2$ and $Cu_3(CO_3)_2(OH)_2$ respectively. These minerals are found in many small occurrences and deposits in most countries. There are virtually thousands of small-scale occurrences of geological Cu-mineralizations in the world, but only the large deposits are being mined at present. Libraries of national geological surveys commonly have compilations of theses occurrences in reports and publications.

Since only small amounts of Cu are needed to correct for Cu deficiencies many of these small deposits should be explored and analyzed for their potential application in Cu deficient soils. But caution in their application is needed since many of these small deposits and occurrences of Cu-ore can also contain other metals, such as the toxic element Pb.

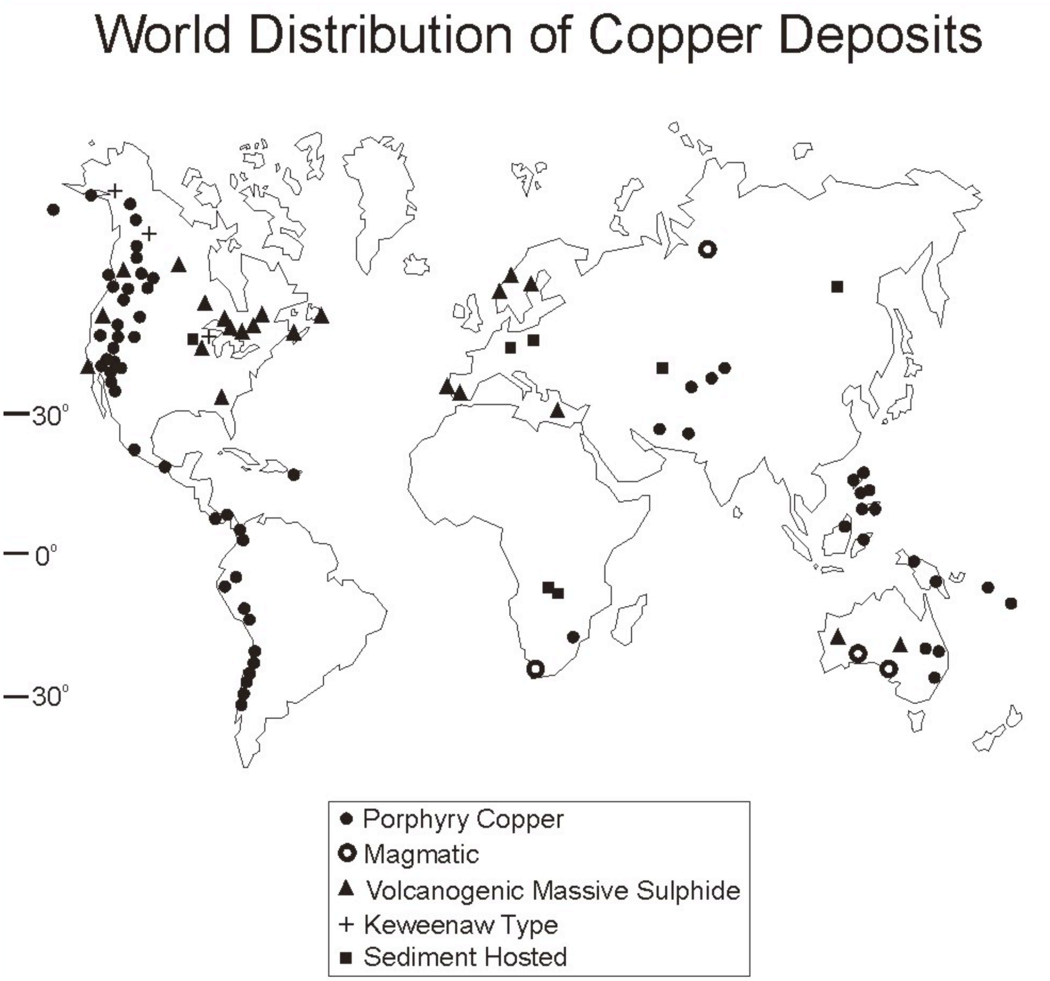


Figure 8.5. *Distribution of Cu deposits according to types of mineralization (after Kessler 1994, with permission).*

Iron

The role of iron in plants

Iron (Fe) is essential for the growth of plants and animals. Although the requirements of Fe in animals and plants are relatively small, Fe is an essential constituent of chloroplasts essential for photosynthesis. The concentration of iron in plants varies. Plants containing less than 50 mg Fe kg^{-1} are considered Fe deficient, the sufficiency range being 50-250 mg Fe kg^{-1} (Havlin *et al*. 1999). In general, plants can take large amounts of Fe without showing toxicity signs. However, rice plants show symptoms of Fe toxicity at concentrations above 300 mg Fe kg^{-1}.

Iron is part of the molecule leghaemoglobin, which is important for biological N-fixation processes. Leghaemoglobin binds oxygen and protects the enzyme nitrogenase, which catalyzes the reduction of dinitrogen to ammonia, from exposure to toxic concentrations of free oxygen. Leghaemoglobin gives active root nodules of leguminous plants their pink colour. Iron has many additional crucial functions, including the formation of many metallo-protein enzymes and is important for protein metabolism.

The pathway of Fe in plants has been followed using ^{59}Fe isotopes. Iron is not very mobile in plants; therefore Fe deficiencies affect the younger part of plants only (Mengel and Kirkby 2001). Iron is taken up by plant roots from soil solution, predominantly as ferrous iron, or as Fe^{III} chelates (for example iron ethylene diamine di(o) hydroxyphenyl acetic acid or *FeEDDHA*). Fe-chelates are organic complexes, which can contain an Fe cation at its core (*chele* = Greek *claw*). The uptake of Fe^{III} chelates by plants is complex. The ferric chelates are reduced at the root cells to Fe^{II}, with an associated break-up of the chelate complex. In general, ferric iron has to be reduced to the ferrous state before it is taken up by the roots.

Although Fe occurs in soils in large amounts, only a very small fraction is taken up by plants. But some plants are more efficient than other plants to utilize Fe and Fe-chelates. Plants have developed different sets of mechanisms to take up Fe (Marschner 2002). While the roots of graminaceous plant species, such as grasses, release specific low weight Fe-chelating amino acids, so-called phytosiderphores that enhance the uptake of ferric iron, roots of dicots and non-graminaceous monocots acquire Fe in the form of ferrous iron through specialized enzyme and acidification mechanisms (Marschner 2002). Iron efficient plants like sunflowers react on Fe stress with morphological changes of the root system, by lowering the pH around the roots and increasing the reducing capacity of root surfaces. Most grasses do not develop morphological changes of their roots but develop different Fe mobilizing strategies to overcome Fe stress (Mengel and Kirkby 2001).

In addition to low availabilities of Fe, imbalances with other metals such as Cu or Mn reduce the uptake of Fe in plants. In addition, excessive P in soils, low soil organic matter and high pH conditions reduce the availability of Fe to plants. Liming soils to pH levels above 7 certainly decreases the availability of Fe, causing so-called 'lime induced Fe-chlorosis'.

The form of N fertilizers commonly used in aerobic soils also plays a considerable role in the uptake of Fe. For example, the application of NH_4^+-containing fertilizers will result in a drop of the pH in the soils for example from 6.5 to 5.0, and under these low pH conditions no Fe deficiencies will occur. In contrast, soils fertilized with NO_3^- as an N source, will likely show no positive effect on Fe availability because the pH of the soil is not decreased.

Iron is not very mobile within plants. Green plants which do not receive sufficient amounts of Fe become chlorotic in the young leaves first, whereas older parts of the plant remain green. Signs of Fe deficiencies are typically green veins and yellow interveinal tissue. In severe deficiency cases, the youngest leaves are completely bleached ('chlorotic').

Crops most likely to be affected by Fe deficiencies are citrus crops, grapes, sorghum, soybeans, deciduous fruit trees (e.g. apple trees) and many ornamentals. Other plants that may exhibit Fe deficiencies are beans, groundnuts/peanuts, cotton, bananas, small grains and grasses, legumes, rice, tomatoes and several other vegetables.

Iron in soils

Soils differ strongly in their Fe concentration, but the general total concentration is often in the percent range. While the total Fe concentration in soils developed from rocks rich in ferromagnesian minerals like basalts and shales are very high, soils developed on granites, sandstones and limestones are considerably lower (Table 8.12). The total Fe content in soils varies from 0.01 to 21%, with a mean of 3.2% (Ure and Berrow 1982).

Despite the high total concentration of Fe in rocks and soils, the concentration of soluble Fe in soils is generally extremely low. Whitehead (2000) pointed out that the ratio of typical Fe concentrations in soils (35,000 mg kg^{-1} = 3.5%) to typical Fe concentration in plants leaves (150 mg kg^{-1}) is extremely low (0.0004), the lowest of all soil-to-plant concentration ratios of plant nutrients. In soils, iron deficient, marginal and sufficient concentrations as determined by extraction with DTPA (diethylenetriaminepentaacetic acid) are 0-2.5 mg kg^{-1}, 2.6-4.5 and > 4.5 mg Fe kg^{-1} soil respectively (Havlin *et al.*1999).

The minerals magnetite (Fe_3O_4), hematite (Fe_2O_3), ilmenite ($FeTiO_3$), inherited mainly from the parent materials, as well as goethite (α-FeOOH) are the least soluble Fe minerals in soils. Most of the Fe in soils occurs as hydrous ferric oxides and hydroxides. The common Fe oxides/hydroxides in soils are, with decreasing solubility: $Fe(OH)_3$ amorphous,> Fe(OH) > γ-Fe_2O_3 maghemite > γ-Fe-OOH lepidocrocite > α-Fe_2O_3 hematite > α-FeOOH goethite.

Iron in soils easily changes its valence level in response to changes of the physico-chemical conditions. Reduced ferrous iron is much more soluble than ferric iron, but ferrous iron is easily and rapidly oxidized into less soluble ferric iron forms. The solubility of Fe^{3+} is strongly pH dependent. The activity of Fe^{3+} in equilibrium with various Fe (III) oxides decreases rapidly with increasing pH (Lindsay and Schwab 1982). Consequently, availability of soluble inorganic Fe in alkaline soils is commonly extremely low. Iron deficiencies are well known in alkaline soils, for example over limestones and in regions with arid and semi-arid climates. The availability of Fe increases however when the conditions become anaerobic and thus conducive for the conversion of the ferric to the more available ferrous form.

Not only does the pH control the availability of Fe, but reduction-oxidation processes in the soils also determine the form and availability of Fe. In general, oxidation takes place in well-drained soils where oxygen is well supplied and reduction processes prevail in waterlogged soils where oxygen is undersupplied. In waterlogged soils, for example in rice paddies, Fe^{3+} is reduced to Fe^{2+}, the form that rice plants take up through their roots. In rice paddies, anaerobic bacteria enhance the reduction of Fe^{3+} as they utilize Fe oxides as electron acceptors. The reduction of Fe^{3+} to Fe^{2+} in these fields often leads to increased Fe^{2+} concentrations. In extreme cases it leads to Fe toxicities in rice plants.

The main problems of Fe toxicity in flooded acid rice soils where the level of soluble Fe increases from 0.1 mg kg^{-1} before flooding to 50-100 mg kg^{-1} after flooding (Ponnamperuma 1972). Iron concentrations as high as 300 mg kg^{-1} cause decreasing uptake of other nutrients and ‘bronzing’, a disorder in leaves of rice plants. The problem of Fe availability is also apparent on degraded sandy soils, specifically on well-drained oxidized soils with low inherent Fe concentrations. However, as mentioned above, Fe deficiencies are most common in alkaline soils. It is well known that over-liming of soils can also induce a reduction in Fe availability.

Large areas of the intermountain region of the USA, as well as large areas west of the Mississippi River are potentially deficient for Fe sensitive crops (Mortvedt 1975), as are large areas with alkaline and alkaline-saline soils in arid areas of the world. In sub-Saharan Africa, Fe deficiencies occur locally in the Congos, Ghana, Nigeria, Kenya and Senegal (Kang and Osimane 1985), and in several countries of South America (Leon *et al.* 1985).

Iron is mainly applied to soils in the ferrous form or as expensive Fe-chelates. On large field operations, a common way of reducing Fe chlorosis is the application of foliar sprays containing ferrous iron.

Despite the fact that soils contain large amounts of Fe (in the percent range) the availability of Fe to crops and finally to food is very low. The main function of Fe in the human body is as carrier of oxygen in the blood, and as crucial element in immune system functions, in energy metabolism and temperature regulation. Over half of the human population of the earth is deficient in micronutrients, and iron, together with zinc, constitute one of the main human micronutrient deficiencies. Iron deficiency, the cause of anemia, affects approximately 2 billion people worldwide.

Geology of iron

Iron is a very abundant component of minerals on planet earth. The total Fe (as FeO) concentration in the upper continental crust is 5.04% (Rudnick 2003). Large portions of Fe in rocks and soils occur in the lattice of primary and secondary minerals. Primary minerals include Mg-Fe silicates like olivine, pyroxenes, amphiboles and biotite, as well as Fe-oxides magnetite (Fe_3O_4), hematite (Fe_2O_3) and Fe-sulphides, especially pyrite (FeS_2) and Fe-carbonates such as siderite. The Fe content in framework silicates like feldspar is very low. Mineral sources of iron are listed in Table 8.11.

Table 8.11. Iron containing minerals.

Mineral	Composition
Magnetite	$Fe_3O_4(Fe(II)O{\cdot}Fe(III)_2O_3)$
Hematite	Fe_2O_3
Goethite	α-FeOOH
Siderite	$FeCO_3$
Pyrite	FeS_2
Vivianite	$Fe_3(PO_4)_2{\cdot}8H_2O$
Glauconite	$(K, Na)(Al,Fe^{3+},Mg)_2(Al,Si)_4O_{10}(OH)_2$
Olivine	$(Mg,Fe)_2SiO_4$
Pyroxene	$(Ca, Na, Mg, Fe^{2+})(Mg, Fe^{2+}, Fe^{3+})Si_2O_6$
Biotite, phlogopite	$(K(Mg,Fe^{2+})_3(Al,Fe^{3+})Si_3O_{10}(OH)_2)$; $K(Mg,Fe)_3AlSi_3O_{10}(OH,F)_2$

Iron concentrations in rocks differ widely. In granites, the average Fe concentration is 2.70%, while in basalts it is 8.56%. Some sedimentary rocks contain considerable concentrations of Fe, but the Fe concentrations in limestones and dolomites are generally very low (0.38% Fe) (Table 8.12).

Table 8.12. *Average abundance of total iron in various common rock types and soil (Ure and Berrow 1982, and other sources).*

Earth's crust	Ultra -mafics	Basalt	Grano-diorite	Granite	Shale	Lime -stone	Soil
5.04 %	9.4%	8.6%	3.3%	2.7%	4.7%	0.38%	3.8 %

Iron ore deposits are widespread over the world with virtually thousands of deposits, but only a few high grade and large tonnage deposits close to oceans and other transport lines are currently extracted. The distribution of large Fe deposits in the world is illustrated in Figure 8.6

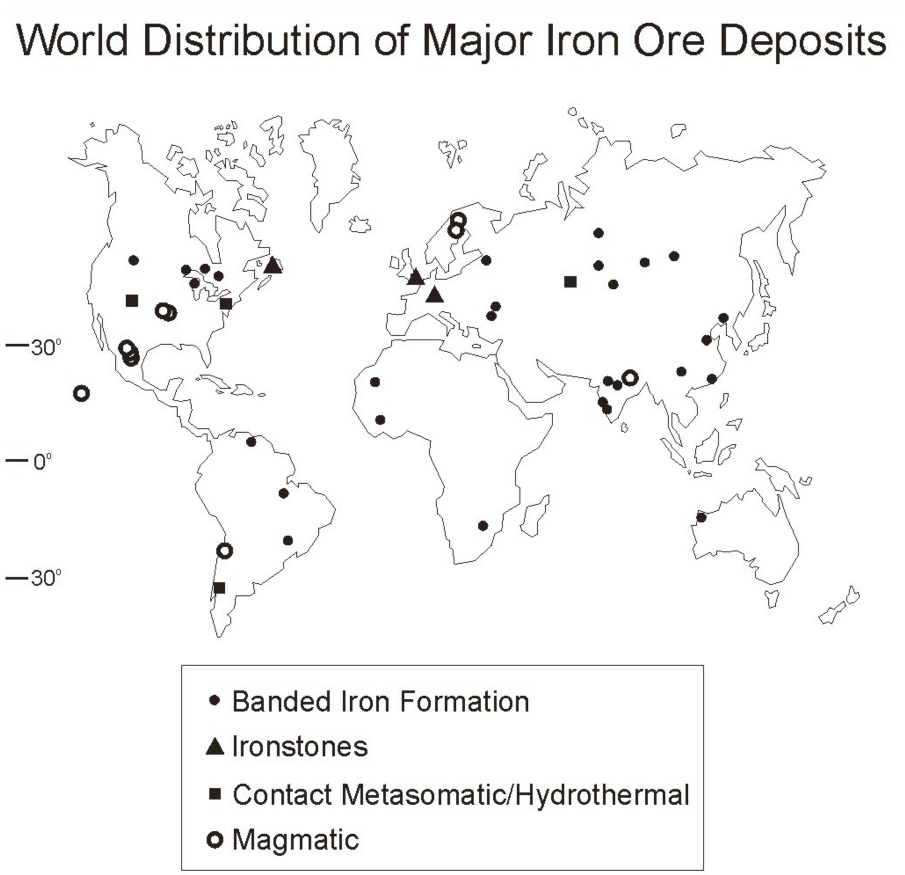


***Figure 8.6**. Distribution of large iron deposits in the world.*

Sedimentary iron deposits are the most important sources of extractable Fe. Most of these Fe deposits consist of layered alternating iron and silica rich layers, so called banded iron formations. They are often found in close proximity to volcanic rocks and have probably formed by volcanic hot springs from which hydrothermal Fe-rich solutions were released into sedimentary basins. Other Fe-rich sedimentary deposits were formed in Precambrian shallow shelf environments (Guilbert and Park 1986). The principal magmatic and contact metamorphic types of Fe deposits are associated with anorthosites and rhyolites. Contact metamorphic Fe deposits occur at the contact with granites, and are a type of skarn deposits. There are several other types of Fe deposits, however none of them being of the same magnitude as the above types of Fe resources.

World iron production in 2003 was about 1,100 million tonnes. Estimates of world resources exceed 800 billion tonnes of crude iron ore, containing more than 230 billion tonnes of Fe (US Geol. Survey 2004).

Commonly, libraries of national geological surveys will provide data on Fe-deposits and occurrences in a given country. Important for the extraction of Fe is the form in which it is found (oxide, sulphide, carbonate or silicate), as well as the ease of extraction, and transportation to the sites where Fe is needed in a plant available form.

Iron occurs in most ferromagnesian silicate minerals in the ferrous form, for example in the minerals olivine, pyroxene and in many common rock types, for example basalts. The applications of these types of ferromagnesian rocks provide simple solutions to Fe deficiencies in soils. Barak *et al.* (1983) successfully used finely ground basalt and volcanic tuff from a local quarrying operation that contain several percent Fe in the ferrous form to remedy chlorosis of groundnuts (*Arachis hypogaea*) in calcareous soils of Israel. Also pyrite-enriched manure proved a good source for Fe on alkaline soils (Barrau and Berg 1977). On a commercial scale, Fe for fertilizer application is used in the ferrous and ferric states in various forms (Table 8.13).

Table 8.13. *Sources of fertilizer iron.*

Source	Formula	Fe (%)
Ferrous sulphate	$FeSO_4 \cdot 7H_20$	19
Ferric sulphate	$Fe_2(SO_4)_3 \cdot 4H_20$	23
Ferrous oxide	FeO	77
Ferric oxide	Fe_2O_3	69
Ferrous ammonium phosphate	$Fe(NH_4)PO_4 \cdot H_2O$	29
Ferrous ammonium sulphate	$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$	14
Iron frits	Varies	Varies
Iron ammonium polyphosphate	$Fe(NH_4)HP_2O_7$	22
Iron chelates	NaFeEDTA	5-14

Manganese

The role of manganese in plants

Manganese (Mn) is an activator of many respiratory enzymes involved in chlorophyll synthesis. Manganese plays a major role in water splitting and the evolution of O_2 in photosynthesis. It also activates a number of enzymes. As Mn can change its oxidation state, it is, like Fe, involved in reduction-oxidation processes. Biochemically, Mn^{2+} resembles Mg^{2+} and substitutes for Mg^{2+} in several enzymes. Mn^{2+} is also known for its role in acceleration of germination and maturity. Typical concentrations of Mn in grasses and legumes range from 30 to 300 mg kg^{-1} (Whitehead 2000). Plant tissue analyses above 300 mg total Mn kg^{-1}

are regarded as excessive. In order to reduce the toxicity of Mn, it is recommended that soils be limed to a pH between 5.5 and 6.5.

Crops susceptible to Mn deficiencies include oats, beans, soybeans, potatoes, wheat, lettuce and onions. To overcome Mn deficiencies it is important to adjust the pH to below 6.5 by using acidifying materials, by applying of Mn-sulphates, Mn-oxides or chelates. Visual signs of Mn deficiencies often resemble those of Mg, specifically interveinal yellowing and chlorosis. However, unlike Mg, the Mn deficiency symptoms start in the younger leaves. This is because Mn is not mobile in plants. Other deficiency symptoms include chlorosis in the younger leaves. Mn deficiencies are also manifested in retarded growth and failure to blossom.

In legumes, small yellow spots and interveinal chlorosis have been reported. Common Mn deficiency symptoms in oats are grey and brown spots and stripes, so-called ‘grey specks’.

The high solubility and availability of Mn at low pH levels and anaerobic conditions may cause Mn toxicity to plants. The tolerance to Mn is different from crop to crop. Some crops can tolerate large amounts of Mn, others, such as leguminous crops and plants of the *Brassica* family, as well as potatoes and tomatoes are susceptible to Mn toxicities.

Manganese in soils

The overall mean of total Mn in soils is 761 mg kg^{-1} (Ure and Berrow 1982). Mn concentrations in soils are higher over basaltic rocks and shales than over granites and sandstones. Manganese has three oxidation states in soils, Mn^{2+}, Mn^{3+} and Mn^{4+}. However, only the Mn^{2+} form is stable in solution. The other two oxidation states form insoluble oxides and hydroxides in soils. The solubility of Mn is largely influenced by the soil pH and the redox potential. Like Fe, the solubility and availability of Mn is highest under acid conditions. In well-aerated soils at pH>7, Mn^{2+} is not available and tends to precipitate as an oxide, sometimes as nodules in the oxidized insoluble form of MnO_2. In contrast, solubility is increased under anaerobic conditions, for example in wet soils. Deficiencies of Mn occur mainly in neutral to alkaline soils as well as in soils with high organic matter contents, for example in calcareous peat and muck soils. With the exception of iron (Fe), Mn concentrations are determined by extraction with DTPA (diethylene-triaminepentaacetic acid). Deficient concentrations in soils generally contain less than 1.0 mg Mn kg^{-1} (Havlin *et al.*1999).

Manganese geology

Manganese occurs in natural minerals in divalent or trivalent forms. In most igneous and metamorphic rocks Mn occurs as divalent Mn, partially substituting other divalent ions, like ferrous Fe or Mg. Rock-forming ferromagnesian minerals have higher Mn concentrations than framework silicates like feldspars and quartz. Therefore, ferromagnesian (mafic) rocks such as basalts have generally much higher Mn concentrations than felsic rocks, such as granites (Table 8.14). The average abundance of Mn in the earth's crust is 950 mg kg^{-1} (Levinson 1974).

In sedimentary carbonate rocks, Mn concentrations can be elevated because of the ionic size of Mn^{2+}, which fits easily into calcite and dolomite. However, as the size of Mn^{2+} is similar to that of Mg^{2+}, it fits better into the dolomite lattice and consequently, the Mn content of dolomite is considerably higher than that of calcite.

Table 8.14. *Average abundance of total manganese (mg kg^{-1}) in various rock types and soil (sources: Levinson 1974; Ure and Berrow 1982).*

Earth's crust	Ultramafics	Basalt	Granodiorite	Granite	Shale	Limestone	soil
950	1300	2200	1200	500	850	1100	761

The distribution of major Mn deposits in the world is illustrated in Figure 8.7. There are three major types of Mn deposits: Sedimentary deposits, volcanogenic deposits and manganese nodule deposits. Of less economic importance are exhalative, metamorphic and residual Mn deposits (Harben and Kužvart 1996). The main Mn deposits are of Cenozoic age, but some important deposits are also known from the Precambrian.

The main Mn ore type (75% of world production) is of sedimentary origin and their weathered products. Depending on the primary depositional environment, Mn ores can be formed in marine, near-shore oxidizing environments or in closed basins at greater depth under anoxic conditions. In aerobic stable platform environments, the layered Mn ores are made up largely of Mn oxides and their weathered products. Manganese accumulations deposited at greater depth include carbonates, and at the bottom of the oceans, Mn nodules. Large sedimentary and meta-sedimentary Mn-Fe deposits are found in Ukraine, Georgia, Russia, India, China, S. Africa and Brazil.

Strongly weathered residual Mn deposits (supergene deposits) make up about 25% of world production. The main Mn minerals in the weathering environment are pyrolusite (β-MnO_2), psilomelane ($BaH_2O)_2Mn_5O_{10}$), braunite ($3Mn_2O_3 \cdot MnSiO_3$) and manganite ($Mn_2O_3 \cdot H_2O \cdot MnO(OH)$. Mixtures of these oxides are often termed 'wad' as they are difficult to differentiate in the field. They consist of relatively easily extractable Mn oxides and hydroxides that accumulated over deeply weathered Mn-rich rocks mainly in tropical countries. Extensive and rich deposits of this kind, so called supergene deposits, are located in Brazil, Gabon, Ghana, Australia and India.

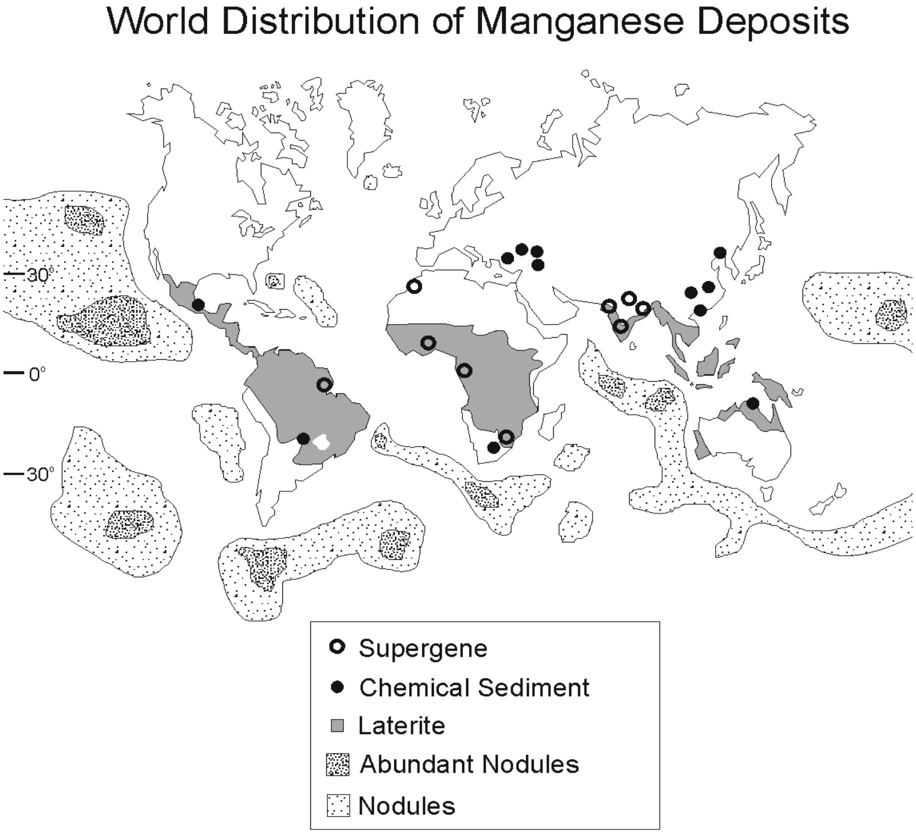


Figure 8.7. Distribution of major Mn deposits in the world (after Kessler 1994, with permission).

Volcanogenic Mn deposits are those where Mn-ore is in close spatial contact with volcanic rocks or interbedded with volcanic rocks. The Mn is thought to be released from volcanic exhalations or as a result of a reaction between volcanic exhalations and seawater. An examples of this kind of Mn deposit is found in Morocco.

In addition to the large Mn resource base on land, there are extensive, unexploited Mn resources at the ocean floors (Heath 1981). Extensive areas of the floor of the Pacific, Atlantic and Indian Ocean are covered with an evenly-spaced carpet of poly-metallic Mn-Ni-Co-Cu rich nodules. These nodules have a concentration of 20 -30% Mn-oxides and 2-3% combined other metals, and are found at the ocean floor at a depth of 5000 m or more. The size of these nodules is commonly a few centimetres across. The origin of these poly-metallic nodules is unclear, but may be related to submarine volcanic exhalations or seawater circulating through volcanic rock and liberating and transporting metals from the underlying oceanic crust (Margolis and Burns 1976).

Manganese for the fertilizer industry is processed into sulphates, oxides and chelates in solid and foliar forms. Finely-ground Mn-oxides are also suitable Mn carriers. On some alkaline soils Mn fertilizers are used in the foliar form at a rate of

1-5 kg ha^{-1}, for example on sugar beet. The amount of Mn used for Mn fertilizers is miniscule in comparison to the global resource base of Mn.

Most Mn is used in the iron and steel industry, but considerable amounts of Mn are also used for the production of dry cell batteries and the chemical industry. The world production of Mn metal was approximately 8 million metric tonnes in 2003 (US Geol. Survey 2004). The main producers of Mn metal in 2003 were South Africa (1,600,000 t Mn), Gabon (1 million t Mn), followed by Australia (990,000 t Mn) and Brazil (950,000 t Mn). The world reserves of Mn, as estimated by the US Geological Survey (2004), are 300 billion tonnes.

Molybdenum

The role of molybdenum in plants

Molybdenum (Mo), nicknamed 'moly', is an essential element for plant growth. Normal plants contain 0.8 - 5 mg Mo kg^{-1} dry weight. Deficient plants contain less than 0.5 mg Mo kg^{-1} dry weight. Molybdenum is essential for nitrogen fixation in legumes and it is an antidote for various heavy metal toxicities. Molybdenum is an important component of enzymes involved in the reduction of NO_3^- to NH_4^+. It is a structural component of the enzyme nitrogenase, which is involved in nitrogen fixation of legumes. One reason legumes tend to grow poorly on acid soils is the low availability of Mo for N-fixation under low pH conditions.

Molybdenum deficient plants often exhibit mottling and death of older leaves as well as suppression of lamina development and marginal necrosis. An example is 'whiptail' in cauliflower, a type of leaf deformation, curling upward of scorched narrow leaves or only the midrib of the leaves. Poor nodule formation on legume roots is another effect of Mo deficiencies. In citrus plants, Mo deficiencies are manifested by 'yellow spots'. Early symptoms of Mo deficiencies resemble that of N deficiencies with general yellowing and pale and yellow leaves.

Molybdenum deficiencies have been identified in many legumes, such as clovers, soybeans, alfalfa, beans and peas. Other crops sensitive to Mo deficiencies include members of the cabbage family, for example broccoli, brussels sprouts and cauliflower. Crops that are less sensitive to Mo deficiencies include maize/corn, beets, lettuce, oats, spinach and tomatoes. As a result of extensive research the application of small amounts of Mo for forage and pasture legumes on acid soils has become a common agricultural management practice in many parts of Australia. The contribution of Mo to Australia's agriculture is very considerable (Donald and Prescott 1975).

Plants can take up Mo in large quantities without apparent toxicity symptoms. However, high levels of Mo in the diet can create toxicity problems for certain animals. Elevated concentrations of Mo in an animal's diet can induce Cu deficiencies, resulting in a serious disease in ruminants called molybdenosis. The symptoms of molydenosis in cattle are stiffness of the back and legs and scouring which leads to dehydration, anorexia and, in some cases, death (Underwod 1962; Ward 1978; McDowell 2003). Other symptoms include stunted growth, dwarfism and bone deformation, diarrhea, loss of weight, depigmentation of hair and loss of libido (McDowell 2003).

Molybdenosis can be cured by providing affected animals with a source of Cu, whether through salt licks, injections (which are expensive) or feed supplements (often copper sulphate at 2 g day^{-1}). Some preventative measures include rotating the use of pastures, providing Cu-rich salt licks, or providing ongoing feed supplements (Stark and Redente 1990).

Molybdenum in soils

The overall mean concentration in soils of total Mo is 1.92 mg kg^{-1} (Ure and Berrow 1982). The soil Mo concentration is largely a function of the bedrock, the degree of weathering, and internal drainage (Reddy *et al.* 1991). Soils derived from granites commonly have higher Mo concentrations than soils derived from basalts or quartz sandstones. Mo concentrations are lowest in ultramafic rocks and highest in shales (Table 8.15). In general, Mo concentrations are low in highly leached, sandy, acid soils, and soils which are high in amorphous Fe and Al oxides.

Molybdenum occurs in soil solution mainly as an anion or non-specifically adsorbed to Fe and Al oxides. In soil solution, Mo occurs as the anion molybdate MoO_4^{2-}. Mo also occurs as soluble thiomolybdates (MoO_4^{2-}, $MoO_8S_2^{2-}$). The availability of MoO_4^{2-} is pH dependent. In oxidizing environments Mo occurs in the oxidation state Mo(VI) and under reducing conditions as Mo(IV). Unlike most other micronutrients, Mo is more available as the pH of the soil increases. Due to its negative charge, MoO_4^{2-} is not likely to be attracted to other negatively charged particles, such as clays and organic matter. The adsorption of Mo to hydrous iron and aluminum oxides is pH dependent and is highest in acids soils ($pH < 5.5$) where the Fe and Al oxides carry positive charges and react with the anion MoO_4^{2-}. Mo availability is thus low in acid soils, for example in Oxisols of Australia and Zimbabwe (Mengel and Kirkby 2001). Therefore, Mo is most available in moist soils with poor drainage and a pH above 6.5.

Molybdenum availability is a major constraint on the growth of legumes on acid soils. Mo deficiencies have been identified in many parts of the world, including the peanut/groundnut growing areas of West Africa, specifically in Senegal, northern Ghana, northern Nigeria and Niger. In Niger, peanut/groundnut growth in acid sandy soils with inherently low concentrations of Mo increased by 37-86% with the addition of small amounts of Mo (Hafner *et al.* 1992).

Response of plants to Mo is relatively good on soils over limestone parent materials. This however is not because of the Mo concentration in the parent material, but because of the enhanced availability of Mo in soils with alkaline pHs. The regional distribution pattern of Mo concentrations in legumes in the USA has been presented by Kubota (1976) (Figure 8.8).

Molybdenum availability can be overcome by increasing the pH, for example through liming. However, if the Mo concentrations in soils are very low from the onset then the addition of small amounts of Mo in the form of sodium molybdate or, in the foliar form, ammonium molybdate is recommended. In many places, seed treatment with Mo is used to correct Mo deficiencies. Application rates are commonly 100–500 g ha^{-1} (for sodium molybdate), or 100–200 g L^{-1} solution of ammonium molybdate. Molybdenized superphosphates and the application of seeds pre-soaked in 0.1% solution of sodium molybdate have been successfully used in legume growth and horticultural production in Australia (Donald and Prescott 1975). Seed priming (soaking seeds in water for 8 hours prior to sowing) and inoculation with *Rhizobium* proved a successful strategy to increase yields of chickpeas (*Cicer arietinum*) in acid soils of Bangladesh and eastern India (Johansen *et al*. 1997). While soil application rates of Mo are in the range of 100 – 500 g ha^{-1}, the application of Mo in seed priming is only 10 g Mo ha^{-1} (Johansen *et al*. 2005).

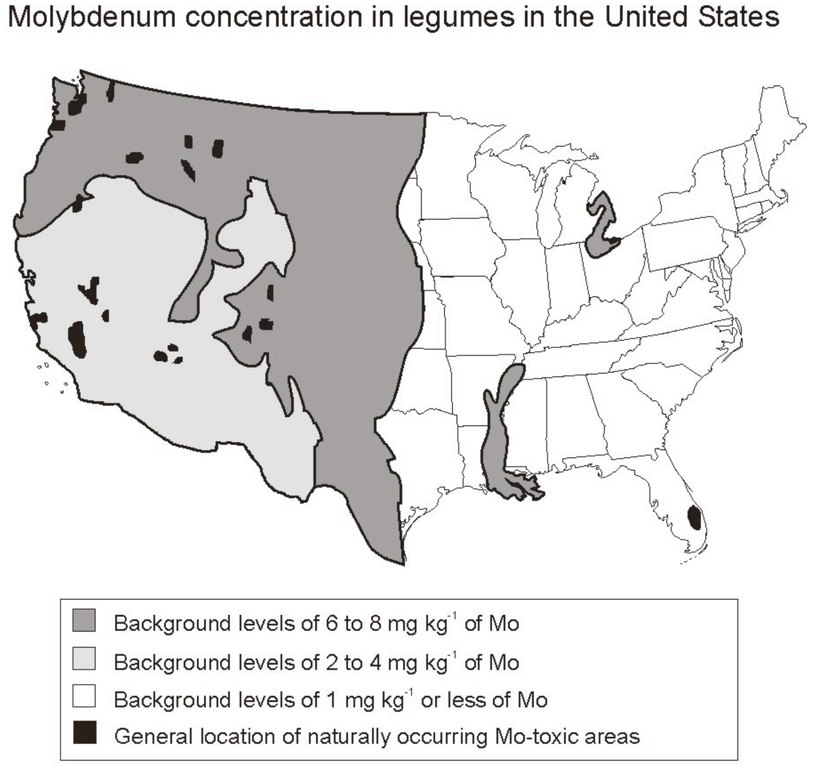


Figure 8.8. *Generalized map of Mo concentrations in legumes of the USA (modified after Kubota 1976).*

High Mo concentrations have been reported in the southwest of the United States from alluvial soils with high water tables, derived from Mo-rich granitic parent materials and from alkaline soils (Kubota 1976). A clear relationship between underlying geology, soil Mo concentration and incidence of Mo toxicity in grazing animals has also been demonstrated by Webb (1971) and Kubota (1976) from areas of central England and Oregon, USA, respectively.

Molybdenum geology

The average concentration of Mo in the upper continental crust is 1.1 mg kg^{-1} (Rudnick 2003). The main inorganic source of Mo in soils is from minerals and rocks. The concentration of Mo in granites is higher than that of more mafic rock types, e.g. basalts and ultramafic rocks (Table 8.15). In rocks, Mo occurs mainly in the sulphide form as molybdenite (MoS_2). This sulphide mineral oxidizes during weathering via a soluble intermediary phase (MoO_2SO_4) to the final form of H_2MoO_4.

Table 8.15. *Average abundance of total molybdenum in common rock types and soil (mg kg^{-1}) (Levinson 1974; Ure and Berrow 1982; Rudnick 2003).*

Earth's crust	Ultra-mafics	Basalt	Grano-diorite	Granite	Shale	Lime-stone	Soil
1.1	0.3	1	1	2	3	1	1.92

High concentrations of Mo are found in mineral deposits containing the mineral molybdenite (MoS_2). High grade Mo deposits (0.3 to 0.5% MoS_2), so-called 'porphyry moly' type and 'climax-type moly deposits' (Guilbert and Park 1986). They are similar to porphyry copper deposits but are found in atectonic extensional rift environments, further away from the colliding oceanic and continental plates. Molybdenite is also extracted as by-product from porphyry type copper sulphide deposits.

Molybdenite occurs frequently in pegmatites and in hydrothermal veins, mainly in high and medium-temperature hydrothermal vein deposits. Sediments deposited under sulphate-reducing unoxic conditions and rich in sulphides and kerogen are reportedly rich in Mo (Ripley *et al.* 1990; Calvert and Pedersen 1993). Elevated concentrations of Mo are also found in the Cu-shales (Kupferschiefer) of Central Europe and high concentrations of Mo have been reported from various coal deposits and sandstone-type U deposits (Smith *et al.* 1997) as well as marine black shale deposits, for example in Korea (Kim and Thornton 1993).

The distribution of economic Mo deposits is confined to only a few countries of the world (Figure 8.6). The total global production of Mo in 2005 was 163,000 metric tonnes (US Geological Survey 2006). The United States of America produced 56,900 t, followed by Chile (45,500 t), China (28,500 t), Canada (9,800 t), Peru

(9,700 t), Mexico (3,500 t) and Russia (3,000 t). The identified world molybdenum reserves are 18.4 million metric tonnes (USGS 2006).

Economically viable, large Mo deposits in the form of Cu and Mo porphyries are commonly found in specific belts related to converging plate margins. In general, they are spatially associated with Cu porphyry deposits. Figure 8.9 outlines the general area in which economically viable Cu and Cu-Mo ores are found.

There are many more occurrences of metal deposits in the world than the ones currently being mined. The Mo mines are usually large-scale operations, and often produce not only Mo minerals, but also other metals and minerals, such as copper. Molybdenum is commonly produced as a co-product from other mining operations, e.g. from copper deposits. Small vein type deposits containing the mineral molybdenite, not economically interesting for the mining industry, may be of interest for agricultural purposes. Libraries of national geological surveys usually list these small deposits and occurrences in reports and mineral inventories.

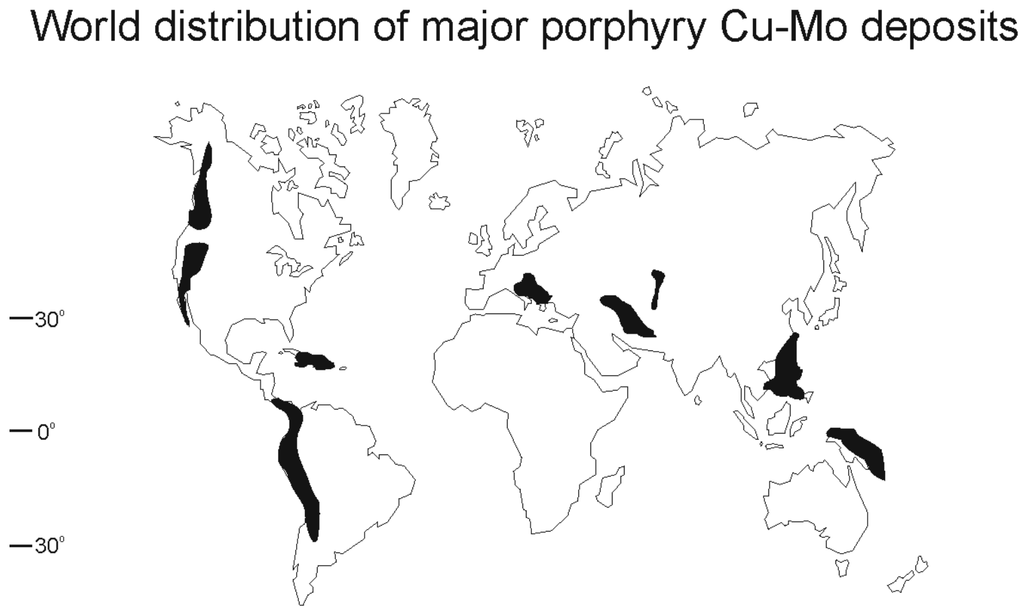


Figure 8.9. Global distribution of major Cu and Mo deposits in porphyry Cu-Mo deposits associated with converging plate boundaries.

Molybdenum is used principally as part of alloys in the steel industry, in cast irons and super-alloys, as well as in chemical applications, including catalysts, lubricants, and pigments. Some 30% of the apparent supply of Mo is recovered from recycled scrap steel and steel alloys (USGS 2004). The average price for Mo in 2003 was US$11.57 per kilogram (USGS 2004), in 2005 it reached US $72.07 per kilogram (USGS 2006).

The agricultural market for Mo is very small. For this market, Mo is recovered from large-scale mining and processing operations and converted into ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 2H_2O$) and sodium molybdate ($Na_2MoO_4\cdot 2H_2O$).

Nickel

The role of nickel in plants

The fact that nickel (Ni) is essential for plant growth has been established only relatively recently (Brown *et al.* 1987). Nickel is chemically closely related to Co and Fe. It is an important element for a number of bacteria (Marschner 2002) and is an essential element for the activation of the enzyme urease that break down urea into ammonia and CO_2 (Krogmeier *et al.* 1991; Gerendás and Sattelmacher 1997). Legumes that grow without Ni supply can accumulate toxic levels of urea in their leaves. A supply of small amounts of Ni enhances urea metabolism and thus reduces urea toxicity. Brown *et al.* (1987) showed that Ni is essential for the germination of barley seeds.

The total Ni concentration in crops is generally in the range of 0.1-1 mg kg^{-1}. Some plants, the so-called Nickel hyper-accumulator plants, can accumulate Ni in excess of 1000 mg kg $^{-1}$ (0.1% Ni). Nickel-hyper-accumulator plants that can accumulate high concentrations of Ni in their leaves include *Alyssum*, *Homalium*, *Hybanthus* (Brooks 1998). The potential of these plants to extract Ni from contaminated soils, so-called phyto-extraction has been described by McGrath (1998).

Initial studies of nickel 'mining', 'phyto-mining' from serpentine soils, has shown some promise and economic potential (Brooks and Robinson 1998). The economic feasibility of using the nickel hyper-accumulator plant *Streptanthus polygaloides* on ultramafic soils in California was demonstrated by Nicks and Chambers (1995, 1998). They showed the potential value of 'a crop of nickel' using the above mentioned plant. The economic return of growing, harvesting and extracting Ni from the 'bio-ore' (US\$ 400-500 ha^{-1}) was similar to that of a cereal crop. These data were based on a 1996 nickel price of US\$ 7.65 kg^{-1}. In September 2005 the Ni price at the London Metal Exchange (LME) was US\$ 15.55 kg^{-1}. The biomass of these plants and their yield of nickel derived from hyper-accumulator plants using phytomining techniques could potentially be increased by the addition of fertilizers and soil amendments (Bennett *et al.* 1998; Brooks and Robinson 1998).

Nickel in soils

The mean concentration of total Ni in soils is 33.7 mg kg^{-1} (Ure and Berrow 1982) but varies with the geological nature of their parent materials. While the total Ni concentration in soils developed from rocks rich in ferromagnesian minerals, such as ultramafic rocks and basalts are generally high (1000 to 5000 mg Ni kg^{-1}), soils developed on granites, sandstones and limestone are especially low in this element. Nickel is easily released from primary ferromagnesian minerals and is commonly adsorbed to Fe and Mn oxides and clay minerals in the soil. In tropical climates, Ni-rich lateritic soils often contain economically important Ni concentrations over ultramafic rocks. In fact, many Ni deposits in the world are Ni-laterite ore deposits, weathered residues (residual soils) of ultramafic rocks.

The application of the micronutrient Ni to soils is not an issue as there are virtually no soils reported that have Ni deficiencies. More pronounced and well known are Ni toxicities in soils, specifically in those soils overlying ultramafic, serpentine-rich rocks.

Serpentinites are rocks, which are formed through alteration processes of ultramafic rocks like dunite and peridotite. Serpentinite massifs are found in many parts of the world and can be recognized visually from far through their sparse vegetation. They are easily spotted on aerial photographs and satellite images. Serpentinite massifs are known in many parts of the world, from New Caledonia, Indonesia, New Zealand, Australia, England and Wales, Italy, France, Switzerland, the former Yugoslavia, Greece, Turkey, Zimbabwe, Cuba, the United States, Brazil and other countries. The serpentinite rocks are chiefly composed of the Mg silicates serpentine ($Mg_3Si_2O_5(OH)_4$. The soils developed on these serpentinite rocks are called serpentine soils and are famous for their soil infertility and minimal vegetation (Brooks 1987).

In serpentine soils the ratio of Mg to Ca is commonly very high, as are Fe, Ni and Cr concentrations (Rabenhorst *et al*. 1982; Brooks 1987). Serpentine soils are toxic to many plants and only a distinctive flora, the serpentine flora, has managed to cope with the unfavourable conditions of these soils. These specific serpentine-adapted plants, also known as serpentinophytes, have developed strategies to exclude Ni or complex Ni with organic acids and take up considerable amounts of Ni in their aerial part (Baker and Walker 1989).

Long-term application of contaminated sewage sludge can lead to increased levels of Ni in soils. Nickel contaminated soils are frequently found in the vicinity of Ni smelters and refineries as well as over contaminated mine sites. Kukier and Chaney (2004) describe the positive crop response of several plant species to the application of large quantities of liming material on acid, Ni-contaminated soils near a Ni refinery in Ontario, Canada.

Nickel geology

Nickel occurs in highly concentrated forms in ultramafic rocks (such as serpentinites) and, to a lesser degree, mafic rocks like basalts. Nickel replaces magnesium and iron in a number of ferromagnesian minerals, for example in olivine and pyroxene. Consequently there is a good correlation between Ni and Mg, Fe and Co in mafic minerals and rocks. Mafic and ultramafic rocks therefore have relatively high Co concentrations, considerably higher than felsic rocks like granite (Table 8.16). The Ni concentration is generally low in limestones, and very low in granitic rocks.

Table 8.16. *Average abundance of total nickel (mg kg^{-1}) in various rock types (Levinson 1974; Ure and Berrow 1982; Rudnick 2003).*

Earth's crust	Ultra-mafics	Basalt	Grano-diorite	Granite	Shale	Lime-stone	Soil
59	2000	150	20	0.5	70	12	34

Nickel in ultramafic rocks is incorporated in silicate minerals, as accessory minerals, in the sulphide form, in ultramafic and mafic rocks and as Ni-sulphide minerals in Ni-Cu and poly-metallic deposits (Guilbert and Park 1986). Considerable Ni resources are found in Ni-rich residual lateritic soils in tropical countries. Here, the nickel is largely found in the mineral garnierite.

Nickel is also concentrated, together with other metals, in manganese nodules found in deep oceans (Heath 1981).

Zinc

The role of zinc in plants

Zinc (Zn) is essential for the activity of enzymes, for example lactic acid dehydrogenase and alcohol dehydrogenase. Zn is an important activator of the enzyme RUBISCO (ribulose biphosphate carboxylase), which has an important role in photosynthesis. Specifically, Zn influences the production of the plant growth hormone auxin (Mengel and Kirkby 2001). Zn is also important for cell elongation and fruit and seed formation.

Zinc is vital for human and animal growth and development, for sexual reproduction, fetal development and a variety of functions of immune system defences (Prasad 1998). Zinc is also important to skin cell development and healing of wounds. It reduces the severity and duration of acute diarrhea and lowers the prevalence of pneumonia in children (Black 2003). Low intake of Zn-rich foodstuff and the consumption of foods that contain high phytate (which inhibits Zn absorption) are widespread in some regions of the world and have grave consequences for human populations. Severe Zn deficiencies result into growth retardation (dwarfism) and immune system imbalances (Prasad 1998). Dietary sources of Zn are seeds, for example pumpkin seeds, meat, poultry, eggs, fish and other seafood.

Zinc is taken up by plant roots in the form of the cation Zn^{2+} and transported in the xylem as a free cation or bound to organic acids. Concentration of zinc in plants ranges from 20–60 mg Zn kg^{-1}.

Zinc deficiencies in plants can be caused by low concentrations of Zn soils and parent material. As Zn is not very mobile within the plants, Zn deficiencies become visible first in younger leaves. Zinc deficiencies are commonly observed in plants by stunted growth and shortened internodes. In maize/corn zinc deficiency can be detected at the four to six leave stage of growth. This deficiency shows broad whitish stripes on both sides of the mid-rib in the second or third leave from the top. Zn deficiencies are commonly noted as interveinal chlorosis of new leaves, ‘rosetting’ (formation of clusters of small leaves) of fruit trees such as citrus and nut trees, and ‘bronzing‘ of rice. Zinc deficiencies in rice can be induced when the concentration of dissolved ferrous iron is very high in the soils and iron plaques, which adsorb zinc, form outside the roots (Zhang *et al*. 1998).

Zinc deficiencies in plants are often mistaken as Mg deficiency with striping between the veins. However, Mg deficiencies start at the bottom leaves while Zn deficiencies are mainly seen in the top half or mid-section of the plants.

Zinc requirements are high in plants such as rice, beans, maize/corn, onions, grapes, citrus and fruit trees, soybeans, and sunflowers. Zinc needs are relatively low in cereals like oats and rye, as well as peas, cabbage, carrots and lettuce.

Zinc in soils

The concentration of total Zn in soils ranges from 1-2000 mg kg^{-1}, but the overall soil mean is, similar to the crustal mean, 60 mg kg^{-1} (Ure and Berrow 1982) (Table 8.18). Zn occurs in soils in only one valence state, as Zn^{2+}. It occurs in soils as Zn^{2+} in solution and complexed by organic ligands and adsorbed onto hydrous Fe and Mn oxides. Goethite adsorbs more Zn than hematite because of the presence of more hydroxyl groups on goethite (Harter and Naidu 1995). Total Zn concentrations in soils can often be correlated with clay content, iron concentrations and organic matter. Considerable amounts of Zn can accumulate in Zn-organic complexes. Zinc deficient, marginal and sufficient concentrations as determined by extraction with DTPA (diethylenetriaminepentaacetic acid) are 0-0.5 mg kg^{-1}, 0.6-1.0 and > 1.0 mg Zn kg^{-1} soil respectively (Havlin *et al.*1999).

The availability of Zn^{2+} in soils is not only dependent on the kind and intensity of weathering of the parent materials, but also on interaction of Zn in solution with other nutrients (for example P) and on environmental growth conditions (soil pH, temperatures, and redox conditions in soils), as well as clay content, iron oxide and organic matter content in soils. It is common that soils containing high concentrations of P tend to be deficient in available Zn. It is well known that the application of high amounts of P can induce Zn deficiencies in plants. Mengel and Kirkby (2001) show that excess P results may affect the physiological Zn availability of plants. The mechanism of the phosphorus-zinc interaction is very complex. Excessive concentrations of P reduce the availability of zinc in root cells. Also, high P concentrations in soils commonly reduce the rate of mycorrhizal infections and may be responsible for reduced Zn uptake. In order to counteract this tendency, some phosphate fertilizers are supplemented with added Zn. Zinc application rates range from 0.5 - 20 kg Zn ha^{-1} yr^{-1}. Zinc is commonly applied together with phosphate fertilizers to overcome the "P-Factor."

Zinc is more available under oxidizing than anaerobic conditions. Consequently, Zn deficiencies are common in submerged soils, for example lowland rice soils. The pH of soils has a dramatic effect on the availability of Zn. Availability is highest in soils below a pH of 7. As pH levels increase the availability of Zn^{2+} decreases. Liming to pH levels > 8 can severely reduce the availability of Zn. Alkaline 'vertisols' are known for their deficiency in Zn, for example in Australia (Donald and Prescott 1975).

In order to correct Zn deficiencies in soils, Zn fertilizers, such as zinc sulphate monohydrate ($ZnSO_4 \cdot H_2O$), zinc oxides or Zn-chelates can be applied. Under unfavourable pH conditions, Zn fertilizers may be applied in the foliar form. Another method to overcome Zn deficiencies is to soak of seeds in water and Zn-sulphate (priming). Optimum solution concentrations of 0.4% Zn for wheat and 0.05% Zn for chickpeas respectively proved successful to overcome Zn deficiencies in alkaline soils of Pakistan (Harris *et al.* 2005). To overcome zinc deficiencies in trees, zinc nails were driven into trees in parts of Australia with marked Zn deficiencies (Donald and Prescott 1975). The trees are able to absorb Zn from the nails and recover normal growth rates. Pine plantations are often sprayed with zinc sulphate monohydrate ($ZnSO_4 \cdot H_2O$) containing 35% Zn to prevent Zn deficiencies from occurring (Donald and Prescott 1975).

Zinc geology

The average concentration of Zn in the continental crust is 72 mg kg^{-1} (Rudnick 2003). Zn occurs predominantly in silicates such as amphiboles and biotite and in ion oxide minerals, specifically magnetite. Zn can substitute for Fe^{2+} and Mg^{2+} in the structures of minerals as the ionic radius of the divalent Zn^{2+} is very close to the ionic radius of divalent Mg^{2+} and Fe^{2+} (Table 8.17). Magnetite (Fe_3O_4) is one of the minerals with the highest concentrations of Zn and the distribution of magnetite and Zn in rocks and soils is often well correlated. In a concentrated form, Zn occurs in the sulphide form as sphalerite (ZnS).

Silica-rich felsic rocks such as granites contain lower concentrations of Zn than basaltic rocks (Table 8.18). This is likely due to the fact that Zn^{2+} can replace Mg^{2+} or ferrous iron (Fe^{2+}) in the structures of many Fe-Mg silicate minerals. These ferromagnesian minerals are more common in mafic rocks than in felsic rocks. Many Fe- and Mg-rich silicates can contain considerable amounts of Zn, for example in biotite, olivine and pyroxene.

Table 8.17. *Ionic radius of Zn^{2+}, Mg^{2+} and Fe^{2+} (1 Ångstrøm = 10^{-10} m).*

Zn^{2+}	Mg^{2+}	Fe^{2+}
0.74 Å	0.78 Å	0.74 Å

Table 8.18. *Average abundance of total zinc (mg kg^{-1}) in various rock types (Levinson 1974; Ure and Berrow 1982).*

Earth's crust	Ultra-mafics	Basalt	Grano-diorite	Granite	Shale	Lime-stone	Soil
72	50	100	60	40	100	25	60

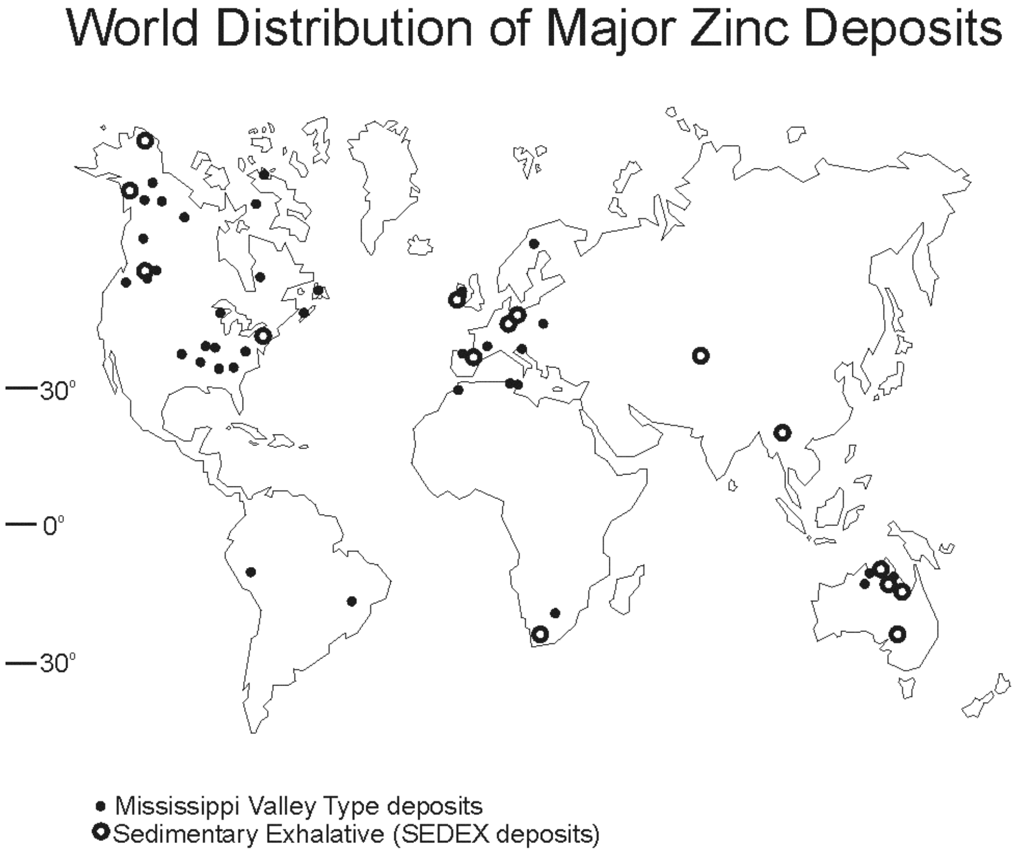


Figure 8.10. *The distribution of major Zn deposits in the world. (excluding non-sulphide deposits). (after Kessler 1994, with permission).*

The distribution of major Zn deposits in the world is illustrated in Figure 8.10. Zinc originates, like most nutrients, from minerals and rocks. In a concentrated form, Zn is found in the sulphide mineral sphalerite (ZnS), which occurs almost entirely in hydrothermal ore deposits. Zinc sulphide deposits, often found together with PbS deposits, are associated with volcanogenic massive sulphide deposits, or in hydrothermal lead-zinc deposits known as Mississippi Valley Type (MVT) deposits, or in sedimentary exhalative (sedex) deposits in many parts of the world (Guilbert and Park 1986). Early sulphide-rich magma accumulates are generally low in Zn, in contrast to late hydrothermal veins. In these hydrothermal veins, ZnS is commonly associated with Cu and Pb sulphides. A compilation of non-sulphide zinc deposits in the world has been presented by Hitzman *et al.* 2003)

The mine production of Zn in 2003 was 8.5 million metric tonnes. The main producing countries are China (1.7 mill. t), Australia (1.6 mill. t), Peru (1.25 mill. t), Canada (1 mill. t) and the USA (0.77 mill. t). Global identified Zn resources are 1.9 billion metric tonnes (US Geological Survey 2004). In 2003, some 370,000 t were recycled and recovered from waste and scrap US Geological Survey 2004). The average price for Zn in 2003 was 36-39 cents per pound, in late 2005, the zinc price reached 63 cents per pound (US Geological Survey 2006).

Common dolomitic limestone contains higher concentrations of Zn than calcareous limestone because the Mg ion in the dolomite structure can be replaced with a Zn ion. Upon weathering Zn is easily adsorbed by clay minerals or organic matter. Plant available Zn occurs to a large extent in the form of zinc-organic complexes. Zinc and cadmium have some similar mineralogical and chemical properties and thus ZnS mineralizations occur commonly with impurities of Cd, which is toxic to plants and humans. Consequently, Zn applications to soils and Zn rich soils should be tested also for Cd.

For agricultural applications, Zn is processed into $ZnSO_4$, ZnO, or Zn-chelates. In these forms Zn is applied to Zn deficient soils and plants in the range of 4 kg ha^{-1}, which is effective for a period of 3-4 years.

8.3 Beneficial elements

In the following section, five nutrient elements will be introduced that have ‘beneficial’ characteristics. They are not essential for plant growth but are beneficial in the sense that they can have favourable effects on plant growth and may be essential for some plants but not all as well as for animal and human nutrition. The selected elements are cobalt, selenium, silicon, sodium and vanadium.

Cobalt

The role of cobalt in plants and animals

In general, cobalt (Co) is non-essential for plant growth, but it is essential for *Cyanobacteria* (blue-green algae) and for the growth of N-fixing bacteria from the genus *Rhizobia* in root nodules of legumes (Mengel and Kirkby 2001). Cobalt is thus important for N-fixation in leguminous plants. It is essential for the formation of vitamin B_{12} as it forms the centre of the B_{12} complex.

Plants take up cobalt as cation Co^{2-} from soil solution. The deficiency, sufficiency and toxicity levels in crops are, according to Bennett (1996), less than 0.2 mg kg^{-1}, 0.2-0.5 mg kg^{-1} and >0.5 mg kg^{-1}. Leguminous crops like beans, as well as other crops like cotton and mustard, are susceptible to Co deficiencies.

Cobalt is important for animal nutrition especially ruminants as it is an integral part of Vitamin B_{12} which is essential for the metabolism of these animals. Forage grasses commonly contain lower concentrations of Co than leguminous forage. Therefore, ruminants that graze on forage grasses require Co supplementation to avoid becoming deficient in Co. Symptoms of Co deficiency include loss of appetite, lack of growth and reduced reproductive vigour (McDowell 2003).

Sheep are very sensitive to both Cu toxicities and Co deficiencies. Without adequate Co supplies in their diet, sheep are subject to the muscular ‘wasting disease’. In New Zealand, this deficiency-induced disease is called ‘bush-sickness;’ in Australia it is also called ‘coast disease’, and in Kenya it is called ‘Nakuruitis’ (McDowell 2003). Cobalt deficiencies in sheep typically produce a loss of appetite, reduced sexual drive and muscular atrophy. The condition of the ‘wasting disease’ in sheep was first recognized in New Zealand. Farmers initially believed that the wasting effect was due to Fe deficiencies and consequently fertilized grazing land with Fe. And indeed, this improved the health of their sheep. But the Fe contained impurities and when the farmers switched to a cleaner source of Fe, the wasting disease re-occurred. Finally, as a result of research in the 1960s and 1970s, farmers turned to Co as they realized that the vital element was not Fe but the ‘trace element’ Co (McDowell 2003). To correct a Co deficiency in sheep, farmers can either feed the animals with Co-enriched supplements, such as Co-fortified salt blocks or Co-bearing rumen pellets, or fertilize the pasture area.

Cobalt in soils

The mean concentration of total Co in soils is 12 mg kg^{-1} (Ure and Berrow 1982) but varies with the geological nature of their parent materials. Cobalt in soils is derived primarily from weathering of ferromagnesian minerals where Co substitutes for Mg. After liberation from the primary minerals Co is often precipitated in the form of oxides, hydroxides or carbonates, all of which are relatively insoluble at neutral to alkaline pH conditions. Strong specific adsorption of Co takes place on Mn oxides, for example on Mn nodules and the Fe hydroxide goethite, as illustrated in Figure 8.11, especially at high pH levels.

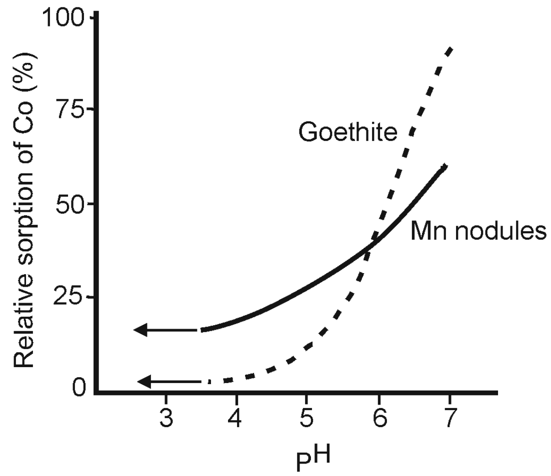


Figure 8.11. *Effects of soil pH on sorption of Co on Mn nodules and goethite (α-FeOOH) (after McKenzie 1975).*

Cobalt is more available in acid soils than in alkaline soils. But as many of the acid soils are also highly leached even these soils are commonly low in Co. Since Co does not accumulate in organic matter, organic rich soils and peat soils also tend to be low in Co. Legumes deficient in Co exhibit severe restriction of growth because they are dependent on Co for symbiotic nitrogen fixation.

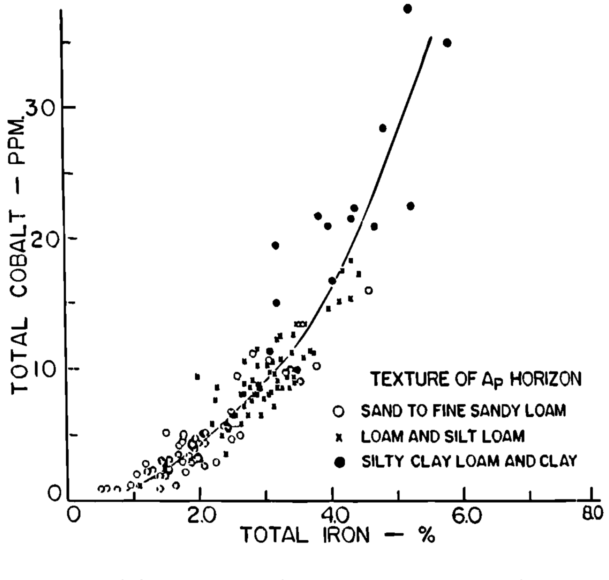


Figure 8.12. *Concentration of Co in soils of New England as a function of Fe and texture (source: Kubota 1972).*

Soils that contain less than 0.01 mg kg^{-1} Co are considered deficient for plant growth. In parts of the NE USA, soils exhibit low Co concentrations (Kubota 1972). Sandy soils of the lower Atlantic coastal plains and areas that are covered with glacial drift derived from the granites of the White Mountains contain low levels of Co. There is correlation between Co concentrations and Fe in these soils. The highest Co concentrations are found in soils rich in clay (Figure 8.12).

Cobalt geology

In nature, there are no common rock-forming minerals of cobalt. However, Co (and Ni) replaces Mg and Fe in a number of ferromagnesian minerals, for example in olivine and pyroxene. Consequently there is a good correlation between Mg and Fe and Co in mafic minerals and rocks. Mafic and ultramafic rocks therefore have relatively high Co concentrations, considerably higher than felsic rocks like granite (Table 8.19). High Co accumulations are also found in sulphide ores and in Mn nodules on ocean floors. In sedimentary rocks, the distribution of Co is closely correlated with that of Fe. Soils developed from granites tend to be low in Co, in particular if they are highly leached. Cobalt concentrations are commonly higher in soils overlying ultramafic and mafic rocks.

Table 8.19. *Average abundance of total cobalt (mg kg^{-1}) in various rock types (Levinson 1974; Ure and Berrow 1982; Rudnick 2003).*

Earth's crust	Ultra-mafics	Basalt	Grano-diorite	Granite	Shale	Lime-stone	Soil
26.6	150	50	10	1	20	4	12

Cobalt is currently extracted from three major ore types: from sedimentary ores, from hydrothermal vein deposits and as by-products from sulphide and laterite nickel deposits. The major Co deposits are found in the 900 million year old sedimentary succession of the 'Copper Belt' of the southern part of the Democratic Republic of Congo and northern Zambia. Here. the sediments are enriched in both Cu and Co, with Co concentrations reaching 0.4%. The ore is vertically and horizontally zoned with various types of copper ores. The cobalt rich ores were probably precipitated under anaerobic conditions far away from the old shoreline (Fleischer *et al*. 1976).

The formation of these Cu and Co ores in carbonaceous sulphide rich shales have long been debated by geologists but seem to be related to some chemical precipitation in shallow mud pools not far away from the ancient shore line. These sediments were subsequently folded and metamorphosed. Similar, but not as rich sedimentary Cu ores with small amounts of Co are those of the 'Kupferschiefer', the 'copper shale' in Central Europe and sediment hosted Cu deposits in Montana, Idaho and southern Canada (Boyle *et al.* 1990).

World cobalt production in 2005 was 52,400 metric tonnes, with the Democratic Republic of Congo (16,000 t), Zambia (9,000 t), Australia (6,600 t), Canada (5,700 t) and Russia (5,000 t) being the largest producers. Identified world Co resources are 13 million tonnes (US Geol. Survey 2006).

Most of the Co is produced as a by-product from copper mining and metallurgical processing, especially from sedimentary Cu-Co ore deposits, such as that mined in Zambia and the Democratic Republic of Congo. Cobalt is enriched during mineral processing of these ores. Cobalt is also recovered as by-product from Ni-(and Co-) bearing sulphide and laterite deposits, for example in Australia, Cuba, Russia and Canada. Small amounts of Co are also found in rather restricted vein-type deposits in various parts of the world, including the famous and longtime mined silver and cobalt-bearing veins of the Cobalt District in Canada. Other potential sources of Co are those of the poly-metallic manganese nodules found at the bottom the major oceans (Margolis and Burns 1976). It can also potentially be extracted and recovered from Co hyper-accumulator plants through the process of ‘phyto-mining’ (Brooks and Robinson 1998). The spot price of refined cobalt reached US $14.20 per pound in June 2006.

Cobalt is used in agriculture in various forms, for example as Co-enriched phosphate fertilizer designed specifically for sheep-grazing lands. Cobalt can also be administered to sheep through Co-enriched feed, Co-enriched vitamin pills or provided through Co-containing salt licks (McDowell 2003).

Selenium

The role of selenium in animal and human health

Selenium (Se) is taken up by plants as selenates, similar to sulphates. Selenium follows the same or similar pathways and metabolic processes as sulphur. Once selenate has entered the cell it is reduced to selenite and subsequently incorporated into organic Se-compounds, mainly Se-bearing amino acids, such as Se-methylselenocysteine, selenocystathione and Se-methyselenomethionine (Mikkelsen *et al*. 1989).

Selenium is important for animal nutrition and deficiencies of Se can result in a form of nutritional muscular dystrophy (NMD) in livestock, widely known as ‘white muscle disease’. Other signs of Se deficiencies in sheep and cattle are premature births or abortions of calves or lambs, as well as growth deficits and infertilities (Maas 1998). In the past, this Se deficiency-related disease was widespread in parts of North America, Australia, New Zealand and Europe (Combs and Combs 1986; Maas 1998). The forages on which livestock with NMD was feeding was generally lower than 0.1 mg Se kg^{-1} in the dry mass. The distribution of Se deficient forages and food grains in North America is shown in Figure 8.13.

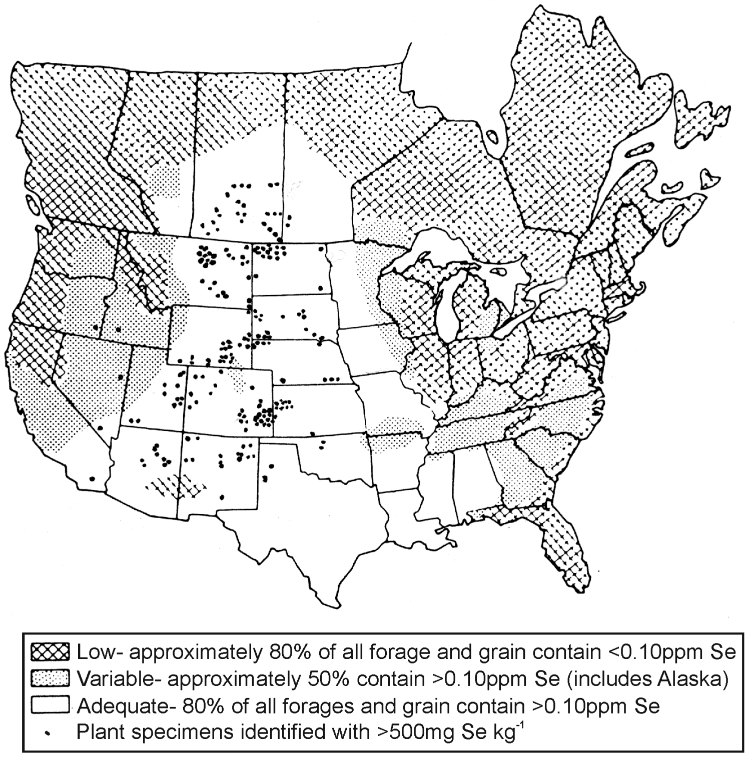


Figure 8.13. Regional distribution of Se concentration in forages and food grain in North America (Source: Kubota and Allaway 1972).

An extensive survey of soils in the People's Republic of China revealed large areas with severe Se deficiencies (Liu *et al.* 1986). The Keshan disease in Keshan County, Heilongjiang Province has been studied extensively as it is in part related to Se deficiencies in soils and vegetation (Tan *et al.* 1982; Su and Yu 1983; Jackson 1988; Fordyce 2005). This human Se deficiency disease is largely a heart disease, which manifests itself in children and women in the child-bearing age. Symptoms of this disease are a significantly enlarged heart. The Se concentrations in cereal grain in areas where Keshan Disease is prevalent is 0.005-0.007 mg kg^{-1} as compared to Se adequate areas (0.020 – 0.040 mg kg^{-1}) and areas with high Se status (0.5-28.5 mg kg^{-1}). The corresponding blood serum concentrations are 0.021 mg L^{-1} (low Se area), 0.095 mg L^{-1} (Se adequate area) and 3.2 mg L^{-1} in areas with selenosis respectively (Yang *et al.* 1983).

Se deficiencies in grazing animals can be treated in different ways. One way is through direct Se supplementation in which the animals are given Se compounds either orally (e.g. in the feed) or directly into the forestomach of ruminant animal as Se-pellets. These two methods are used predominantly in the United States and Australia.

The addition of Se-based fertilizers is recommended in Finland, where the soils are rather homogenously Se deficient (0.2-0.3 mg Se kg^{-1} dry matter). In 1990, the Finish government made it compulsory to add 6 g Se per hectare in the form of Na-selenates added to fertilizers. This intervention raised the Se concentrations in grain and fodder and finally in blood and serum of humans. The Se intake in Finland's population increased threefold within a period of two years bringing the Se intake of a whole population to the recommended Se level (Aro *et al*. 1998).

Other Se-rich sources (for example fly ash) or foliar application to Se deficient plants could also be considered to increase the Se concentration in soils and plants. In the case of endemic Se deficient nutrition, e.g. in Keshan and other places with low Se concentrations in soils, other strategies, such as direct food supplements (in the form of pills) or by using Se-rich food (for example broccoli) from other than local sources are advised.

Selenium in soils

The total Se concentrations in soils vary from 0.1 to 2 mg kg^{-1} (Fordyce 2005). Selenium enters the soils mainly as a result of weathering of Se-containing rocks and minerals. The Se content in soils is largely a function of the underlying rock formations. But other Se inputs also contribute to the total Se concentrations in soils, specifically inputs from volcanic ash and fine particles from coal burning operations, as well as through the application of some fertilizers and irrigation water. Total Se concentrations in soils vary. The mean concentration of total Se in soils from around the world is 0.4 mg kg^{-1} (Ure and Berrow 1982; Fordyce 2005), but the total concentration is less important than the plant available form, which is commonly only a small fraction of the total Se in soils.

Selenium can replace sulphur in many sulphide minerals, for example in pyrite. In soils, Se occurs in soils in organic and inorganic forms, mainly cationic forms. The four major solid forms in soils are selenate (SeO_4^{2-}), selenite (SeO_3^{2-}) selenide (Se^{2-}) and elemental Se (Se^0). Selenium also occurs in volatile forms such as dimethyl selenide and dimethyl diselenide.

Selenite is the predominant form found in acid soils under aerobic conditions. However, it is easily adsorbed by iron oxides or forms ferric selenites, and is only slightly available. Plants that contain toxic concentrations of Se are rarely found on acid soils. Selenate is the most prominent form of Se found in aerated alkaline soils. This is the most direct source of Se for plant uptake and is the most available form responsible for Se toxicities. Selenate rich alkaline soils are found predominantly under arid climatic conditions overlying seleniferous geological formations. Removal and subsequent oxidation of seleniferous shales associated with pyritiferous coal, uranium and in some cases phosphate rocks can result in pollution due to excess of available of selenates. Toxic concentrations of Se are mainly found in alkaline, well-aerated soils.

Under anaerobic conditions and with the help of soil micro-organisms, selenates and selenides can be reduced to the solid but insoluble forms of selenide and elemental selenium. Microbial reduction of selenides and selenates can also produce volatile forms of Se, for example dimethyl selenide, which can be easily released into the atmosphere. Various methods have been tested or have been proposed to overcome Se toxicities in soils, either naturally enriched in Se (from Se-rich parent material) or anthropogenically polluted soils and waters, for example from tailings of coal mining operations or certain phosphate rock and associated shale deposits. These methods reach from constructed wetlands to phytoremediation and microbial reduction and volatilization of Se-complexes (Terry and Zayed 1998).

In contrast to Se deficiencies in soils, vegetation and finally animals and humans, there are serious problems related to Se toxicity. In several countries including the United States a fatal disease was recognized on alkaline rich soils. It was originally called the ‘alkali disease’ as it was assumed that it was caused by animals drinking alkaline water. However, it was later recognized that the alkali disease is caused by large intakes of Se from seleniferous plants that grow on Se-rich soils. The Se toxicity has been noted mainly in those animals, horses, cattle, and sheep that are grazing on forages that contain Se in excess of 5 to 40 mg kg^{-1} dry matter (McDowell 2003). Symptoms of Se toxicity are deformed hoofs, loss of hair and mane, lameness and lack of vitality. Alkali disease of livestock is generally associated with the consumption of Se-rich grains and grasses (Rosenfeld and Beath 1964).

Another sickness related to the forage of even larger dosages of Se from seleniferous plants are called ‘blind staggers’ as the animals are stumbling and staggering as if they were blind, with ears drooped. These animals consumed so-called Se-accumulator plants, which can accumulate several thousand mg Se kg^{-1}. There are a number of Se-accumulator species, for example *Astralgus* (milk vetch), *Stanleya*, *Xylorrhiza, and Oonopis* that have the ability to convert large amounts of Se from the soils or geological resources into available forms. Plants that contain more than 4 to 5 mg Se kg^{-1} are considered potentially toxic to animals. These accumulator plants commonly grow on specific soils overlying shales, and glacial till derived from shales or Se-contaminated pyritiferous and clay rich material. The seleniferous soils are generally neutral to alkaline in reaction and well drained.

Selenium geology

The average abundance of Se in common igneous rocks (Table 8.20) shows that Si-rich rocks like granites and rhyolites have low concentrations of Se in comparison to mafic and ultramafic rock types. High concentrations of Se are commonly found in sediments especially shales, and in some limestones. Very high concentrations of Se (up to several hundred mg kg^{-1}) are found in Cretaceous shales in the central western United States. Other areas with known naturally occurring high Se concentrations and chronic or acute selenosis are described by Rosenfeld and Beath (1964) from Canada, Colombia, Ireland, Israel, South Africa and Australia. Most of these highly seleniferous occurrences are related to the underlying rocks and climatic factors.

Table 8.20. *Average abundance of total Se (mg kg^{-1}) in various rock types (Levinson 1974; Ure and Berrow 1982; Rudnick 2003, and others).*

Earth's crust	**Ultra-mafics**	**Basalt**	**Grano-diorite**	**Granite**	**Shale**	**Lime-stone**	**Soil**
0.13	0.022	0.103	0.059	0.005	0.6	0.08-0.1	0.4

The global consumption of Se is about 2,700 t (USGS 2005). The price of Se has climbed from about US$ 5 per pound in 2003 to US$10.50 per pound at the end of 2004 (US Geological Survey 2005). The main use of Se is in the glass industry (35%), followed by metallurgy (24%), chemical and pigment industry (20%), electronic industry (e.g. photocopier) and others. The use of selenates (mainly Na-selenates) as additives to fertilizers and their use as dietary supplements for livestock and humans are included in the category of chemical uses. The principal use of Se in the pharmaceutical industry is in shampoo to control dermatitis and dandruff.

Selenium does not occur in high enough concentrations in rocks and minerals to justify for mining them solely for Se content. Selenium is recovered mainly as by-products from refining copper ores, specifically from the slimes left behind at the anodes in electrolytical copper refining.

Environmental issues

Selenium is rarely found in toxic concentrations in surface waters. A well researched exception is the case of the San Joaquin Valley in California where the irrigation of seleniferous soils increased the Se load in downstream water systems. Selenium enriched irrigation runoff was diverted to evaporation ponds and managed wetlands in the Kesterton National Wildlife Refuge where it caused, amongst others, high concentrations of Se in fish, frogs and other animals and deformities and mortalities in water fowl (Ohlendorf *et al*. 1986).

Naturally occurring high concentrations of Se are found in pyritiferous shales associated with coal deposits and sedimentary phosphates. The recent case of Se poisoning of animals grazing in phosphate mine areas in Idaho, USA, has attracted some public attention. The average Se concentration in some PR deposits of the Permian Phosphoria Formation in Idaho is 30 mg kg^{-1} in PR but can reach as high as

800 mg kg^{-1} (United States Geological Survey 1977). The Se concentration in shales and mudstones associated with these PR deposits averages 14 mg kg^{-1} but can reach maximum levels of 1500 mg kg^{-1}. These high concentrations of Se, particularly when available as soluble selenite or selenate are a matter of health and environmental concerns. The death of a few horses and sheep as a result of grazing on highly seleniferous plants from this area highlighted these environmental and health concerns. It should be noted however, that the use of seleniferous phosphate rock resources can also have positive effects, particularly in areas where Se concentrations in soils are inherently low, such as in areas in sub-Saharan Africa. The burning of high S-coal with associated high Se concentrations is expected to contribute to aerial deposition of Se over large areas. Fly ash commonly contains considerable amounts of Se.

Silicon

There is a surprising discrepancy between abundance of silicon (Si) in rocks, soils and plants and its importance given in plant nutrition and its application in agriculture and horticulture, for example in nutrient solution culture (Epstein 1999). It is also surprising how few groups of organisms have actually utilized large parts of this omnipresent element in nature.

In an important review article Epstein (1999) questions the definition of essentiality for Si. Silicon is not regarded as essential nutrient element (as yet) as no association of Si to metabolic or physiological activities could be proven. Increasing evidence shows that plants can fulfill their life cycle without Si, albeit with reduced growth, and that Si might be essential for lignin synthesis (Epstein 1999). Epstein calls silicon a ‘quasi-essential’ element.

The role of silicon in plants and animals

The total amount of Si in plants is similar to those of the major nutrients Ca, Mg, and P, but the abundance of Si within higher plants differs sharply. In some plants, such as rice (*Oryza sativa*) and horsetail (*Equisetum arvense*) the Si content is very high, reaching 10-15% dry weight. In general, the Si content of *Monocotyledoneae* (monocots) like grasses and wheat is by far larger than that of *Dicotyledoneae* (dicots) such as soybeans.

Jones and Handreck (1967) proposed a division in plants into three groups:

- members of the *Cyperaceae* such as horsetail and wetland *Gramminaea* such as wetland rice with the highest Si concentration (10-15%),
- dryland grasses such as sugarcane and most of the cereal species like rye and oats (1-3%),

- dicots, especially legumes (<1%).

Plants take up Si in the form of silicic acid but the exact uptake mechanism is still unclear (Mengel and Kirkby 2001). Some plants actively take up Si, e.g. Si accumulators, while others, like many dicots actively exclude Si at the root surface. When Si has entered the plants, the Si is deposited predominantly in cell walls in the form of amorphous silica, $SiO_2 \cdot nH_2O$ as so-called opal phytoliths (Sangster and Hodson 1986). Detailed description of the types and shapes of opaline silica depositions in various grasses and plants have been provided by Parry and Smithson (1964) and Carnelle *et al*. (2001).

The Si deficiency and sufficiency level of plant materials have been rated by Bennett (1996) as <0.2% and 0.2-2.0% respectively. Si is generally not regarded as toxic for plants.

The addition of silicon to soil solution can have positive physical and chemical effects on plant and animal growth. Epstein (1999) and Ma (2004) summarize the effects of Si that enhance the resistance of plants to biotic and abiotic stresses.

The addition of silicon has physical and chemical functions for plant growth. The main physical function of Si in plants is the increase in mechanical strength of the leaves and stem through the deposition of silica in cell walls. The added strength prevents the plants from ‘lodging’ after heavy winds and the reinforcement of cell walls by silica protects some plants against diseases and pests (Epstein 1999). Ma *et al*. (2001) have shown that the incorporation of Si in cuticle cells reduce transpiration rates in rice by 30% and thus contribute to the reduction of drought stress of this crop. The application of Si to soils for rice cultivation resulted in increased resistance to insect pests, it promoted photosynthesis through reduction of excessive transpiration and enhanced light interception (Kato and Owa 1997). Also cucumber, containing high concentrations of Si, is more efficient in light interception (Adiata and Besford 1986).

The use of soluble Si not only contributes to enhance the physical defenses of plants like rice, sugarcane, and cucumber, it also has chemical functions that enhance the plants’ resistance to stresses, including fungal stress.

Silicon has been proven to be essential for animals. It is essential for growth and skeletal development of chicken and rats (Schwarz and Milne 1972). High silicon concentrations in animals and humans are found in connective tissue, such as tendons but also in the aorta and in tracheae (Carlisle 1986; Underwood and Suttle 1999).

Silicon is an essential constituent of diatoms, small unicellular floating aquatic algae that dependent upon Si for growth and formation of their siliceous skeletons, or frustules. It has been established that diatomites require Si not only for the formation of the silica frustules but also for a number of other complex metabolic processes (Sulivan and Volcani 1981).

Silicon in soils

Although the total Si concentration in soils is in the percent range, with a mean concentration of 33% (Ure and Berrow 1982), it is not the total SiO_2 that matters for soil solution Si and related reactions in the soil, it is the available Si portion, the Si in the form of silicic acid (H_4SiO_4) that is important. Silicon occurs in soil solution in the form of a very weak acid, ortho silicic acid, H_4SiO_4, or $Si(OH)_4$, commonly as low as 30 to 40 mg L^{-1} (Jones and Handreck 1967).

In Japan, a strong relation between the geology and the Si concentration in river water is reported. The SiO_2 concentration of river water draining from volcanic areas was consistently higher than river water Si concentration draining from granites and sedimentary rocks. Ma and Takahashi (2002) report SiO_2 concentrations in rivers draining from volcanic area as 47.5 mg L^{-1} versus SiO_2 concentrations of 13.9-11 mg L^{-1} in rivers draining from granites and Paleozoic and Mesozoic sedimentary rocks. The relationship between geological bedrock and Si supplying capacity showed a similar picture. Volcanic parent material and shales have high Si-supplying capacity versus granites and Paleozoic and Mesozoic sedimentary rocks that have low Si-supplying capacity. Since irrigated rice requires on average 14,000 t of water per hectare per growing season the concentration of Si in the water is an important factor. Ma and Takahashi (2002) showed that the Si concentration in rice straw can be correlated with the Si concentration in irrigation water. The SiO_2 concentration in rice straw was generally in the range of 11-18% when irrigated with water that contained 15 mg L^{-1} SiO_2 and more, whereas the rice straw SiO_2 concentration in rice straw was as low as 6-10% when irrigated with water that contained less than 15 mg L^{-1} SiO_2. The average dry weight SiO_2 percentage in rice straw was 16.8% in soils over volcanic parent material versus 6.7 -7.2% SiO_2 (dry weight) in soils over granite.

The analysis of Si is not part of routine soil investigations and a database of soil Si in the world is insufficient. It is well known that tropical areas are commonly Si depleted but a comprehensive survey and identification of soil types where Si addition might be useful, is missing.

Soluble Si, predominantly ortho-silicic acid, is present over a wide pH range (pH 2 -9) until a pH of 9 when soluble Si sharply increases in soil solution. Silicic acid is the dominant species that is found in rivers and stream. The worldwide median Si concentration in rivers is 13 mg SiO_2 L^{-1} (Ure and Berrow 1982). The source of Si is largely from weathering of minerals and from biochemical cycling of Si (Moulton *et al*. 2000; Derry *et al*. 2005).

The effects on plants of increasing Si in soil solution are:

- ○ Reduced pathogen attacks,
- ○ Reduced Al toxicity,
- ○ Increased Mn tolerance,
- ○ Increased uptake of available P.

Chérif *et al*. (1994) showed that the use of soluble silica reduced fungal attacks by *Pythium* ssp. Silicon seem to provide protection against pathogens through the intensification of physiological barriers at the root site and accumulation of phenolic and lignin-like compounds. Outlining recent research results, Bélanger *et al*. (1995) show the prophylactic effects and advantages of using soluble Si based fertilizers in greenhouses to reduce *Fusarium* wilt and incidents of powdery mildew and other diseases.

There are several field and laboratory studies that demonstrate that the addition of Si to soil solution decreases the effects of Al toxicity (Galvez *et al*. 1987; Barceló *et al*. 1993; Baylis *et al*. 1994; Hammond *et al*. 1995; Hodson and Evans 1995; Corrales *et al*. 1997; Cocker *et al*. 1998; Ma 2004). However, it is apparent that the actual mechanism and interaction between Al and Si and other elements is complex.

Corrales *et al*. (1997) discuss some of the proposed mechanisms such as reduced binding of Al in the cell wall and the formation of aluminum-silicate complexes in the apoplast. According to Baylis *et al*. (1994), the interaction of Si with Al can result in the formation of subcolloidal hydroxyaluminuno-silicate species. Hammond *et al*. (1995) showed that increased Si in solution caused enhanced uptake of P from soil solution and that Si reversed the inhibitory effects of Al on the uptake of Ca into the roots. In a review on the amelioration of Al toxicity by Si in plants, Cocker *et al*. (1998) discusses the potential mechanisms responsible for Si amelioration of Al toxiticity.

The fact that the application of plant available Si-sources can ameliorate Al toxicity is extremely important because Al toxicity is one of the main barriers for optimal plant growth in acid soils.

Another beneficial effect of the addition of Si to soil solution is the increased tolerance to Mn. The addition of Si prevents the development of brown speckles, the typical signs of Mn toxicity by spreading out the distribution of Mn in the leaf and thus increasing tolerance to high concentrations of Mn (Williams and Vlamis 1957).

Experience has shown that the addition of Si enhances the uptake of P in low-Si tropical soils. It has long been assumed that silicic acid would blanket Fe-oxyhydroxy surfaces or desorb phosphate ions ‘fixed’ on Fe-oxide surfaces. But Ma and Takahashi (1991) showed that the fixed P was in fact not desorbed by silicic acid but that the enhanced P uptake and growth was caused by depressing the toxicities of other elements such as Al and Mn. This, in turn, increased the availability and uptake of P. The application of Si resulted in a considerable decrease in Al uptake and in an increased translocation of available P to the plant.

Most of the above experiments were carried out in controlled greenhouse experiments but field evidence has been gathered over the years as well. The agronomic yield increase through the application of Si-based fertilizers has been demonstrated in many places and with several plants. Increased yield of sugarcane has been shown on highly weathered Si deficient soils (e.g. in Hawaii) (Fox *et al*. 1967) and on organic soils (e.g. in the Everglades of the Florida) (Anderson 1991; Anderson *et al*. 1991). The positive effect of Si fertilization on sugar cane yield has also been established in Brazil, Australia, South Africa and India (Epstein 1999). Many examples of successful application of silicate fertilizers on rice yield have been provided from Japan (Ma and Takahashi 2002).

Silicon geology

Silicon is the second most abundant element of the earth after oxygen (28.15%). It occurs as silicate in almost all rocks on the earth surface, either in common igneous rocks like granites or basalts, in metamorphic rocks like amphibolite or gneiss and most clastic sediments, like sandstones and shales.

The Si concentration in rocks and minerals is commonly expressed as SiO_2. The average SiO_2 concentration of upper continental crust is 66.6% (Rudnick 2003). The chemical compositions of the main rock forming minerals are provided in Chapter 2 in Table 2.2 and the composition of the main igneous rock types is illustrated in Figure 2.1. The SiO_2 content of common igneous rocks ranges from 35 -80%. The SiO_2 content of metamorphic rocks, such as gneisses, schists is about 60 -70%, and amphibolites 40-55%. The SiO_2 content of sedimentary rocks varies widely, from pure carbonate rocks with only small SiO_2 contents to cherts that can be close to 100%. Depending on the source of the sand particles, sandstones can contain as much as 80% SiO_2. Biogenic sediments containing large amounts of diatoms are diatomites with Si concentrations almost reaching 100% SiO_2.

The stabilities of silicate minerals differ strongly and thus influence the release of Si. The behaviour of minerals and rocks during weathering and the release of silicates is illustrated in Figure 2.8. The release of silica from minerals and rocks into solution is a function of many variables including temperature, aqueous chemistry (including pH), biology and time.

The release rate of silica and the stability of common minerals can be grouped into three major groups:

- ○ Minerals that easily break down during weathering, e.g. olivine and pyroxene,
- ○ Minerals that break down moderately fast such as feldspars and the dark micas (biotite and phlogopite),
- ○ Minerals that do not break down easily during weathering such as quartz.

It is these resistant minerals that are often enriched in detrital sediments, for example in quartz sandstones, arkoses and conglomerates.

There are several organic and inorganic Si sources that are used to fertilize Si-accumulator plants such as rice and sugarcane. Organic sources include composted rice straw and rice husks. The main inorganic Si sources are Si fertilizers mainly calcium silicate slags from metal processing plants, mainly steel industries (Ayres 1966; Anderson *et al.* 1991) and K-silicate fertilizers (Tokunaga 1991; Ma and Takahashi 2002). In Japan, the K-silicate fertilizers are produced in a fusion process using fly ash, K-sources and Mg sources.

Other sources of relatively available Si sources are fused magnesium phosphates (FMP), described in Chapter 4, and porous hydrate calcium silicates (used in the construction industry of Japan) and silica gel (Ma and Takahashi 2002).

Other potential but not tested Si-rich resources could include biogenic silica, for example uncalcined diatomite. The global production of diatomite in 2004 was 1,960,000 t (US Geological Survey 2005). Currently they are used mainly for filter purposes (purification of vegetable oils, wine and beer) and for removal of microbial contaminants in drinking water, and fillers. In agriculture, diatomite, also called diatomaceous earth, is mainly used as grain protectant and non-toxic insecticide (Korunic 1998).

Other not yet tested Si-rich resources include perlite, pumice, fine silica-rich volcanic ash, volcanic silicic glass, fly ash, and olivine-rich sources and cement waste products. However, it is expected that due to the low solubility of silica in water these materials will provide very little available Si into solution in a short time, if not chemically or biologically processed.

Sodium

The role of sodium in plants

Sodium (Na) is an essential micro-nutrient for the growth of blue-green algae, for example *Anabaena cylindrical*. Sodium is essential for plant species possessing the C_4-pathway as it allows for the uptake of pyruvate which is essential for the C_4-pathway of photosynthesis (Brownell and Bielig 1996). Prominent C_4-plants are maize/corn, sugar cane, sorghum, and dicots of the families *Amaranthaceae* and *Chenopodiaceae*, e.g. quinoa (Wilson *et al*. 2002).

Physiologically, Na can fulfill the functions of K, especially when the concentrations and supplies of K to the plant are low. Beneficial effects of Na in the absence of K lie in the ability of Na to perform functions in plants usually done by K. Asher (1991) discusses the nature of the substitution of Na for K and reasons that the supply of Na under restricted availability of K could enhance stomatal functions in leaves. Na is important for osmotic regulation in both C_3 and C_4 plants especially in halophytes, plants that like salts and accumulate salts in order to maintain turgor.

Plants require Na in small concentrations only. However, it is difficult to provide some general concentration data on deficiencies, sufficiencies and toxicities of Na in soil solutions and growth media. External Na concentrations of < 100µM (2.3 mg kg^{-1}) are required for C_4 plants and much lower concentrations (0.07µM) are needed for C_3 plants (Asher 1991). However, some plants, especially halophytes, require high concentrations of Na (>10mM = 230 mg Na kg^{-1}) to increase their turgor and growth.

Critical toxicity levels are commonly expressed as percentage of the cation exchange capacity (CEC) of a soil. The CEC and the exchangeable sodium percentage (ESP) are critical parameters determining toxicity levels of Na in soils. The ESP is the degree to which the exchange complex is saturated with Na and is expressed as ESP=exchangeable Na (cmol kg^{-1}) / CEC (cmol kg^{-1}). Saline soils are soils in which salts interfere with the growth of plants and where the ESP is below 15. Sodic-saline soils are those soils where the ESP is greater than 15, which means that Na occupies more than 15% of the CEC sites.

Net uptake of Na differs between plant species. High and medium Na-uptake crops include sugar beet, swiss chard, spinach as well as cabbage, coconut, cotton, potatoes, rubber. Low to very low Na-uptake crops include most cereal crops, rapeseed and soybeans (Mengel and Kirkby 2001).

Sodium in soils

The abundance of total Na in soils varies strongly, form 0.1 to 10%, with an overall mean of 1.06% (Ure and Berrow 1982). In general, the concentration of Na in soils is lower than in the earth's crust because of weathering, leaching and transport of Na to the sea. Soils in dry climates with high evaporation rates have significant higher Na concentrations than soils in tropical and temperate climates.

Sodium geology

Sodium is one of the most abundant elements in the earth's crust. The mean concentration of Na in the earth's crust is 2.37%. As seen in Table 8.21, the Na concentration in granitic rocks is higher than in basaltic and ultramafic rocks. The Na concentration in clastic sediments and limestones is generally low. High concentration of Na is found in chemically precipitated sediments, in salts.

Sodium occurs mainly in complex rock forming silicate minerals and in soluble salts. The geochemistry of Na is largely controlled by its ionic size. The ionic radius of Na (0.98 Å) is closer to that of Ca (0. 99 Å) than to K (1.33 Å). Common Na silicate minerals in igneous environments include plagioclase feldspar in which there is solid solution and isomorphous substitution of Na for Ca, from $CaAl_2Si_2O_8$ (anorthite) to $NaAlSi_3O_8$ (albite). Other Na-rich silicates include pyroxenes, amphibolites, feldspathoids, such as nepheline. Sodium-rich minerals in metamorphic environments include Na-rich plagioclases, glaucophane and other rare Na-silicates.

Table 8.21. *Average abundance of total sodium (in dry weight %) in various rock types (from various sources in Wedepohl 1970).*

Earth's crust	Ultra-mafics	Basalt	Grano-diorite	Granite	Shale	Lime-stone	Soil
2.37	0.42	1.65	2.75	2.40	0.59	0.13	1.06

The main naturally occurring soluble sources of Na are derived from salts. High Na salts include NaCl (halite), glauberite, $Na_2SO_4 \cdot CaSO_4$, trona $Na_2CO_3 \cdot NaHCO_3$, $NaNO_3$ and borax $Na_2B_4O_7 \cdot 10H_2O$.

Environmental issues

In large parts of the world agricultural productivity is severely reduced due to the excessive accumulation of Na salts in the soil, especially in irrigated agriculture. Salinization and sodification of soils lead to poor physicochemical properties of soils, decreased yields and even crop failure in large parts of the world. The accumulation of Na salts in soils is a major type of land degradation and a major challenge to world agriculture.

Vanadium

The role of vanadium in plants

The essentiality of Vanadium (V) for higher plants is not yet conclusive, but low concentrations of V are needed for the growth and photosynthesis of green algae (Kabata-Pendias 2001). Vanadium is required in green algae for the synthesis of the organic compound porphyrin, a compound found in bituminous complexes of crude oil and tar sands (see below). Vanadium may play a role in N_2-fixation and may replace Mo (Kabata-Pendias 2001). Minute concentreations of V are considered beneficial for animals and humans.

Vanadium in soils

Total V concentrations in soils vary from 20-500 mg kg^{-1}, with a mean of 108 mg kg^{-1} (Ure and Berrow 1982). There are several forms of V in aqueous solutions in soils, depending on soil pH, V concentration, redox potential and ionic strength. The cationic form of V, vanadyl, VO^{2+} (in the +4 oxidation state) seems to be stable at low pH ranges (below pH 4). The vanadate anionic form (VO_3^-) (in the +5 oxidation state) is stable in the pH range of 5 to 8 (Welch 1973). Plant uptake by roots from labeled V nutrient solution showed that the highest uptake rate of V was from the cationic vanadyl form under acid soil conditions. The uptake of the anion VO_3^- is inhibited by the presence of PO_4^- (Welch 1973). The anionic (vanadate) form of V is more mobile in soils than the cationic, reduced from of V (vanadyl) and is relatively more toxic to plants and soil microorganisms (Kabata-Pendias 2001). Morrell *et al.* (1986) provide some insights in the biotransformation of vanadate to vanadyl during plant uptake.

The general critical level of V in common plants is less than 0.2 mg kg^{-1} dry weight, the sufficiency concentration ranges from 0.2 to 0.5 mg kg^{-1} and toxicity levels are above 1 mg kg^{-1} (Bennett 1996). Other researchers state toxicity concentrations as 10-20 mg kg^{-1} (Wang and Liu 1999). Elevated concentrations of V also decrease P-uptake by maize/corn (Singh 1971, Sklenar *et al.* 1993). Studies by Wang and Liu (1999) on the effect of V on the growth of soybean seedlings showed that a V concentration in soils exceeding 30 mg kg^{-1} reduced dry matter yields of shoots and roots of soybeans. However, these effects were mainly found in fluvial soils. In Oxisols with high Fe and Mn oxide concentrations no toxic effects of V concentrations up to 75 mg V kg^{-1} could be discerned. This indicates a high V adsorption on Fe and Mn oxides (Wang and Liu 1999).

Many V toxicity studies have been carried out in glasshouse and nutrient solution experiments. Under natural field conditions, Gough *et al.* (1979) found no obvious toxicity symptoms in plants. In fact, some plants (e.g. mosses and sagebush) seem to be able to accumulate considerable amounts of V without showing toxicity symptoms. *Allium* and some species of *Astralgus* are accumulators of vanadium (Cannon 1963).

Vanadium geology

Vanadium occurs in nature in four oxidation stages, +5, +4, +3 and +2. But as there are rarely any V minerals, V rather replaces other elements. On account of its similar ionic radius V^{3+} can replace Fe^{3+} in various minerals in the igneous environments, e.g. in magnetite.

Vanadium abundances in different rock types are summarized in Table 8.22. The average concentration of total V in the earth's crust is 138 mg kg^{-1}, almost the same as the average abundance in soils (108 mg kg^{-1}) (Ure and Berrow (1982). Elevated V concentrations are generally found in mafic rocks, such as basalts, but also with alkaline complexes, carbonatites, and with chromite, iron and manganese mineral deposits.

Vanadium is strongly concentrated in organic matter rich marine sediments, especially black shales. Ripley *et al*. (1990), Coveney *et al*. (1987) and Patterson *et al*. (1986) showed that most of the V in black shales is bound in clay minerals, possibly as a result of biodegradation of organic matter and diagenesis.

Very high concentrations of V (with an average of 0.8-0.9 % V_2O_5 and in some areas up to 2.5% V_2O_5) have been reported from the extensive vanadiferous black shales in the Permian Phosphoria Formation of the western United States (McKelvey *et al*. 1986), and in tar sands, for example in Canada and Venezuela. Also phosphorites contain commonly elevated concentrations of vanadium. Khiari *et al*. (2004) report V concentrations in sedimentary phosphate rocks of Saudi Arabia varying from 23 to 457 mg kg^{-1}. Slansky (1986) considered the elevated V concentrations in phosphorites to be probably associated with organic matter.

The V concentrations in crude oil vary from less than 1 mg L^{-1} to 1400 mg L^{-1} depending on the source of the oil. High V concentrations (300-1400 mg L^{-1}) occur in heavy crude oils from western Venezuela (National Research Council 1974).

Table 8.22. *Average abundance of total vanadium (mg kg^{-1}) in various rock types (Levinson 1974, Ure and Berrow 1982, Rudnick 2003).*

Earth's crust	Ultra-mafics	Basalt	Grano-diorite	Granite	Shale	Lime-stone	Soil
138	50	250	100	20	130	15	108

The few V bearing minerals, most of them secondary minerals in the weathering environment, are mainly of interest mostly for collectors and mineralogists. One of the main uranium ores, carnotite $(K_2(UO_2)_2(VO_4)_2{\cdot}3H_2O$ contains 12% vanadium.

Other V-bearing minerals are roscoelite ($K(V, Al)_2(OH)_2AlSi_3O_{10}$) and vanadinite ($Pb_5(VO_4)_3Cl$).

Vanadium concentrations are high in ashes of spent fuel oils and coal. A large amount of V is and will be recovered from petroleum and tar sand refining as well as from spent V catalysts. The global resources of V are very large. According to the US Geological Survey world vanadium resources exceed 63 million t (USGS 2006).

Environmental issues

Vanadium is a vital metal in various special steels, in the aerospace industry as V-Ti alloy, and high value machinery. In the production of sulphuric acid for the production of P fertilizers vanadium pentoxide (V_2O_5) is used as catalyst. After use, these 'spent' V catalysts are either recycled or disposed of. The disposal of spent V catalysts needs special containments for safe storage.

Vanadium occurs also, in small concentrations, in basic slags. When these slags are used as soil amendments and are not ploughed into the soil, they can cause V poisoning in grazing cattle (Frank *et al*. 1996).

Vanadium occurs in industrially polluted sites and in areas where fossil fuels (coal and oil) are burnt. Soils close to these sites are highly enriched in V in the soils. However, it is the V-bearing aerosols from coal and oil burning as well as from industrial pollution that forms the highest risk of V exposure to humans.

Chapter 9

Multi-nutrient rock fertilizers

Fertilizers are substances intended to supply one or more plant nutrients to the soil in order to promote plant growth, increase crop yields, and improve crop quality (Cooke 1982; Finck 1982). Most conventional fertilizers consist of substances that have been synthesized industrially and made soluble as a result of chemical reactions in industrial processing plants. These fertilizers contain highly soluble nutrient sources for immediate use by plants and increased production of crops. The use of nutrients from soluble fertilizer sources is one component in the strategy of improving soil health and food security.

Despite their proven fast reaction and effectiveness, many farmers in developing countries have been unable to access conventional fertilizers. Due to infrastructural constraints and high transportation costs, these fertilizers, which are produced mostly in industrialized countries, often do not reach farmers in remote locations. Even if the fertilizers reach market outlets, farmers often do not receive the fertilizers when they need them. Furthermore, in some parts of the world, synthetic fertilizers are simply not affordable for smallholder farmers.

In recent years, environmental and ecological concerns have arisen over the long-term effects of using conventional synthetic fertilizers. Many of these concerns stem from the high energy costs for the production of conventional fertilizers using non-renewable resources (e.g. natural gas for N fertilizers), concerns about low fertilizer use efficiency of many of the soluble fertilizers in the first year of application (Balliger *et al*. 2001) and environmental pollution, (for example eutrophication), associated with improper use of soluble fertilizers.

Other concerns are related to the fact that most chemical fertilizers introduce only one or two nutrients and often lack the whole spectrum of nutrients including micronutrients, which are necessary to enhance soil quality. The application of chemical fertilizers also does not introduce organic matter, which is important for soil structure, biodiversity, soil ecology and soil health in general. Furthermore, purely chemical interventions into soil systems often change the chemistry, physical properties and biological activities in soils, as well as the dynamics of this system and the soil ecology.

One of the pioneers of modern agrogeology, Keller (1948) was an early voice of caution to the use of chemical fertilizers. He noted that high external input conventional agricultural practices require the addition of commercial soluble fertilizers, which are made of a selected few moderately pure, relatively concentrated, highly soluble elements that quickly supply the mineral-derived nutrient substances most acutely needed by the crops. He compared this practice with the "dosing of the ailing soil-patient with a quickly-assimilated, concentrated, processed, stimulating food to revive its strength."

In response to these concerns, the fertilizer industry is trying to find and develop more efficient 'slow release', multi-nutrient options to replenish soil nutrients more efficiently. However, the use of synthetic, soluble fertilizers is not the only options to treat soil fertility problems. Natural fertilizers, those substances that release nutrients from natural organic and rock and mineral substances together with organic matter have been used for centuries to counter soil fertility declines and should be seen as an alternative option. Natural fertilizers include organic and mineral substances that supply nutrients to soils, enhance soil physical and biological properties and soil health as well as promote plant growth. These natural nutrient resources include poultry and cattle manures, green manures, leaf litter, and other organic residues as well as ashes, and geological resources such as phosphate rocks and multi-nutrient silicate rock fertilizers.

Weathering minerals and rocks have the same tendency as slow release fertilizers. Without going through chemical synthesis in industrial processing complexes they slowly release a whole array of nutrients. However, the release rate is very slow. The release of nutrients can be increased through a variety of means such as the physical grinding of rocks into smaller particle size, and/or reaction with organic acids.

Natural fertilizers have become attractive to those farmers that try to follow natural pathways of more sustainable 'soil building.' Keller (1948) promoted a strategy which he coined a natural, long-term, geological practice in which clay, silt and fine-sand sized fractions of rocks and minerals would release nutrient elements slowly to the soil as "long-lasting, full-diet, soil builders". The intention of this strategy would be to build up the soil "as nearly as possible according to the principles followed by nature" (Keller 1948).

More recently, integrated nutrient management (INM) systems have been promoted as part of broad-based, practical farm management strategies that aim at improving soil fertility and reducing the excessive use of soluble nutrient inputs. These strategies take account of the complex mineral-organic interactions in soils and include rocks and minerals as part of the system (Reintjes *et al.* 1992; Scoones *et al.* 1996; Smaling and Braun 1996; Deugd *et al.* 1998). INM is based on the 'judicious' manipulation of nutrient stocks and flows in an agricultural system that aims at reaching a 'sustainable' level of agricultural production (Deugd *et al.* 1998). In the scheme of low external input agricultural (LEIA) practices the use of natural, rock- and mineral-based fertilizers plays a considerable role for more sustainable soil fertility management practices.

While the use of rock- and mineral-based fertilizers has been advocated by some farmers and scientists, many questions remain, especially the effectiveness of applying silicate rock fertilizers to soils. The main concern is the generally low solubility of most rocks and the subsequent low availability of nutrients to plants. Another constraint is related to the practicality of applying large amounts of ground rock to agricultural land (Hinsinger *et al.* 1996; Von Fragstein *et al.* 1988; Bolland and Baker 2000; Harley and Gilkes 2000). In addition, some rock fertilizers are diluted with minerals that have no practical nutrient value, such as quartz (Harley and Gilkes 2000; Bolland and Baker 2000). Nevertheless, rock- and mineral-based fertilizers have proven useful in some agricultural systems and climate conditions, particularly under tropical wet conditions (Leonardos *et al.* 1987; Harley and Gilkes 2000; Theodoro and Leonardos 2006).

9.1 Multi-nutrient silicate rock fertilizers

Multi-nutrient silicate rocks are made up of a variety of naturally occurring silicate rock materials containing a multitude of plant nutrients. The objective of using ground whole rocks is to mimic natural conditions of soil fertility regeneration through weathering. The process of weathering and subsequent nutrient release from minerals is enhanced mainly through physical grinding, partial breakdown of minerals in rocks with subsequent exposure of fresh surface areas of rocks and minerals. Part of the newly exposed mineral surfaces will react with soil solutions and organic compounds over time and will slowly release some of the nutrients contained in the minerals.

The use of various ground silicate rocks as nutrient sources for agriculture has been researched for a long period of time. Research with finely ground rocks and minerals, based on the concept of 'bread from stones,' started as early as the 19th century by Missoux (1853/54), and Hensel (1890, 1894). Renewed interest in this concept started in the middle of the 20th century with research by Keller (1948) and Keller *et al.* (1963). A growing body of research on this topic continues to be carried out in many countries with temperate and tropical climates (see Table 9.1).

The application of multi-nutrient silicate rock fertilizers as part of more lasting, more 'sustainable' soil fertility replenishment strategies has received renewed interest in recent decades due to advances in the understanding of geochemical weathering processes, root exudate chemistry, nutrient cycling and biochemical processes in soils. In the past, most of the fundamental research focused on dissolution rates of single minerals, and pathways and processes that minerals and rocks undergo in soils. While there is a great deal of knowledge regarding the dissolution kinetics, nutrient cycling and biochemical processes at root surfaces, the pathways and reactions in soil systems have still not yet been fully understood. Soils are complex natural systems that depend on a myriad of factors.

Whole rock multi-nutrient silicate fertilizers offer potentially low-cost geological nutrient sources for low external input agricultural systems. They are often locally available and usually contain a large number of nutrients in comparison to soluble fertilizers, which commonly only contain the main macronutrients N, P and K. Many whole rock fertilizers are silicate rocks that commonly contain K, Ca, Mg and an array of micro-nutrients as well as small amounts of P. In contrast to commercial soluble fertilizers, whole rock silicate fertilizers are slow release multi-nutrient fertilizers and attractive largely for use in agricultural practices in highly weathered soils of the tropics and subtropics (Fyfe *et al.* 1983; Leonardos *et al.* 1987; Theodoro and Leonardos 2006) and for forestry and ecological restoration. They are especially useful for application in situations where leaching rates of conventional fertilizers are high, e.g. in sandy soils under wet climatic regimes (Harley and Gilkes 2000) as well as for some acidic forest soils in temperate climates (Hildebrand and Schack-Kirchner 2000).

Table 9.1. Published research work on ground silicate rock for agricultural application.

Counry or region	Publication
USA	Keller 1948; Keller *et al.* 1963
Mauritius	D'Hotman de Villiers 1961
Zimbabwe	Roschnik *et al.* 1967
Australia	Gillman 1980, Gillman *et al*. 2001; Coroneos *et al.* 1996; Hinsinger *et al.* 1996; Harley and Gilkes 2000; Bolland and Baker 2000; Gillman *et al.* 2001, 2002; Lim *et al.* 2003; Priyono and Gilkes 2004
Brazil	Fyfe 1981, 1987, 1989, 2000; Fyfe *et al.* 1983; Leonardos *et al*. 1987, 2000; Theodoro and Leonardos 2006.
East Africa	Chesworth 1982, 1987, 1993; Chesworth *et al.* 1983, 1985; van Straaten 1987; van Straaten and Chesworth 1985; van Straaten and Pride 1993
Israel	Barak *et al.* 1983; Silber *et al.* 1999
Germany	Von Fragstein *et al.* 1988; Hildebrand and Schack-Kirchner 2000; von Wilpert and Lukes 2003
Austria	Blum *et al.* 1989a,b
United Kingdom	Appleton 1990; Mathers 1994
Sri Lanka	Weerasuriya *et al.* 1993
Norway	Bakken *et al.* 1997, 2001

The main hindrance to a more widespread acceptance of whole rock fertilizers is their slow release rate of nutrients (Hinsinger *et al*. 1996) and the high application rates required. Blum *et al*. (1989a,b) demonstrated that under laboratory conditions the release rate of nutrients from most ground silicate rocks was very slow and that most ground silicate rocks contain a high proportion of elements that have no apparent importance for plant nutrition. Most of the tested rock samples showed very low solubilities and nutrient releases and were regarded as agronomically ineffective, at least for conventional agriculture where highly soluble fertilizers are required for short-term effects. However, the same researchers showed that certain rock types, for example smectite-rich volcanic ashes, have relatively high cation exchange capacities and nutrient levels that could be used in nutrient poor acid forest soils. In similar studies, Von Fragstein *et al*. (1988) found that the highest cation release rates were from phonolitic volcanic rocks followed by basaltic rock types. Ground granite rock powder released the least amounts of nutrients.

9.1.1 Application of multi-nutrient silicate rock fertilizers in temperate climates

There is a small but steady market for multi-nutrient silicate rock fertilizers in Central Europe, e.g. Germany, and parts of North and South America, especially on organic farms (von Fragstein *et al*. 1988; Blum *et al*. 1989a,b). So far, only few scientific studies on the effectiveness and practicality of using multi-nutrient silicate rock fertilizers have been carried out in these regions.

In Norway, Bakken *et al*. (1997, 2000) studied the nutrient release of various K-bearing silicate rocks and residues from mine tailings on grasslands. The results of these trials under field conditions showed that only 30% percent of the K bound in biotite concentrate (from a feldspar processing plant in Lillesand, Norway) was taken up by plants, as compared to 70% from soluble KCl. Bakken *et al*. (1997, 2000) reached the conclusion that the weathering rate of the rock and mineral products was too slow to replenish the native pool of plant-available K within a three-year period with five harvests.

To combat declining acid neutralization capacity (ANC) and nutrient imbalances in forest soils, researchers have tested the application of ground volcanic silicate rocks as liming materials (e.g. Evers 1991; Hildebrand 1991; Fakengren-Gerup and Tyler 1992; Huettl and Zoettl 1993). The pH of ground rock samples is generally alkaline, with ground phonolitic rocks reaching a pH > 10, basalts pH 8-10, granites pH 7-10 (Von Fragstein *et al*. 1988). Keller and Reesman (1963) showed that the pH of rock slurries from glacial moraines were all alkaline, with the pH ranging from 8.2 to 9.4. These natural rock materials should thus be regarded as potential slow nutrient releasing ‘liming materials’. In fact, most whole rock fertilizers are multi-nutrient liming materials.

In a comparative study on acid forest soils, Hildebrand and Schack-Kirchner (2000) demonstrated the effectiveness of finely ground basaltic rock in comparison to liming materials. Applied basalt fines caused more beneficial nutrient flows into the mineral soil than limestone additions. However, to achieve good nutrient release rates an application of 6 t ha^{-1} basalt fines had to be applied. The application of these volcanic silicate rock fertilizers provided additional Ca and K to long-term tree nutrition in the Black Forest of Germany (Hildebrandt and Schack-Kirchner 2000).

In K-deficient forest soils of SW Germany the application of 10 t ha^{-1} phonolite rock increased the concentration of Ca and increased the soil pH. However, the high application rate of Na-rich phonolite rock also resulted in high rates of Na release. High rates of Na release can cause increased Na loading of groundwater and potentially contribute to a loss in structural stability of soils (von Wilpert and Lukes 2003). This result demonstrated the importance of carefully selecting the type of rock fertilizers to avoid potentially harmful element concentrations and new ecological imbalances.

The results of testing ground silicate rocks on soils in temperate and very dry climates consistently show that granitic rocks and other silica-rich rock materials are not effective to meet the nutrient demands of most agricultural crops. However, the application of ground volcanic silicate rocks does show a good potential for soil nutrient release enhancement and liming effects, specifically for long-term crops and trees, as well as for ecological restoration.

9.1.2 Application of multi-nutrient silicate rock fertilizers in tropical climates

Trial results of ground silicate rocks in tropical climates indicate better dissolution rates and better effectiveness than trials in temperate climates (d'Hotman de Villiers 1961; Roschnik *et al.* 1967; Leonardos *et al.* 1987, 1991; Gillman 1980, and Gillman *et al.* 2000, 2002; Theodoro and Leonardos 2006). This is largely due to the high temperatures and moisture regimes in these climates, in which the reaction between mineral surfaces and soil solution is enhanced and dissolution kinetics increased. In addition, tropical soils themselves are often low in nutrient concentrations due to high degrees of weathering and leaching and are commonly acid. Consequently, these soils are largely receptive to the addition of nutrients and to liming through the application of suitable silicate rock fertilizers.

In particular, the rate of dissolution and weathering of mafic minerals (e.g. olivines, pyroxenes) and rocks (mainly fine-grained mafic to ultramafic rocks, e.g. basalts, and rocks with high volcanic glass components) are increased under these climatic conditions. Fine-grained rocks with high proportions of olivine, pyroxene, amphibole, Ca-rich plagioclase feldspar and a significant glass fraction, as well as low concentrations of free quartz, have the highest natural weathering capacities and commonly increase the pH of soils. These rock and mineral resources can thus be used effectively in tropical areas as slow-release nutrient-supplying materials for crops in degraded tropical soils and also for forestry and pastures. Researchers from countries with tropical climates report positive results from tests using ferromagnesian-rich silicate rock fertilizers, such as basalts or ultrapotassic/potassic lavas and tuffs (d'Hotman de Villiers 1961, Roschnik *et al*. 1967, Leonardos *et al*. 1987, 1991, Gillman 1980, Gillman *et al*. 2000, 2002, and Theodoro and Leonardos 2006).

In Brazil, Leonardos *et al.* (1987) tested various ground rock materials on strongly-leached, acid lateritic soils. They found that the application of ultrapotassic, ultramafic volcanic rock resulted in higher yields of beans (*Phaseolus vulgaris*) and napier grass (*Pennisetum purpureum*), as well as slow-growing trees. In subsequent studies, Leonardos *et al.* (1991) and Theodoro and Leonardos (2006) reported good agronomic responses to the application of ultrapotassic K, Mg, Ca, P and micronutrient rich lavas and tuffs. Figure 9.1 shows a farmer applying ground ultrapotassic rocks in combination with manure on nutrient depleted acid soils

Figure 9.1. *Farmer in Bazil using manure in combination with ground ultrapotassic rocks on nutrient depleted acid soils (Photo courtesy of Dr. S. Theodoro, University of Brasilia).*

The application of these ground rocks on the severe nutrient deficient acid soil conditions found in Brazil showed increased soil nutrient status (Ca, Mg, P, K) and reduced the aluminium toxicity. Consequently crop production and the livelihood of farmers should improve in this area. These results are particularly encouraging because the rock material used in these studies was taken from the nearby Mata da Corda formation. The volume of these unconsolidated easily extractable geological resources are truly enormous, the Mata da Corda formation stretches over large areas (250 km x 50 km) of Brazil, in the state of Minas Gerais.

In Zimbabwe, Roschnik *et al.* (1967) tested finely ground basaltic rocks in strongly weathered Kalahari sands in glasshouse experiments. They reported exponential growth increase of two slow-growing legumes with high application rates. The yield increase of sunflowers grown on Kalahari soils following treatment with 5-40 tons per acre of finely ground basalt showed a linear response curve (Roschnik *et al.* 1967).

In Mauritius, large, one-time application (up to 180 tonnes per hectare) of ground basalt applied to sugar cane fields consistently showed increased yields (d'Hotman de Villiers 1961).

In tropical parts of Australia, Gillman (1980) and Gillman *et al.* (2000, 2002) showed a raised pH, increased the cation exchange capacities, and enhanced cation levels with the application of large amounts of ground basaltic rocks to weathered and nutrient depleted soils. In contrast, the application of K-feldspar in a dry area of Western Australia showed negative agronomic results (Bolland and Baker 2000). The lack of benefit in the latter study stemmed primarily from the release rate of K from K-feldspar, which is extremely slow, especially in this dry region.

In Colombia, K-feldspars have also proven ineffective because of neglible K-release rates (Sanz Scovino and Rowell 1988). K-minerals that are more suitable for chemical and biological weathering and K-release include leucite and other feldspathoid or K-zeolite bearing volcanic rocks as well as biotite and phlogopite mica. The best agronomic effectiveness is achieved with the application of fine-grained silica-undersaturated volcanic rocks, such as basaltic lavas or unconsolidated tuffs with varying amounts of volcanic glass.

Also some minerals, which show slow release rates can be transformed into effective agrominerals. For example, the release of elements from phlogopite and biotite, both micas, is generally slow. However, it can be effectively accelerated through biologically induced activities or chemical modification. Berthelin *et al.* (1991), Hinsinger and Jaillard 1993, and Hinsinger *et al.* (1993) demonstrated increased K-release from phlogopite by biologically induced transformations in the rhizosphere.

9.1.3 Mine ‘wastes’ turned ‘by-products’

Fine grained and physically ground rock materials from quarrying and certain non-metallic mining operations can also be turned into effective rock fertilizers. An example of this is the successful agricultural use of a ‘by-product’ of vermiculite mining at Namekara, 30 km north of Tororo, Uganda. Vermiculite is mined in this area, part of the extensive alkaline Bukusu complex, by a private company (Uganda Vermiculite Ltd.). The fines of the weathered, vermiculite-rich silicate rocks, originating from the underlying phlogopite pyroxenites, were previously discarded and seen as ‘mine wastes’. Chemical analyses of the fine ‘mine wastes’ showed that these previously ‘wasted’ rock fines contain considerable concentrations of exchangeable magnesium, some plant available phosphorus and micronutrients. The usefulness of this by-product as a fertilizer was discovered by accident when ‘wastes’ from this mining operation were planted with corn/maize and showed high yields (see Figure. 9.2 and picture on front cover).

While the coarse and medium grade vermiculite is extracted, processed and shipped to various consumers in North America, Europe and Africa, the fine grained ‘mine waste turned by-product’, is slightly processed through the removal of magnetite and through exfoliation. It is currently used primarily in areas of Uganda where cotton, sunflower and other crops are grown and in greenhouses in Uganda producing flowers and herbs. Application of this by-product rock-fertilizer results in early seed germination and seed emergence.

Figure 9.2. *Maize/corn growing on vermiculite mine ‘waste’ heap (centre) as compared to maize/corn grown on nutrient deficient acid soils. Photo taken 2005 close to the open pit Namekara vermiculite mine, Eastern Uganda.*

Another multi-nutrient silicate rock fertilizer that occurs as a mining by-product has been used in Sri Lanka (Weerasuriya *et al*. 1993). In this case, scrap phlogopite 'waste' from pegmatite mines is ground and acidulated with various acids, including nitric and sulphuric acid. The acidulation process releases up to 65% of K and Mg, less than 13% of Ca, and 15-100% Mn and Zn. As little as 200 $kg{\cdot}ha^{-1}$ of this acidulated, non-hygroscopic granular phlogopite mica results in an increase in rice yield of over 41% in comparison with recommended application rates of muriate of potash (KCl) and dolomite. However, the agronomic effectiveness of acidulated feldspars in combination with dolomite has been negligible (Weerasuriya *et al*. 1993).

In Israel, Barak *et al*. (1983) tested the application of ground Fe-rich basaltic rocks and lapilli tuffs (volcanic pyroclastic material), by-products of local quarrying operations, on calcareous soils where peanuts (*Arachis hypogaea*) often show low yields due to a lack of iron (Fe-chlorosis). Application of this rock-fertilizer resulted in significantly improved iron nutrition, chlorophyll production and growth of peanuts. Further tests with black and yellow volcanic tuffs illustrated that these materials should not be applied to soils with very low pH levels as some Al (from alumino-silicate minerals) might become available in soils with a pH below 4 (Silber *et al*. 1999).

Figure 9.3. *Quarry operation near Haikou, Hainan Province, China, with olivine basalt quarry wastes.*

Many fine-grained 'wastes' of industrial mineral mining operations and rock crushing operations need to be assessed for their agronomic potential in tropical nutrient depleted acid soils. Figure 9.3 provides an example of potential Mg-rich silicate rock fertilizers with liming qualities from a quarry operation in Hainan Province, southern China. Here, the quarry fines from an aggregate operation using olivine basalts are currently discarded. The fines are now tested on acid Mg-deficient soils on a rubber plantation in Hainan Province, China.

Several locally available silicate rocks and minerals, mainly of mafic composition, lend themselves as potential rock fertilizers. Locally available rock 'wastes' and by-products from non-metallic mining and quarry operations need to be investigated on their potential use as slow-release multi-nutrient silicate fertilizers in nearby farming areas, especially in tropical and sub-tropical environments. However, for effective results, it is important to characterize the selected rocks and minerals, and match specific soil and plant requirements with that of the nutrient supplying capacities of the whole rock fertilizers.

9.2 Challenges and opportunities of applying multi-nutrient rock fertilizers

9.2.1 Challenges

Challenges to the use of multi-nutrient rock and mineral fertilizers are multi-faceted. The agronomic effectiveness of whole rock fertilizers is a function of rock factors (e.g. mineralogy and chemistry), soil factors (e.g. organic matter content, pH, texture), crop factors, other environmental factors, and management factors.

The main challenges to the application of these nutrient containing rock and mineral materials are:

- They have generally low nutrient concentrations.
- They are not very soluble.
- They have a high percentage of minerals that have no practical nutrient value, such as quartz.
- For agronomic responses they have to be applied at high application rates.
- They require high energy inputs (mainly crushing).
- On a nutrient base, they are very expensive.
- They have, in general, low agronomic effectiveness.

Each of the above characteristics can negatively influence the agronomic effectiveness of short-term crops, particular in temperate climates. Therefore, careful selection and characterization of rocks and minerals as well as characterization of soils and selection of crops is needed prior to the use of these materials to avoid using rock materials that have potentially only low or negligible agronomic effects.

The greatest challenge in the use of whole rock fertilizers is to increase the solubility of rocks and minerals in order to enhance nutrient release from the rock and mineral surfaces. This can be achieved by physically modifying and/or chemically changing the mineral surfaces. Physically changing the surface area of the minerals, e.g. through fine grinding, can enhance the release of nutrients (Lim *et al*. 2003; Priyono and Gilkes 2004; Priyono 2005). Chemically modifying the surfaces, e.g. through acidulation can also enhance the solubility and nutrient release from minerals. The release of K and Mg from phlogopites through acidulation is an example of how nutrient release can be enhanced (Weerasuriya *et al*. 1993).

The general challenge is to match the nutrient supplying capacities of the multi-nutrient rock fertilizers to the soils and to the plant requirements. Research is needed on the application of the right type and amount of rock fertilizers at the right time to the right crop. Many failures that occurred with the use of multi-nutrient rock fertilizers were caused by the poor selection of the appropriate rock fertilizer compositions and specific crop requirements, as well as from the poor selection of climatic environments. Mafic rocks, for example, contain large amounts of ferromagnesian minerals with high concentrations of plant nutrients such as Ca, Mg, Fe and micronutrients and are thus suitable for many degraded and acid soils. They are usually free of quartz. On the other side, felsic rocks and mica-bearing rocks contain less of the above nutrients but more of the plant nutrient K and are thus more suitable for soils and crops that have higher K requirements.

In order to overcome the low solubility and thus release rate of nutrients from minerals and rocks it is necessary to apply large volumes of rock fertilizers to the soils. While this might be possible where the rock materials are regarded as ‘waste’ and/or available close to the area where it is needed, it is probably uneconomic to extract and transport large volumes of these materials over long distances. A way out of this situation is to modify the rock fertilizers in such a way as to increase the release rates and thus reduce the amounts of materials that must be applied to the soils. Experiences could be gained by testing some of the modification techniques applied to increase P release from otherwise unreactive phosphate rocks (see below: opportunities). Challenges also include the economics of transportation and grinding and other modification techniques of the rock fertilizers.

9.2.1 Opportunities

There are several general advantages and opportunities for improving soil fertility issues with multi-nutrient whole rock fertilizers, and specifically mafic rock fertilizers:

- Whole rock fertilizers contain a large number of macro- and micronutrients which upon weathering can contribute to the improvement of nutrient deficient soils and poor crop production, over a long time span.
- They have favourable properties to raise the pH of soils (liming effect).
- They are suitable for application on sandy soils under wet climatic regimes.
- They are suitable as slow-release fertilizers in nutrient depleted acid soils.
- Their application has low environmental impact.
- Many of them are locally available, some of them as quarry ‘wastes’ and mine ‘wastes’ from other non-metallic, industrial mineral mining operations.
- They are inexpensive with regards to mining.

The whole rock fertilizers have to be chosen carefully and well characterized in order to meet the nutritional requirements of the degraded soils and the crops grown on them. The selection of rock and mineral materials as whole rock fertilizers depends largely on the nutrient deficiency and the need to replenish nutrients in the soils. While fine grained mafic silicate rock fertilizers are more suitable to release various nutrients (e.g. Ca, Mg, micronutrients) they are generally low in K and therefore less suitable in K-deficient soils.

Multi-nutrient rock fertilizers and many single nutrient rock fertilizers will not replace conventional fertilizers that react fast in soil solution for easy access to plant roots. However, there seems to be a large potential of applying appropriate rock and mineral fertilizers in combination with organic matter to highly weathered and degraded soils in the long-term. In fact, the combination of ground rock materials with organic materials likely resembles natural systems and are in the words of Keller (1948), “long-lasting, full-diet, soil builders.”

In tropical environments, the use of mafic rock fertilizers as slow-release fertilizers is particularly useful in degraded soils, and in soils where long-term ameliorative effects are needed, e.g. in forest and pasture management systems. The release of macro- and micronutrients from rocks and minerals in these situations is enhanced due to high temperature and moisture regimes.

However, in most of experiments the multi-nutrient rock fertilizers have been applied directly to the field without modifications (apart from grinding).

Consequently, there are only limited experiences of multi-nutrient silicate rock fertilizer modifications, such as fine milling (Priyono and Gilkes 2004; Priyono 2005) and acidulation (in the case of mica, Weerasuriya *et al.* 1993). It seems evident that other modification such as composting, mixing with acidulating sulphur, partial acidulation and heap leaching, as well as blending with organic acid producing compounds should also be tested with various multi-nutrient rock fertilizers to enhance soil fertility on nutrient deficient acid soils.

The application of ground silicate rock fertilizers together with organic residues needs to be researched rigorously as they represent more natural pathways of replenishing soils. This will involve studies of inorganic-organic interactions and transformations from mineral to organic compounds. More laboratory studies, greenhouse and field experiments are needed to test rocks and minerals that possess high cation concentrations and relatively high weathering potential, like feldspathoids, as well as mafic, ultrapotassic and olivine-rich volcanic rocks. It is also important to better understand which soils and which plants may promote the dissolution of silicate rock fertilizers. More research and development on microbially induced nutrient release from multi-nutrient bearing rocks and minerals should be carried out to produce biologically enhanced rock fertilizers.

Rock fertilizers represent inexpensive and environmentally friendly fertilizer options that can be included in low external input and organic agricultural systems in areas of the world with infertile soils and unsuitable climates. With the right choice of locally available rock materials for the right soils and the right crop, these materials have shown to be of benefit to local agriculture, especially when modified or blended with locally available organic materials, and in the long-term can contribute to sustainable land management and soil restoration.

Large research gaps have to be covered from the scientific perspective. But it is evident as well that more collaborative investigations with all stakeholders, including geologists, soil scientists, extensionists and farmers, are needed to get a better understanding of ecosystem functions and the agricultural functions within this ecosystem to maintain or enhance the natural environment. And there are other social and cultural dimensions that have to be included to make a more holistic research effort towards a more sustainable agricultural future. As Sherwood and Uphoff (2000) stated, we have to engage farmers rather than change farmers. We should involve farmers as partners in improving soil health. Soil researchers, geoscientists, extensionists and farmers should solve soil related problems together and develop and spread better practices and methods, including agrogeological ones, to ultimately provide better livelihoods for farmers.

A special case of rock resources ‘out of place’: reservoir sediments

A special ground rock resource with added organic matter is reservoir sediment, made up of weathered and unweathered rock material, of usually silt and clay sizes as well as organic matter that have been eroded in the catchment area of the reservoir and settled behind a dam. Soils and weathered rocks eroded by water usually end up in rivers and large volumes of sediments, either in the open sea or in reservoirs. These sediments derived from upland soils and weathered rocks have been seen as ‘resources out of place’ (Darmody and Marlin (2002).

While sediment accumulations in reservoirs are a challenge to reservoir managers as they reduce the volume of water stored behind the dam, dredged out reservoir sediments may become an asset to improve soils in the immediate surrounding, particular when the soils in the surrounding of the reservoir are infertile and/or sandy.

The chemical and mineralogical compositions as well as the clay/silt/sand ratio within the reservoir sediments depend largely on the geological source material in the catchment area. Reservoir sediments containing transported soils and weathered rocks with mafic silicate minerals and organic matter represent potential resources for agricultural application under certain conditions. The sediments have to be easily extractable, not contaminated with heavy metals and have a good fertilizing value for soils close to the reservoirs. By their nature, these sediments are mainly fine grained and have thus a high water holding capacity.

Careful selection of sites with sediments derived from suitable parent materials, e.g. rocks of volcanic origin is important. The river sediments of the River Nile which used to be ‘harvested’ by the Egyptian farmers for centuries are to a high proportion derived from the Blue Nile that brings its fertile sediment load from the volcanic highlands of Ethiopia (Smith 1990). But also sediments of small fish ponds charged with animal excreta are being harvested for their high nutrient content, their high water holding capacities. The dredged out sediments are used on nearby fields.

Chinese farmers have harvested the accumulated sediments from waterways and reservoirs for many centuries (King 1911). In the 1970s, it was estimated that more than 25% of the fertilizer values used in Chinese crop production derived from dredged channels, reservoirs and fish ponds (Ryding and Rast 1989). Chinese farmers also practiced sediment compost systems, whereby muds extracted from the canals and reservoirs were mixed with organic matter.

Reservoir sediments cont.

Usually animal manure and green manures, and mud were fermented in pits before application to rice fields (Anonymous 1998). Reservoir sediments are also applied in North America. Dredged sediments from Lake Paradise, Illinois, USA were applied to nearby maize/corn fields (Lembke *et al*. 1983). No nutrient deficiencies were discovered in subsequent crops. The sediments showed a good spectrum of macro- and micronutrients and had high water holding capacities. They found that adding sediments to local soils resulted in good yields. The application on local soils had technical merits, but the costs of dredging, transportation and application was expensive relative to conventional fertilizers.

Darmody and Marlin (2002) and Darmody *et al*. (2004) demonstrated that the application of dredged fine-grained sediments from the Peoria Lakes of the Illinois River, USA, are potentially capable of supporting crop production due to their high natural fertility and their high water holding capacity. However, because of their initial poor soil physical characteristics (poor soil structure and very fluid consistency immediately after dredging) Darmody *et al*. (2004) advised a combination of drying, tillage methods and the addition of materials to improve the tilth, e.g. perlite, compost, biosolids to avoid compaction in the field. Darmody *et al*. (2004) tested the plant uptake of various metals from the Illinois sediments in tomato, barley, snap bean, lettuce and radish and found no difference from control garden soils in Illinois and well below those from industrial areas. They concluded that, properly managed, uncontaminated dredged sediments should make excellent plant growth media.

A research team from Portugal, Brazil and Canada (Fonseca *et al*. 1993, 1998) studied the mineralogy, chemistry and agricultural suitability of specific reservoir sediments in Portugal and Brazil. In particular, they evaluated the clay mineralogy and the organic matter contents in these sediments and compared the agronomic response and suitability of these dredged sediments to that of potting media for flowers. In addition, the research provided valuable data on the usefulness and agronomic effectiveness of these ‘wasted’ soils. The concentrations of micronutrient values in reservoir sediments in Portugal and Brazil were relatively high in comparison to nearby agricultural soils.

Further work needs to be done to determine and evaluate concentrations and availability of anthropogenically introduced heavy metals and pesticides in order to avoid inappropriate use of these fertile organic and ground rock resources. Reservoir sediments, ‘resources out of place’, have a high potential to enhance soil fertility and increase water holding properties of soils close to reservoirs, especially when added to infertile and sandy soils.

Chapter 10

Other minerals and rocks for use in agriculture

While the foregoing chapters dealt primarily with geological macro- and micronutrient resources and their use to enhance soil fertility, this chapter deals with minerals, rocks and mineral-based products used in agriculture, horticulture and floriculture that improve soil and growing conditions by physical means. Most of the minerals and rocks described below are soil amendments, a term that denotes those mineral and organic materials that modify the physical characteristics of soils but do not contribute directly to increasing nutrient concentrations in soils.

10.1 Soilless growth media

The production of vegetables and flowers in greenhouses is rapidly growing around the world. The growth and packaging of plants for this industry requires enormous amounts of plant growth media as well as light-weight sterile packaging media. A large number of plants are grown in shallow-drained container soils each year.

The trend of using soilless practices started in response to the rising costs of practises,to reduce pathogen infestation of soils, as well as soil-degradation (e.g. salinization) and the high costs of chemical fumigation, energy and water. Controllable, energy and water efficient practices in pathogen-free environments are the main advantages for farmers using soilless systems. Also, vegetables and ornamentals can be grown at sites with unsuitable soils and unsuitable climates, e.g. in areas with saline soils, or in deserts (Schwarz 1995). Constructed growth media containing various organic and inorganic rock and mineral materials are used in containers and flower pots, in greenhouses, on sport fields and restricted landscapes, rooftop gardens, courtyards, patios and other spaces.

Soilless growth conditions are created using minerals, rocks, sterile organically-based growth media, together with nutrient solutions. Constructed growth media provide anchorage for plants, good water-holding and drainage characteristics, and adequate oxygen/gas exchange for roots. Common soilless growth media of natural provenance, both organic and mineral based, include peat, vermiculite, perlite, pumice, and expanded clays. Rockwool, another rock-based material that is widely used as soilless growth medium in the greenhouse industry, is a material that has been fused at high temperatures from a mixture of rock materials. Other soilless growth media, used more rarely in greenhouse operations, include humate, scoria, and natural zeolites.

Growth media typically include mixes of lightweight, bulky and sterile mineral and rock materials together with sterile sand or other material with higher bulk density to stabilize the pots and prevent them from toppling when dry.

10.2 Organic growth media

10.2.1 Peat

Peat is a major non-mineral-based soil amendment and growth medium. It is made up of various species of sphagnum moss, in varying stages of decomposition. The main agriculturally important characteristics of peat are: high water holding capacity, high cation capacity (60-180 cmol (+) kg^{-1}), low bulk density (0.07-0.1g cm^{-3}), low pH (3.5-4.5) and dark colour (useful for heat absorption). Peat is a major ingredient in commercial growth media, commonly making up more than 50% of the volume.

10.2.2 Coco-Peat

An increasingly popular organic-based growth medium is ‘coco-peat,’ a product which has been widely used in the greenhouse industry since the 1980s. ‘Coco-peat’ is also called ‘coir dust’ and is a waste product from the coconut industry. Similar to peat, the main agriculturally important properties of coco-peat include: high water-holding capacity, high CEC (100-150 cmol (+) kg^{-1}), very low bulk density (0.05 – 0.06 g cm^{-3}), as well as high porosity (95-96%), (Verdonk *et al.* 1983; Awang and Ismail 1997). A key advantage of coco-peat (or coir-dust) over peat is that it is not mined from peat bogs, which are seen by many as valuable components of the natural environment. The main exporter of coir dust for the greenhouse industry is Sri Lanka.

10.2.3 Humate

Another soil amendment is humate, a material made up of oxidized coals and lignites, and organic-rich claystones. Leonardite is the name used for naturally oxidized lignite (Broughton 1972). Humates are mined and processed in various parts of the world (Roybal and Barker 1986). This black to dark brown material contains high levels of humic acids, has a high CEC (200-500 cmol (+) kg^{-1}), a slightly acid pH, and good physical properties such as a high water holding capacity (Hoffman and Austin 1994; Hoffman *et al.* 1996).

A typical chemical composition of humates (ash-free) is carbon 50-60 wt.%, oxygen 30-40 wt.%, hydrogen 3-5 wt.%, nitrogen 1-3 wt.% and sulphur 1-3 wt.% (Hoffman *et al.* 1996). Humic acid polymers have good chelating properties, they easily bind to clay minerals to form stable organic-clay complexes.

10.3 Rock and mineral based soil amendments

Inorganic mineral and rock based soil amendments that occur naturally and that have undergone physical processing, e.g sizing and heat treatment, are major components of soilless growth media. In the following section the soilless rock and mineral based growth media vermiculite, perlite, pumice, scoria, natural zeolites and expanded clays will be discussed along with rockwool. The latter is a material that has been fused in a blast furnace at high temperatures (approximately 1600^{o}C) using geological raw materials (diabase and limestone) as principal feed material and coke as energy source for the blast furnace.

10.3.1 Vermiculite

Vermiculite is a laminar hydrated ferromagnesian sheet silicate mineral with a permanent negative charge. It occurs in all sizes, from fractions of millimeters to centimeters. Large crystals look like mica. However, vermiculite has the ability to 'exfoliate', to expand perpendicular to the sheet-like structure of the layer-like structure, under high temperatures. The resultant concertina or worm-like shape of vermiculite provides the name to this mineral group (from the Latin word: 'vermiculus' meaning 'little worm').

In the greenhouse industry exfoliated vermiculite is commonly used as 10-30% additive in potting media, but is also used for seed germination, and as a carrier of pesticides, fertilizers, and bacterial inoculants, for example for *Rhizobium* strains (Sparrow and Ham 1983, Graham-Weiss *et al.* 1987, and Lin 1989). The main properties of vermiculite are its:

- light-weight (0.06-0.16 g cm^{-3}) ,
- good water retention,
- good aeration,
- high buffer capacity,
- high cation exchange capacities (50-150 cmol (+) kg^{-1}),
- high total and available Mg,
- good thermal properties.

Because of these properties exfoliated vermiculite enhances early germination with favourable environments for growth and provides a head start in early root development (Handreck and Black 1986; Lin 1989; Yu *et al.* 2000; Tsuda *et al.* 2003). The nature of the exchangeable cations plays a major role in its usefulness in horticultural applications. Most vermiculites contain considerable amounts of exchangeable Mg. However, when vermiculites contain high concentrations of exchangeable Na it reduces its usefulness due to salinization of the growth medium.

Geology of vermiculite

Geologically, vermiculites are found in various environments, specifically associated with carbonatites, mica pyroxenites and ultramafic intrusives. In its crude unexfoliated form, vermiculite represents a group of platy sheet-silicate minerals with the general formula: $(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$. Unexfoliated vermiculite in ultramafic rocks and carbonatites expands into vermiculite during weathering. Consequently, vermiculite is found mainly in weathered environments, in the upper 100-200 m of the weathering land surface. At greater depths, vermiculite changes into incompletely altered vermiculite, and ultimately into the micas phlogopite or biotite. The transition from biotite mica to hydrous clay mica ('illite') to vermiculite is depicted in Figure 5.5. Vermiculite, the end product of this transformation is largely found in weathered environments.

Figure 10.1. *High-grade vermiculite deposit under laterite crust, Namekara, E. Uganda.*

Vermiculites have been discovered in various geological environments, but economic deposits are mainly associated with strongly weathered biotite or phlogopite bearing rocks, such as carbonatites and ultramafic bodies. In 2001, a new vermiculite mine, associated with weathered biotite-pyroxenites from the Bukusu alkaline ring complex, opened in Uganda (Figure 10.1). The largest known vermiculite deposit is Phalaborwa in S. Africa, associated with an ultramafic/ carbonatite complex. Other vermiculite deposits are mined in China, Brazil, Russia, and Zimbabwe.

Processing of vermiculite

The common treatment of crude vermiculite involves flash heating in vertical furnaces at high temperatures (> 900^{o}C). Here, the particles of crude vermiculite exfoliate by expanding at right angles to the cleavage of the mineral, resulting from mechanical separation of the layers by the rapid conversion of the contained water to steam. The exfoliation results in larger volumes and lower bulk density of the expanded vermiculite (Figure 10.2). The difference of unexfoliated and exfoliated vermiculite is illustrated Figure 10.3. Other potential methods of exfoliation include the use of microwaves (Obut *et al*. 2003), Figure 10.4.

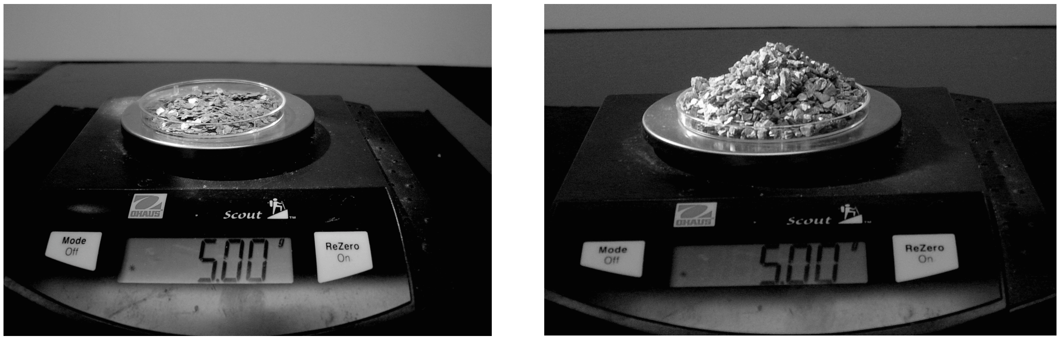


Figure 10.2. *Difference in volume of 5 g unexfoliated (left) and 5 g exfoliated vermiculite (right).*

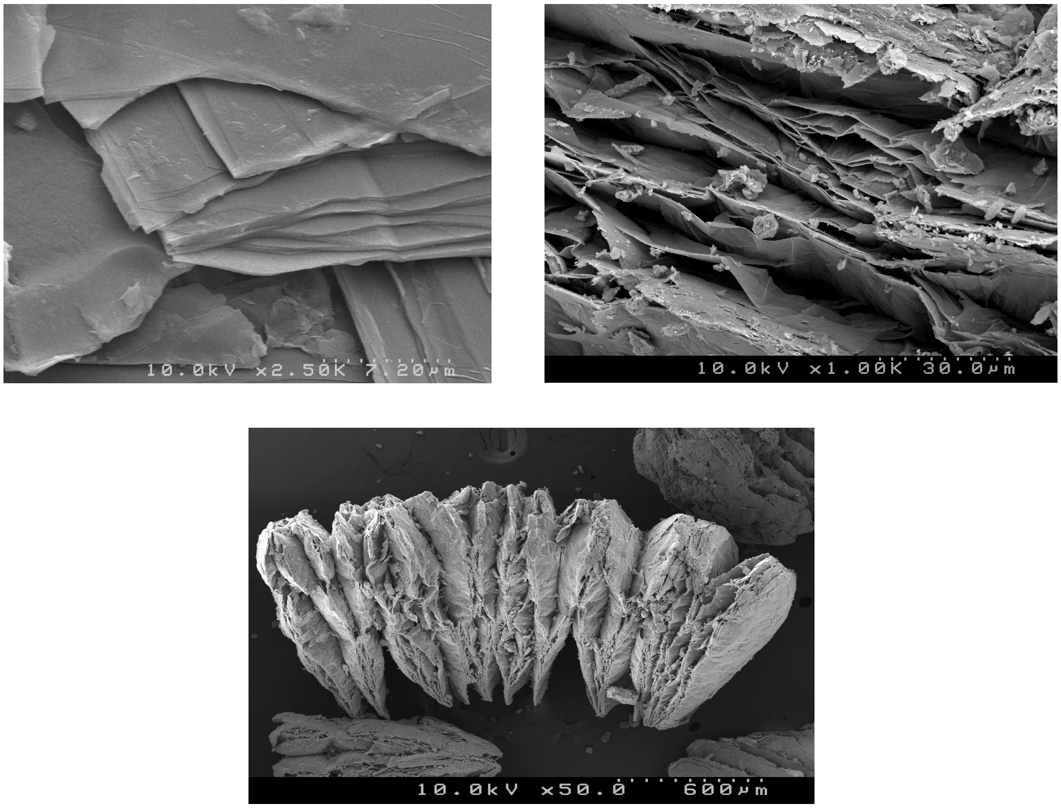


Figure 10.3*. Scanning electron micrographs of unexfoliated and exfoliated Uganda vermiculite. Magnification is shown in scale bar.*

Figure 10.4 *The same block of Uganda vermiculite before and after exfoliation in a household microwave oven; microwave time 2 minutes.*

Vermiculite is commonly transported in its crude state and exfoliated at a treatment plant close to an area of high consumption. Exfoliation is an energy intensive process, requiring mainly oil or natural gas, both non-renewable resources. The price of expanded vermiculite varies with size and bulk density. The prices in 2006 ranged from US$ 75-85 t^{-1} for superfine (< 0.6mm) vermiculite to US$ 225-250 t^{-1} for coarse grade (4.75-2.36mm) vermiculite.

Environmental considerations of vermiculite

The chief environmental problem associated with vermiculite does not stem from the vermiculite itself but instead from potential contamination with asbestos. Asbestos that was found in the vermiculite deposit of Libby, Montana, USA, forced the largest mine in the United States to close in 1994.

Vermiculite products currently on the market are tested in special laboratories on potential health risks including asbestos. The procedures followed are outlined by the Environmental Protection Agency (EPA) and various international institutions of occupational medicine, e.g. the Institute of Occupational Medicine (IOM) in Scotland, UK, or the National Institute for Occupational Safety and Health (NIOSH). The methods involved in detecting asbestos in samples include: polarized light microscopy, scanning electron microscopy, energy dispersive spectroscopy and x-ray diffraction. Detection limits for asbestos concentrations are <0.001%. Current vermiculite producers provide data to the public showing that the asbestos concentrations are below these levels. Currently produced vermiculite is virtually asbestos-free and poses no health concern.

10.3.2 Perlite

Perlite is the term used for both the processed (expanded) and the unprocessed forms of a specific silica-rich volcanic glassy rock material. This volcanic glass in the 'crude' unprocessed form is a meta-stable, amorphous, silica-rich (75-77.5% SiO_2) volcanic glassy rock of rhyolitic composition that contains approximately 2 -5% meteoric water.

In its natural state, this glassy rock material is formed by the gradual hydration of obsidian glass in or near the earth's surface. The hydration process of obsidian involves a volume increase which results in concentric fractures resembling onion skins. Figure 10.5 illustrates the gradual transformation from obsidian (Figure 10.5a) to pure crude perlite (Figure 10.5d). Figure 10.6 shows a detailed view of the surface of obsidian nuclei embedded in greyish-white perlite rock. Crude perlite is chemically inert, has a pH of about 7, and a specific gravity of 2.2-2.4 g cm^{-3}.

Expanded perlites are perlites that have been flash-heated and in the process expanded 10-20 times their original volume (see below). Expanded perlites consist of microscopic bubbles and pores separated by thin walls of volcanic glass. They are porous, light-weight, chemically inert, physically stable silicate materials with good thermal insulation properties and a neutral pH. They are used in the greenhouse and growth media industry because of the following properties:

- light-weight,
- good absorption characteristics,
- good drainage,
- excellent aeration characteristics,
- low bulk density,
- moderate physical strength and resilience.

Increasingly, perlite is being used in commercial plant growing and hydroponic operations (Szmidt *et al*. 1988), and in special perlite 'bag systems' or 'grow-bags', in the production of tomatoes and cucumbers (Wilson 1980, 1985, Grillas *et al*. 2001). Horticultural perlite can be re-used for several years. The application of steam sterilization is the most effective method of sterilization of perlite (Wilson 1988).

Expanded perlite is also an effective carrier of bacterial inoculants, for example strains of *Rhizobium* for legumes (Daza *et al*. 2000). An interesting use of perlite is that of finely ground white perlite powder sprinkled onto the surface of seed blocks to aid early plant growth. The high brightness and reflectance of light onto the underside of leaves of the growing seedlings promotes plant growth (Power 1986).

In the construction industry expanded perlite is valued because of its light weight, low thermal conductivity, high sound absorption and resistance to heat. Over half of the perlite production goes into the construction industry, for insulation and special light-weight cements. Approximately 10% of the expanded perlite produced in the United States is used for horticultural purposes.

Table 10.1 *Mineralogical and physico-chemical characteristics of vermiculite and perlite.*

Charactersitic	Vermiculite	Perlite
Geological origin, setting and age	Weathered carbonatites, biotite/ phlogopite bearing igneous and sedimentary rocks of various ages	Si-rich volcanic dome- shaped extrusives, mainly at plate collision zones and diverging plate margins; Tertiary to mid-Quaternary
Rock/mineral type	Hydrated Mg-Al-phyllo-silicate mineral	Glassy volcanic rock
Structure	Sheet silicate, sheets separated by water	Macro and micro-concentric structure (onion-like), granular, pumiceous
Colour (unexpanded)	Bronze to light brown	Light grey to dark grey
Hardness (Mohs scale)	2.1 - 2.8	5.5 – 7.0
Expansion characteristics upon flash heating	Individual sheets forced apart at right angles, forming 'concertina' shapes	Softened grains swell into light, fluffy foam-like particles
Cation exchange capacity	50-150 cmol (+) kg^{-1}	Negligible
Buffer capacity	High	Negligible
Expansion temperature	850-1100°C	750-1100°C
Expansion ratio	12-20	10-20
Bulk density of expanded material (g cm^{-3})	0.06-0.16	0.03-0.15
Physical resistance of expanded material	Low-Medium	Medium-High
Drainage properties of expanded material	Medium	High
Colour of expanded material	Light brown, silverfish	Bright white

Expanded perlite is sold in various grades, from coarse (-20 mesh) to fine (-100 mesh). In a screened form it is used successfully in many horticultural and floricultural applications as a component in various growth media, for example together with peat and vermiculite. Coarse grained perlite provides good drainage and excellent aeration. Fine grained perlite at sizes <250 microns can however reduce drainage and promote water-logging of growth media (Martyr 1981).

Exfoliated vermiculite and expanded perlite share a number of common characteristics. Table 10.1 provides a comparison of the physical and chemical characteristics of perlite and vermiculite. While vermiculite has a high CEC and buffer capacity (ability to resist changes in pH) as well as water-holding capacity, perlite has greater hardness, physical and chemical resistance as well as better aeration and drainage characteristics. The CEC of expanded perlite is negligible. Because of these differences, perlite and vermiculite are often used to complement one another (Power 1986).

Importantly, the open structure and vesicles of expanded perlite provide the roots with good access to air and thus to oxygen, which is crucial to respiration and early root growth of plants (Handreck and Black 1986). Consequently, its main function in growth media is to provide aeration for roots, and drainage. Since the vesicles in expanded perlite are mostly interconnected it is highly absorbent and consequently used to absorb liquids carrying fertilizers and pesticides.

Perlite and pumice have similar chemical composition. Table 10.2 shows the similarity of selected perlite and pumice samples.

Table 10.2. *Chemical composition of selected perlite and pumice samples (compiled from Harben and Kužvart 1996).*

Chemical analysis	**Perlite (%)**	**Pumice (%)**
SiO_2	73-76	70-74
Al_2O_3	12.5-13.2	12.5-13.5
K_2O	4.1-5.1	1.8-4.8
Na_2O	3.3-4.3	1.6-3.5
Fe_2O_3	0.5-0.75	0.9-2.0
CaO	trace	0.8-2.3
MgO	trace	trace

Geology of perlite

Perlites are young volcanic rocks, usually of Tertiary to mid Quaternary age. Large deposits of perlite occur in continental volcanic fields associated with plate collisions or rifting. Large natural perlite deposits consist of steep-sided, aerially confined, mushroom-shaped and dome-like structures overlying high-silica rhyolitic vents. Perlites form thick glassy envelopes around rhyolitic lavas associated with complex caldera structures. But perlite is also found as dikes and sills. The very high viscocity and quick quenching of the extruding rhyolitic lava produces thick glassy zones on the top, bottom and sides of slowly extruding lava. The glassy, transparent light grey to black rock has a generally pearl-like lustre (from the French *perle* for pearl). However, there are several different types of perlites: dense perlites, with 'onion skin' type concentric fractures, granular types and pumiceous perlite (Chamberlin and Barker 1996). Perlites are formed through hydration of obsidian. The transition from pure obsidian with water content of less than 0.5% (a) to obsidian nuclei embedded in greyish-white perlite (b and c) to pure perlite, water content 2-5% (d) is illustrated in Figure 10.5.

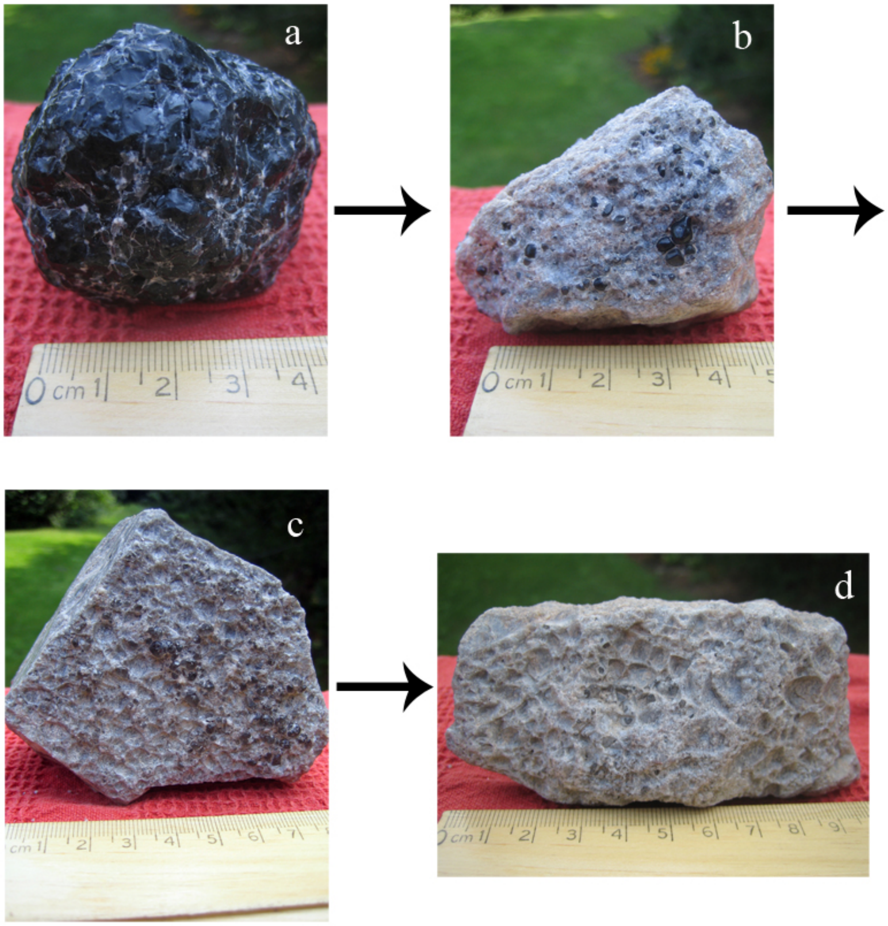


Figure 10.5. *Sequential illustration of transformation from obsidian (a) to obsidian nuclei embedded in greyish-white perlite, 'Apache tears' (b and c) to pure crude perlite (d).*

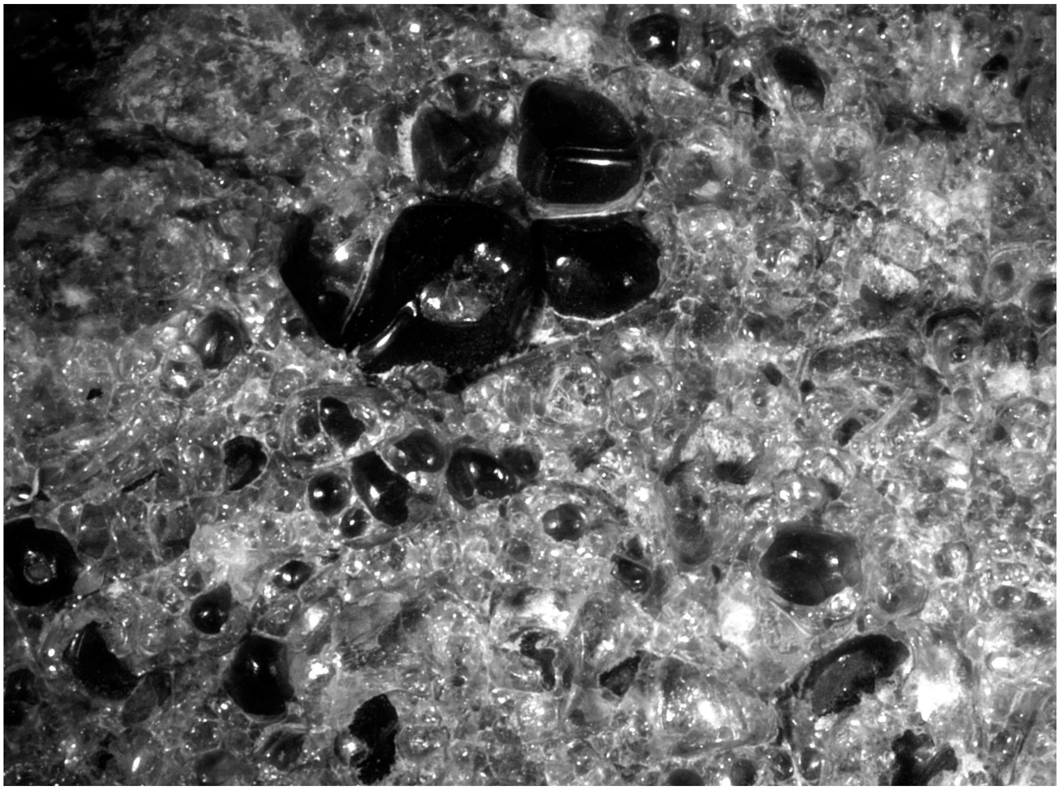


Figure 10.6. *Detailed view of obsidian nuclei embedded in hydrated perlite (scale of picture = 2.5 cm).*

Circular, mushroom-form or elongate perlite deposits associated with high-silica rhyolite lava flows and domes were formed at specific times and in specific locations.

The Si-rich volcanic activities, which produce the ‘sticky’ glass-rich phase, later hydrated to perlite, are commonly Tertiary to mid-Quaternary in age. While older volcanics are usually devitrified, very young flows and domes have not yet had enough time to hydrate from obsidian to perlite.

Major perlite deposits are located in geologically ‘young’ volcanic terrains, mainly in plate tectonic collision zones, e.g. along the west coast of North, Central and South America, Japan, Indonesia, New Zealand as parts of the Circum-Pacific ‘Ring of Fire’, as well as in an East-West trending zone, from the Mediterranean to the Himalayas and the Carribean, and in zones where plates are diverging, such as the East African Rift system and in Iceland.

The largest known, economically extracted perlite deposits are located in the plate collision belt in the Mediterranean, in Greece, and in the Rio Grande rift zone of New Mexico, USA.

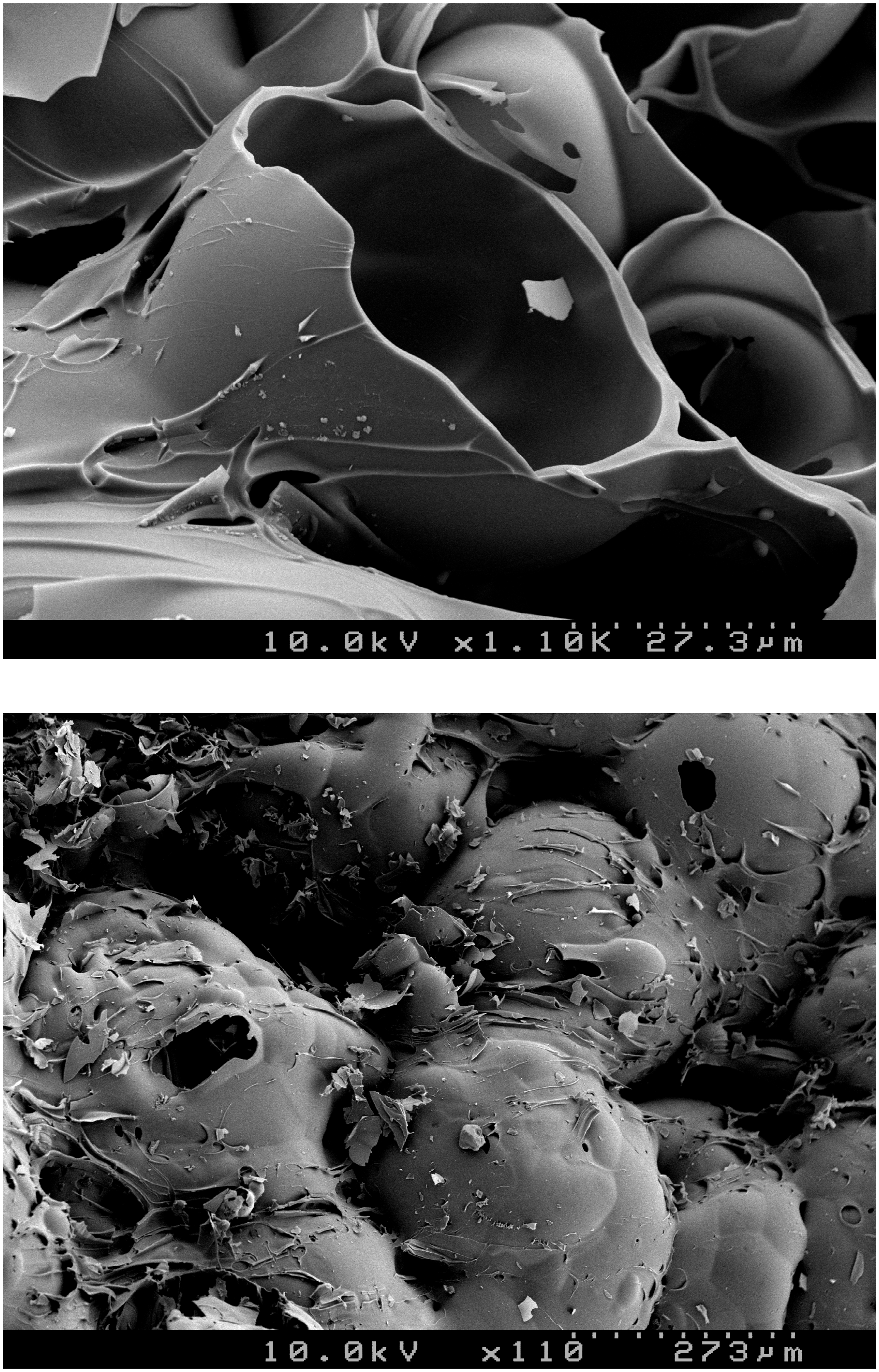


Figure 10.7. *Scanning electron micrographs of expanded ('popped') perlite from Greece. Magnifaction is shown in scale bar.*

In 2005, the main countries that produced perlite were Greece (525,000 t a^{-1}), and the United States (506,000 t a^{-1}), followed by Japan (200,000 t a^{-1}), Turkey and Hungary. The total production of perlite in 2005 was 1,920,000 t (US Geol. Survey 2006). In 2004, crude perlite was sold in the USA to expansion operations at US$ 40.94 t^{-1}. The average price of expanded and sized perlite for horticultural application was US$ 324 t^{-1} in the United States (US Geol. Survey 2004).

Processing of perlite

Industrial processing of perlite requires several steps, including milling, drying and flash heating. Upon flash-heating at temperatures between 900°C and 1100°C, the rock starts melting and the contained water is converted to steam. Due to the sudden vaporization of the trapped water the perlite 'pops' like popcorn, expanding 10 to 20 times its original volume. The rapid expansion of perlite by flash-heating is performed in special furnaces, commonly vertical furnaces. In the furnaces, the glassy crude perlite rock is transformed into a mass of low bulk density, glassy foam with thin walls (Figure 10.7). The light expanded perlite has a brilliant white colour. Figure 10.8 demonstrates the difference in volume between crude, unexpanded and expanded perlite.

Figure 10.8. *Difference in volume of 5 g unexpanded perlite (left) and 5 g expanded perlite (right).*

Environmental considerations of perlite

The main environmental concerns with the production of perlite are high energy requirements and 'nuisance dust'. Expansion of crude perlite in furnaces requires considerable energy. This generally comes from non-renewable oil or natural gas to achieve the required high temperatures (750°C – 1300°C). However, most studies related to exposure to perlite conclude that perlite does not pose any significant health risk to workers and consumers. Some concerns have been raised about the presence of small portions of crystalline silica (<1%), and low concentrations of fluorine. However, both concentrations are usually very low and of little concern during application. The Occupational Safety and Health Agency of the United States (OSHA) concludes that perlite is non-toxic when airborne total particulate concentrations are maintained at levels of 15 mg m^{-3} or below, and when the quartz content is limited to less than 1% crystalline silica.

10.3.3 Pumice

Pumice is a naturally occurring, light-coloured, cellular, frothy, chemically inert and physically resilient volcanic glassy rock. It is similar in appearance and properties to the artificially expanded perlite. Currently, only a small amount of pumice is used for horticultural purposes, but in some places the horticultural use of pumice is growing. An example is the use of pumice (shipped from Iceland) as substrate in hydroponic operations for fruit, vegetable and flower growing operations in the Netherlands (Boertje 1994). Other uses for pumice include the building industry, and the abrasive industry, as an additive in soap and dental polishes, and stonewashing of jeans (McMichael 1990; Geitgey 1994).

Pumice is used in the greenhouse and growth media industry, in a similar fashion as perlite. It has the following properties:

- light-weight,
- moderate water holding capacity,
- good, free drainage properties,
- chemically sterile and inert,
- good aeration properties,
- good physically stability.

In general, pumice has similar physico-chemical properties to those of perlite and can thus be used as an inexpensive substitute for perlite in greenhouses and plant nurseries in soilless culture (Noland *et al.* 1992). Differences of pumice and expanded perlite are mainly related to the range of pore sizes, shape and independent particle size as well as physical resilience.

Pumice rocks and fragments have vesicles <1mm in size, separated by volcanic glass walls (Figure 10.9). Vesicle shapes in pumice are more irregular than in perlite, from round to elliptical to elongate and irregular shape. In some pumice deposits, the vesicles are closed and in others they are open. The glass walls in pumice are also thicker than in expanded perlites. This gives pumice higher physical strength and higher bulk density than expanded perlite, commonly 0.5-0.7 g cm^3 (Geitgey 1994). Pumice, commonly brittle with sharp edges with a Mohs' hardness of 5-6, is also used as mild abrasive.

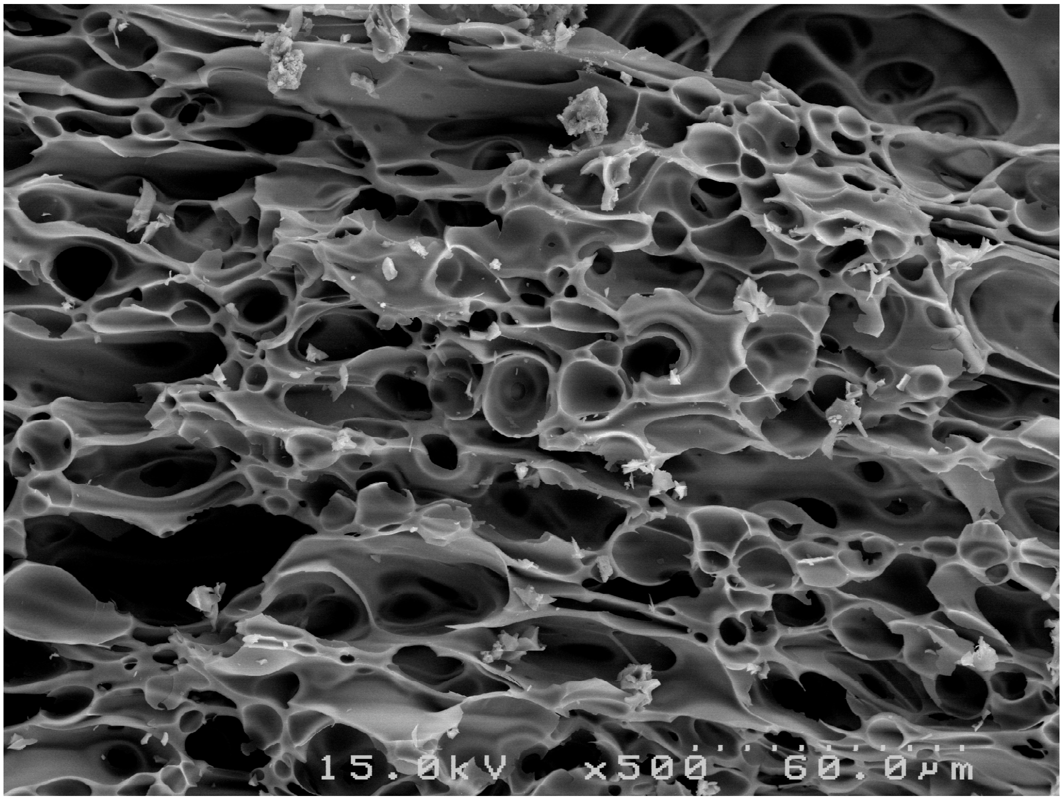


Figure 10.9. *Scanning electron micrograph of pumice fragment, a framework of pores, sealed and open. Magnification is shown in scale bar,*

As can be seen from Table 10.2 the chemical composition of perlite and pumice is similar. It differs slightly with regards to K, Na and Ca as well as Fe concentration. The Fe content makes pumice often grey to pale yellow to brown. However, it is important to note that from the total chemical composition of these two silicate rocks almost none of the nutrient elements is plant available and released for uptake by the roots.

Pumice can easily be steam-sterilized and re-used (Gunnlaugsson and Adalsteinsson 1999). Einarsson *et al.* (1993) used the locally available pumice from Iceland as a carrier for *Rhizobium* bacteria for the legume *Lupinus nootkatensis*, which is used in Iceland for soil stabilization.

Each pumice deposit differs in composition, grain size distribution and characteristics of vesicles, shapes and connectedness of vesicles. In Turkey, the pumices with rhyolitic composition have typically closed pores, while other Turkish pumices of dacitic composition have more open pores (Gündüz and Uğur 2004) and have thus different use. Pumice rocks with closed vesicles are often seen as floating pumice. Pumice fragments from the 1883 Krakatau eruption in Indonesia were still seen floating on the Indian Ocean up to two years after the eruption (Geitgey 1994).

The costs of extraction of pumice are generally very low making pumice a useful product, particularly when growth operations are close to pumice deposits or when transport is cheap, e.g. sea transport from source close to the oceans. Greek scientists compared the use of pumice with that of coco-peat and rockwool as growth media in hydroponic operations and found that productivity of lettuce and flowers was not significantly different from other growth media (Syros *et al*. 1999; Siomos *et al*. 1999).

Figure 10.10. *Pumice mulched papaya tree, Melkassa, Rift Valley, Ethiopia.*

Pumice has also been tested for use as rock mulch, together with other rock types as described below (Woldeab *et al*. 1994). A practical observation with pumice mulch was made in a papaya plantation in the drought prone Rift Valley of Ethiopia near the town of Melkassa. Here, locally available ‘floating pumice’ was applied as mulch on papaya trees that were watered in basinal structures at the base of the tree (Figure 10.10). The amount of irrigation water used for papaya trees could be reduced by approximately 50% without compromising the growth of the above trees and the papaya fruit yield (van Straaten, unpublished). The main reason for the increased water use efficiency is reduced evaporation loss (see section on rock mulch below).

Geology of pumice

Pumice forms as result of violent expansion of dissolved gases in viscous, silica`-rich lavas. Pumicite has the same origin and composition but is only of smaller grain size (particles <4 mm in diameter). The mineralogical compositions of the silica-rich lavas range from rhyolitic to dacitic. The chemical composition of pumice is similar to the composition of perlite (Table 10.1).

Pumice is found in large consolidated and unconsolidated layered deposits close to the volcanic vents from which it was ejected. Pumicite occurs further away from the volcanic vent. In general, the extent of pumice and pumicite deposits is much larger than the more confined deposits of perlite. Pumice and pumicite are mainly air-fall deposits, ejected from volcanoes during violent eruptions. Some pumice deposits are derived from turbulent ash flows. The thickness of pumice deposits and particle size usually decreases with increasing distance from the volcanic vent. The thickness varies but is typically in the meter to tens of meters range. Other pumice deposits are transported by water and usually mixed with other sedimentary debris and are thus less clean.

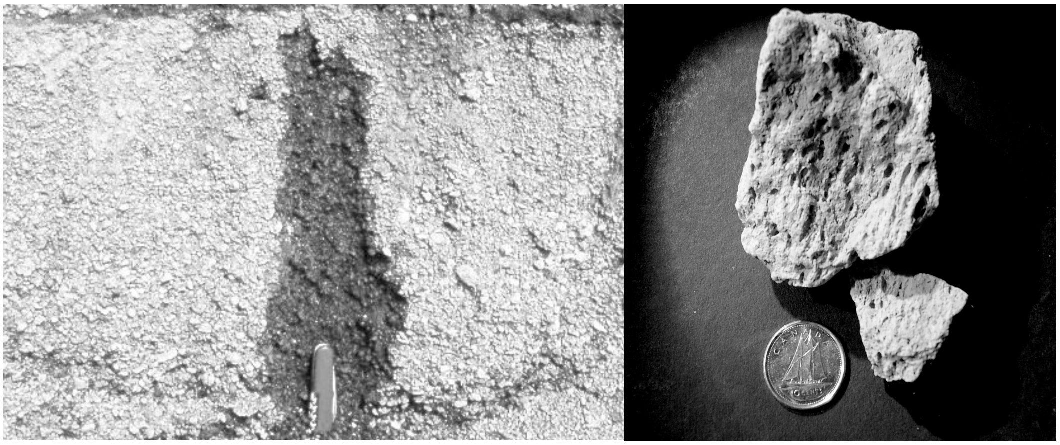


Figure 10.11 *(left) pumice deposit in Rift Valley of Ethiopia indicating good natural water holding capacity; (right) pumice fragments.*

Unconsolidated pumice deposits are found in many parts of the world where Tertiary to younger silicic (Si-rich) volcanic rocks occur. Areas where large unconsolidated pumice deposits can be found are young volcanic areas along the Pacific Rim and in other plate collision areas. Countries in Europe with sizeable pumice deposits are located are Greece, Turkey, Spain, Italy. Other major occurrences and deposits of pumice are located in the western United States, in Canada and some Caribbean countries in geologically young, continental volcanic areas, as well as in Central and South America, New Zealand, Indonesia, Japan and other countries along the Circum Pacific rim. Extensive pumice deposits are also found in diverging plate tectonic settings, for example in the Rift Valley of Eastern and Southern Africa, in the Rio Grande Rift of the USA, and in Iceland.

More than 50% of the world's 5.8 million tonnes annual pumice production comes from the Mediterranean, mainly Greece, Turkey, Spain and Italy, with an additional 12% of world production coming from the United States. Most pumice is mined by open pit methods, using bulldozers to push the unconsolidated pumice into stockpiles for further processing.

In a rare case, pumice is mined from river deposits, for example in New Zealand, by barge pumping, where pumice, mixed with sand, is separated by screening and gravity methods (McMichael 1990; Harben and Kužvart 1996).

In 2005, the average price of pumice and pumice for horticultural applications was US$ 16.30 per tonne (US Geological Survey 2005).

Processing of pumice

Processing of pumice itself consists primarily of crushing, screening and bagging according to grain size. In many unconsolidated deposits sizing is the only processing technology required, generally making it a very inexpensive material.

Environmental considerations of pumice

The production of pumice is more 'environmentally friendly' than that of perlite or vermiculite as it does not require high-energy inputs for thermal expansion, as nature has already completed this process. Although this is an environmental advantage, the shipment of pumice to the consumers requires greater transport energy inputs.

Pumice is shipped in its bulky, expanded form, while perlite is transported in the crude perlite form to be expanded in processing plants close to the point of use. In distant markets this translates to a competitive disadvantage for pumice.

The mining and processing of pumice can create 'nuisance dust', according to Occupational Safety and Health Standards (OSHA) criteria. However, proper handling and dust control can reduce the dust problems considerably. Chemically, pumice is non-toxic. It is not considered hazardous as defined by OSHA Hazard Communication Standards.

10.3.4 Scoria

Scoria is the basaltic-andesitic equivalent to pumice, with approximately 50-60% SiO_2 or less. Scoria rocks are used as growth media mainly because of their favourable physico-chemical characteristics and their large local availability in volcanic areas of the US (e.g. Hawaii), on the Canary Islands of Spain (Caldas and Tejedor 1987; Tejedor *et al*. 2003), in Italy and in Israel (Feigin *et al*. 1980).

In general, scoria is a chemically and physically stable rock, but with a higher bulk density than expanded perlite, pumice or exfoliated vermiculite. Scoria has thicker walls than pumice and has thus a greater structural strength than either pumice or expanded pearlite. The vesicular, dark scoria rock type contains a great amount of vesicles that give the rock a coarse, black, sponge-like appearance. The density of the basaltic material is about 2.9 g cm^{-3}, but the bulk density of this vesicular rock is about 0.7 to 1.1 g cm^{-3} depending on the grain size. Scoria has a very low cation exchange capacity (up to only 5 cmol (+) kg^{-1}) and a pH close to neutral (Luque 1981).

Unconsolidated and easily to extract natural scoria rocks with various grain sizes can be readily mined and sized. Locally available scoria rocks have been tested as materials for rock mulch in Ethiopia (Woldeab *et al*. 1994). The main reason for the increased water use efficiency is reduced evaporation loss (Tejedor *et al*. 2003) as described below. Scoria rocks are applied on the Canary Islands of Spain as rock mulch (Caldas and Tejedor 1987; Tejedor *et al*. 2003). The yield of roses in greenhouse experiments in Italy revealed there was no significant difference between roses grown in pots with perlite or scoria (De Pascale and Paradiso 2001).

Geology of scoria

Natural accumulations of unconsolidated scoria in thousands to millions of tonnes occur in many areas with young volcanic activities, especially of basaltic to andesitic volcanism. Since scoria fragments are relatively heavy, they fall close to the volcanic vent. Scoria fragments are typically found in thick layers in and around conical hills made up of pyroclastic rocks, so-called cinder cones (Figure 10.12). Fragments of scoria with size ranges between 2 and 64 mm (lapilli) can be easily extracted from these cinder cones and sized by simple screening.

Figure 10.12. *Steep-sided cinder cone with scoria, Grábrók, Iceland.*

10.3.5 Natural zeolites

Zeolites consist of a group of crystalline, hydrated, alumino-silicate minerals with negatively charged sites in their structure. Zeolite structures are open and filled naturally with water and positively charged ions for electrical neutrality.

- Zeolites have the following properties:
- High degree of hydration,
- High void volume (up to 50%),
- High internal surface areas (several hundred m^2 g^{-1} of zeolite),
- High cation exchange capacity (CEC): 150-300 cmol (+) kg^{-1},
- Cation selectivity, specifically for cations like NH_4^+, K^+, Cs^+, and others,
- Excellent molecular sieve properties,
- High physical stability.

The name zeolite is derived from the Greek words *zein* and *lithos*, meaning boiling stones, because of their bubbling nature when heated by a blow pipe (Mumpton 1978). Historically, crystals of zeolites were found only in small amounts, in vesicles of volcanic rocks, and were regarded as mineralogical curiosities. Their microscopic grain size makes identification difficult however, improved identification methods in the last few decades, specifically X-ray diffraction (XRD) and scanning electron microscopy (SEM), resulted in the discovery of more fine-grained zeolite deposits, many of which were previously identified as fine-grained 'vitric tuffs' or fine-grained 'ash-fall tuffs'. In the last fifty years, extensive deposits, made up of highly concentrated accumulations of zeolite minerals in predominantly layered rocks formed from volcanic ash, have been discovered in many parts of the world (Mumpton 1973, 1978, 1999; Holmes 1994).

A scanning electron micrograph of a zeolite (clinoptilolite) (Figure 10.13) illustrates the crystalline nature of this mineral at high magnification.

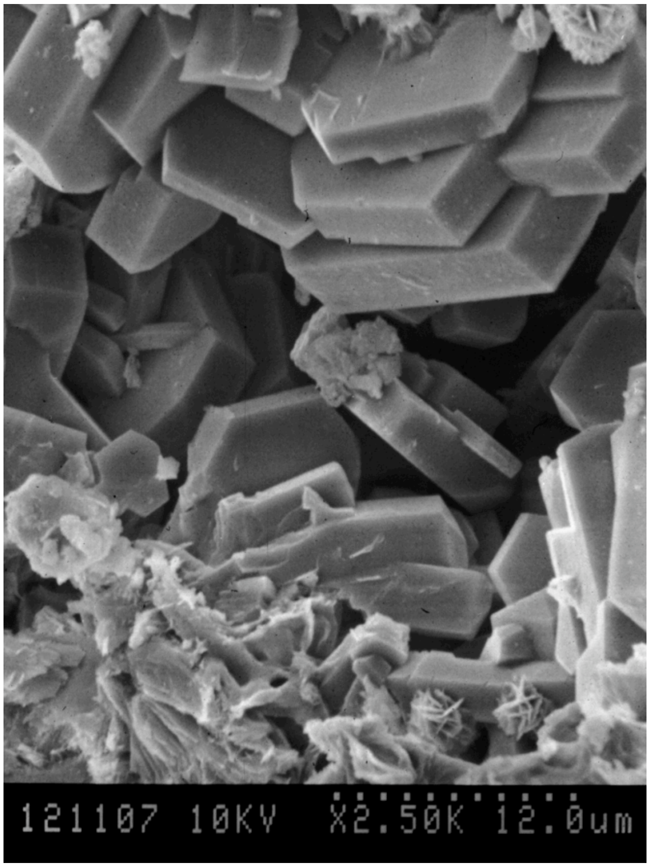


Fig 10.13 *Scanning Electron Micrographs (SEM) of clinoptilolite, Ash Meadows, California,USA. Magnification is shown in scale bar.*

Each zeolite has a special selecitivity for specific cations, for example clinoptilolite has the following cation selectivity:

Cs > Rb > K > NH_4 > Ba > Sr > Na > Ca > Fe > Al > Mg > Li (Ames 1960).

Zeolite Geology

Natural zeolites are geological resources that are formed when reactive Si-rich source materials are subjected to circulating alkaline solutions (Sheppard and Hay 2001). The multi-stage processes usually take place under low temperature-low pressure regimes. An important factor in the formation of zeolite is the reaction of alkaline pore water with the glassy Si-rich starting material (Sheppard 1973; Mumpton 1999). Volcanic glass of intermediary composition is the most common source material. Other, less known precursor materials include biogenic silica-rich sediments, and poorly crystalline clays. The pH of the reacting solution and the concentration of dissolved species of Na^+, K^+, Ca^{2+} , and H^+ and silicic acid (H_4SiO_4) of the reacting aqueous phase also play major roles in the subsequent formation of zeolites.

The formation of zeolites depends on:

- chemistry of pore water,
- activities of dissolved species like Na^+, K^+, Ca^{2+}, etc.
- composition of starting material.

Sheppard (1973), Mumpton (1973) and Munson and Sheppard (1974) classified natural zeolite deposits into six classes. Detailed accounts of the 6 major zeolite classes are described by various authors in Reviews in Mineralogy and Geochemistry (Bish and Ming 2001).

- Closed systems: Zeolites formed from glass-rich volcanic materials in hydrologically closed saline/alkaline lakes, e.g. in playa lake systems in rift valleys. Zeolites form as a result of saline, alkaline solutions reacting with and replacing vitric tuffs that fell into these closed basins. The distribution of authigenic mineral zones is typically lateral, with unaltered vitric ash deposits found at the edges of the playa lake environment, followed by zeolitized ash, and finally, in the centre, K-feldspar (Surdam 1977; Langella *et al*. 2001).
- Open systems: Zeolites formed in hydrologically open systems, as a result of meteoric water percolating in open hydrological systems. The zoning is typically vertical (Sheppard and Hay 2001).
- Burial metamorphic systems: Zeolite deposits formed under low-grade, burial metamorphic conditions, in rocks that were subjected to specific pressure and temperature regimes, the so-called zeolite facies (Utada 2001a).
- Hydrothermal or hot spring systems: Zeolites formed as result of hydrothermal alteration (Utada 2001b).
- Deep marine systems: Zeolites formed in deep marine sediments (Iijima 1978, 2001).
- Weathered systems: Zeolites formed in soils from mainly but not exclusive volcanic source materials (Ming and Mumpton 1989; Ming and Boettinger 2001).

In addition to natural zeolites, there is also a very large production of synthetic zeolites, produced largely for the detergent and chemical industries, for use as molecular sieves. Synthetic zeolites are 'custom-made' for the market. They are uniform in composition, but much more expensive, and commonly less physically stable than natural zeolites.

The general formula of zeolites is:

$$\underbrace{(M_x^{+}, M_y^{++})}_{\text{exchangeable cations}} \qquad \underbrace{(Al_{(x+2y)}Si_{n-(x+2y)}O_{2n})}_{\text{structural cations}}\cdot nH_2O$$

The typical formulas, void volumes and cation exchange capacities are shown in Table 10.3.

Table 10.3. *Representative formulae, void volumes and theoretical cation exchange capacities of seven naturally occurring zeolites and one synthetic zeolite (Linde A) (source: Mumpton 1999).*

Zeolite name	**Representative unit-cell formula**	**Void volume (%)**	**CEC* (cmol+ kg^{-1})**
Clinoptilolite	$(Na_3K_3)(Al_6Si_{30}O_{72})\cdot 24H_2O$	34	216
Mordenite	$Na_8(Al_8Si_{40}O_{96})\cdot 24H_2O$	28	229
Phillipsite	$(NaK)_5(Al_5Si_{11}O_{32})\cdot 20H_2O$	31	331
Chabazite	$(Na_2Ca)_6(Al_{12}Si_{24}O_{72})\cdot 40H_2O$	47	384
Analcime	$Na_{10}(Al_{16}Si_{32}O_{96})\cdot 16H_2O$	18	454
Laumontite	$Ca_4(Al_8Si_{16}O_{48})\cdot 16H_2O$	34	425
Erionite	$(NaCa_{0.5}K)_9$ $(Al_9Si_{27}O_{72})\cdot 27H_2O$	35	312
Linde A (synthetic)	$Na_{12}(Al_{12}Si_{12}O_{48})\cdot 27H_2O$	47	548

* Cation Exchange Capacity calculated from unit-cell formula

Although more than fifty different species of the zeolite group of minerals have been identified, only seven zeolite minerals make up the major part of volcano-sedimentary zeolite deposits: analcime, chabazite, clinoptilolite-heulandite, erionite, laumontite, mordenite and phillipsite (Table 10.3). The structure of each of these minerals is different but they all have large open 'channels' in the crystal structure that provide large void spaces for the adsorption and exchange of cations. Primary building units of zeolites are SiO_4 and AlO_4 tetrahedra. These primary building units are linked together into simple geometric forms (secondary building units), e.g. rings.

Permanent electronegative charges result when either Al^{3+} or Fe^{3+} (trivalent) structural cations replace Si^{4+} (tetravalent) structural cations. The net negative charges must be balanced for electro-neutrality by additional monovalent (M^{+}) and divalent (M^{2+}) cations, e.g. Na^{+}, K^{+}, Ca^{2+}, but also Cs^{+}, or Pb^{2+}. Counter-ions – cations – are held loosely in zeolite channels and can be exchanged. Important cations of agronomic importance that can be added and released in the zeolite channels are ammonium (NH_4^{+}), and K^{+}. The high cation exchange capacities of zeolites are a function of the degree of substitution of structural cations (trivalent Al or Fe for tetravalent Si). The greater the substitution, the greater the negative charge, and therefore the greater the amounts of other cations that are required to achieve electric neutrality.

Relatively pure zeolite deposits have been discovered in more than 50 countries. Most of the major deposits have been found in or close to volcanic areas in saline, alkaline lake environments, in weathered volcanic zones, hydrothermal alteration zones and in rock sequences of deep sea sediments. Outcrops of massive natural zeolite deposits in Ethiopia are depicted in Figure 10.14. Many natural zeolite deposits are yet to be discovered, especially in less investigated volcanic areas of the world.

Fig 10.14. *Massive bedded zeolite deposit, Rift valley, near Melkassa, Ethiopia.*

High probability areas for zeolite deposits are primarily in converging and diverging plate margin areas with active volcanism. Diverging plates include the Rift Valley in East Africa and the Rio Grande Rift in the western United States. Converging plate boundary areas include the Pacific Rim (“Ring of Fire”), from

South America to New Zealand, Indonesia, Japan and North America. Zeolite deposits are also known from Caribbean countries and other relatively young plate margin areas with volcanic activites.

The use of natural zeolites in agriculture

Natural zeolites are increasingly used in agriculture and horticulture, as feed additives, N-carriers, manure handling and odour control materials, in horticulture as slow release N-carriers, and in aquaculture for ammonia control. Among the many applications of natural zeolites are pet litter (odour control, desiccation), water treatment, animal feed, pollution control (heavy metals, Cs adsorption), oil and gas industry (molecular sieve), building industry (e.g. dimension stone, light-weight aggregate), and as 'zeoponic' plant substrate for long-term space missions (Ming 1989).

Natural zeolites are particularly useful in agriculture because of their large porosity, high cation exchange capacity and their selectivity for NH_4^+ and K^+ cations, as well as their physical stability (Mumpton 1984). They can be used both as carriers of nutrients (e.g. NH_4^+ and K^+) and as a medium with free exchangeable nutrient ions. Some natural zeolites contain considerable amounts of exchangeable K^+ that can enhance plant growth in potting media. For example, Hershey *et al*. (1980) provided data on the slow release effect of K from K-zeolites.

The main use of natural zeolites in agriculture is, however, for ammonium (NH_4^+) exchange, storage and slow release. It has been shown that zeolites, with their specific selectivity for NH_4^+, can take up NH_4^+ from farmyard manure, composts or NH_4^+ from ammonium bearing fertilizers, and store it temporarily in the internal void spaces before slow release (Mumpton 1977, 1999). Many laboratory and field experiments carried out over the past decades show that NH_4^+-charged zeolites can act as slow-release fertilizer. Several studies have shown increased plant growth, in response to greater availability of NH_4^+ and decreased losses of N through nitrification, with the addition of zeolites (Barbarick and Pirela 1984; Pirela *et al*. 1984; Witter and Lopez-Real 1988; Eberl *et al*. 1995; Mumpton 1999; Ming and Allen 2001). Increasing fertilizer use efficiency by adding natural zeolites to soluble N-fertilizers such as ammonium nitrate and urea as well as K fertilizers has been summarized by Ming and Allen (2001). The application rates of zeolite amended fertilizers are relatively high, ranging from 400 kg ha^{-1} to several tonnes per hectare.

Lewis *et al*. (1984) showed the effectiveness of the zeolite clinoptilolite as a slow release N fertilizer, preventing injury to urea-sensitive radish plants. The injury to seedlings upon application of clinoptilolite plus urea is lowest in sandy soils (Lewis *et al*. 1984). Park and Komarneni (1998) demonstrated the slow release of NH_4^+ from various zeolites treated with molten $NH_4^+NO_3$ and KNO_3 over time.

This modified zeolites with ‘occluded’ ammonium and nitrate shows good promise to be a slow-release N fertilizer.

Most of the examples of slow-release nutrient-charged zeolites have been used for horticultural applications and only few experiments have been conducted on field-based agriculture. Recent experiments with ammonium-loaded zeolites on sandy Aridisols demonstrate slow release of zeolite-amended NH_4-fertilizers (Perrin *et al.* 1998). Application rates in these experiments varied from 112 to 336 kg N ha^{-1}. In comparison to unamended N-fertilizers, the N use efficiency of zeolite amended N-fertilizers is generally high, ranging from 72-95.2%. However, no significant differences in maize/corn yield have been observed among the various N fertilizers (Perrin *et al.* 1998).

Leggo (2000) demonstrated the nutritional and ecological features of ‘organo-zeolites’, mixtures of manures with zeolite and ammoniated zeolite over time under greenhouse conditions. The data show an exponential decrease of NH_4^+ from charged zeolites, whereby about half of the lattice-bound NH_4^+ in orgono-zeolitic substrate was released within the first week. The total residence time of NH_4^+ in zeolites is two months (Leggo 2000).

In Cuba, zeolites are successfully used in small-scale, peri-urban as well as large-scale ‘zeoponic’ systems, where NH_4^+-charged zeolites provide vegetables with substrate and nutrients for growth. The experience from Japanese research and development shows that significant returns can be achieved, albeit at high application rates (Torri 1978).

The application of natural zeolites requires a good understanding of both, the chemical characteristics, e.g. exchange properties of the zeolites, and the soils where the zeolites are going to be applied. It has been shown that zeolites that contain a high percentage of exchangeable Na (e.g. sodic clinoptilolites) can cause yield reductions due to Na toxicity and osmotic problems within the plants (Barbarick and Pirela 1984). Therefore it is prudent to characterize the zeolites prior to application as to avoid high Na zeolites or to modify (exchange Na^+ with NH_4^+ or K^+) prior to application. While most of the naturally occurring natural zeolites are beneficial in improving animal and plant growth, there are cases where zeolites do not perform effectively. For example, it has been demonstrated that certain zeolites with Na as the main exchangeable cation can actually decrease rather than increase plant growth and yield (Barbarick and Pirela 1984). Soils where the application of zeolites are most suitable are generally coarse grained sandy soils with low cation exchange capacities and low water holding capacities.

Another agricultural area with substantial potential to apply natural zeolites is as animal feed additive and in manure treatment systems. Mumpton (1999) and Ming and Allen (2001) report on the predominantly positive experiences from research in many countries, where small dosages (3-6%) of zeolites were incorporated in animal feed stuff for swine, ruminants and poultry. The effectiveness of using zeolites seems to be related to the ion exchange characteristics of zeolite to preferentially adsorb NH_4^+ from the breakdown of proteins and N components in feed (Mumpton and Fishman 1977; Mumpton 1999). According to reports from various researchers, the addition of zeolites into the feed did not only increase growth and feed efficiency but also reduced the incidence of intestinal diseases among young animals. In addition, the use of zeolites as feed additive reduced the evolution of ammonia and odours in animal wastes. Hale (2006) studied the effects of using small amounts of zeolites in combination with gypsum in feed additions to laying hens. Results of large scale trials in laying operations show that the addition of 1-1.5% zeolite and 5.25% gypsum could reduce ammonia emissions to the environment by 66-85%.

Bernal *et al*. (1993) and Witter and Lopez-Real (1988) studied the N losses during composting processes and the effectiveness of natural zeolites in adsorbing the volatilized ammonia. Ammonia (NH_3) concentrations in chicken houses and other intensive, confined animal growth operations can be high and a threat to animal (and human) health. In order to reduce high concentrations of NH_3 in these confinements and the outside environment, Koelliker *et al*. (1980) developed a simple system that removed NH_3 concentrations by 15-45%. A simple scrubbing device has also been developed at the University of Guelph, Canada, in which the NH_3 in the air from chicken houses is transformed into NH_4^+ and then adsorbed with very high efficiency onto zeolites (van Straaten, unpublished). Mumpton (1999) summarized experiences from Japan on the reduction of odours and associated pollution from chicken and swine operations and on the reduced moisture content of animal excrements.

Zeolites are also successfully used in aquacultural operations, e.g. in fish hatcheries, but also in aquaria and during transport of live fish (Mumpton and Fishman 1977; Mumpton 1999). The zeolites remove the NH_4^+ produced by decomposition of fish excrements and unused food from recirculating waters and thus provide a healthier environment for fish.

Zeolite amended sand is also used as medium for turfgrass operations especially for germination and establishment of various grasses (Ferguson *et al*. 1986). Simulating the growth of grasses, such as creeping bentgrass on golf greens, Huang and Petrovic (1994) showed that sandy rooting media amended with 5-10% clinoptilolite with optimum particle size of 0.1-1 mm promoted better N use efficiency, and reduced N leaching into the environment as well as high water availability and aeration.

Ammonium-charged zeolites have also been tested successfully for their ability to increase the solubilization of phosphate minerals (Lai and Eberl 1986; Chesworth *et al.* 1987; Eberl *et al*. 1995; Allen *et al*. 1996), leading to improved phosphorus uptake (see Chapter 4).

Several compilations and conference proceedings covering occurrences, properties and use of zeolites have been published in recent years, including Mumpton (1977), Sand and Mumpton (1978), Pond and Mumpton (1984), Holmes (1996), Mumpton (1999), Bish and Ming (2001) and proceedings of conferences held by the International Natural Zeolite Association (website: http://icnz.lanl.gov/). In these publications the reader can find research results on the geology, mineralogy and use of zeolites in various applications including agriculture.

Zeolite production, prices and environmental considerations

World production of zeolites in 2005 was estimated between 2.5 to 3.0 million tonnes. The largest annual production of natural zeolites comes from the People's Republic of China (approximately 1.5 to 2 million tonnes), followed by the Republic of Korea (150,000 t), Japan (140,000 to 160,000t), USA (65,500 t) Cuba (37,500 t), Hungary and Turkey (30,000 t each) and other producers (US Geol. Survey 2005).

The prices of natural zeolites vary widely, with zeolites being commonly sold between US$ 30 and 140 per tonne, with granular agricultural grade (40 mesh) ranging from US$30-70 (US Geol. Survey 2005). However, speciality high quality natural zeolites, for example the 20 cm thick, high-grade chabazite deposit at Bowie, Arizona, USA fetch high prices for their use in gas purification (Holmes 1994). Some zeolites, for example for pet litter, or fish tank additions or odour control are sold at prices between US$ 0.5 – 4.50 kg^{-1} (US Geol. Survey 2005).

From the >50 naturally occurring zeolites there is only one zeolite mineral, the fibrous zeolite erionite, that has been classified as carcinogenic (Suzuki and Kohyama (1988). With the exception of this one zeolite, all other zeolites do no show detrimental environmental or health effects.

10.3.6 Expanded clay

Expanded clay is widely used in hydroponics operations (Figure 10.15) and landscaping. It is made up of various clays that have been calcined in rotary kilns at temperatures above 1000°C. Expanded clay is an inert, physically stable product that provides free drainage and good aeration. Expanded clay has low cation exchange capacity (10-30 cmol (+) kg^{-1}), and bulk density (around 0.6-0.7 g cm^{-3}) (Steinberg *et al*. 2005). The pH is neutral to slightly alkaline (pH 7-7.5).

Light-weight expanded clay aggregates (LECA) are produced from clays mixed with organic compounds that have been calcined in rotary kilns at temperatures exceeding 1000°C. It is widely used as a growth medium in plant containers. It is made up of round or oval-shaped light-weight product that is very porous inside and that has a sintered, brown surface. Sintered clay ‘pebbles’ are chemically inert and physically stable, have good drainage and aeration properties and have bulk densities of around 0.3-0.8 g cm^{-3} with a neutral pH.

Figure 10.15. *Expanded clay (here Turface) (left); Light-weight expanded clay aggregate (LECA) (right).*

10.3.7 Rockwool

Rockwool (or mineral wool) is widely used in the construction industry as insulation material, and in the soilless greenhouse industry. In Denmark, the use of rockwool (termed ‘Grodan’) started in the early 1970s. “Grodan’ was used as an alternative to soils, which suffered from pathogen infestation, poor moisture control, and salinization due to intense fertilization. The use of this growth medium spread fast into other geographical areas with intensive agriculture on a small footprint, for example to the Netherlands (Welleman and Verwer 1983; Welleman and Smulders 1988; da Silva *et al*. 1995). Like with other growth media, the use of rockwool in greenhouses enables farmers to produce vegetables and flowers all the year round (Noordam 1988). Rockwool is a sterile, porous, non-degradable growth medium with a very low bulk density (0.07-0.1g cm^{-3}) and a pore volume of about 96%. Rockwool has a high water retention capacity (da Silva *et al*. 1995). The initial pH of this growth medium is alkaline (pH 7-9) but due to the lack of buffer capacity it can be easily corrected (Schwarz 1995).

Rockwool is made from several geological materials and is produced in a blast furnace at high temperatures. The main components of rockwool are diabase (with basaltic composition) (60%), limestone or steel slag (20%) and coke (20%). The coke is used as fuel in high temperature blast furnaces. At a temperature of about 1600°C the rock blend melts. This liquid, molten material is then extruded onto a series of high-speed rotors and forms 5 μm fine fibres. These fibers are then rapidly cooled by an air stream and phenolic resin and wetting agents are added. The extruded and spun fibrous material is then pressed into blocks or slabs, cut into shapes, and packaged. Slabs of rockwool are usually 90-100 cm long, 15-25 cm wide and 5-10 cm thick but are also produced as propagation plugs and blocks of various shapes.

The chief disadvantage of rockwool is its environmental costs. Rockwool production requires high energy inputs and since rockwool is not biodegradable it finally ends up on landfills. However, recent developments show that rockwool slabs can also be reused in chopped forms as a component in potting media (T. Blom, University of Guelph, pers. comm. 2005).

10.4 'Wastes' from selected mineral-based industries

Some of the 'wastes' or 'by-products' of mineral-based industries offer a potential 'resource' for various crop production systems. Several 'wastes' from mining and mineral-related industries may be useful for low-input agriculture. They include:

- Waste from incomplete calcining in lime operations,
- Calcium carbonate wastes from cement and other industries using $CaCO_3$,
- Tailings from diamond mining from kimberlites,
- Wastes from 'black granite' operations,
- Waste from phosphate mining,
- Wastes from phosphate processing,
- Pyrite wastes,
- Wastes from steel production, such as basic slag and calcium silicate slag,
- Wastes from coal burning operations, for example fly ash, bottom ash, the by-products of fluidized-bed combustion and materials from flue gas desulphurization scrubbers.

Examples of 'waste utilization' for agricultural purposes include the use of incompletely calcined limestones or carbonates, and 'dust' from the cement industry as liming materials. Other already ground up and reprocessed 'dumps' include the tailings fines from kimberlite operations. These resources, characterized by rapidly weathering olivine-rich rocks and other Mg-rich rocks, might be useful as potential liming materials and local Mg sources, for example, on pastures.

Calcium silicate slags, by-products of the steel industry, have caused considerable yield increases for sugar cane, specifically on low-Si soils (Ayres 1966; Anderson *et al.* 1991). Magnesium-containing fluidized bed combustion by-products have proved to be effective liming materials with a high effectiveness to reduce subsoil

Al phytotoxicity (Stehouwer *et al.* 1999).

Basic slag is a known P resource that has been used widely in European agriculture. It used to be a by-product from the steel industry, either from the basic Bessemer or the basic open-hearth process, and was used in a ground form as a phosphatic fertilizer and liming material since the late 1800s. In 1970/71 about one third of the phosphate used by German farmers was in the form of basic slag (Fleischel 1972). Basic slag was also widely used in Brazil (Sanchez and Uehara 1980). However, with the change of steel making processes and different ores, these P-rich basic slags are less available.

The agronomic effectiveness of basic slag as a fertilizing and liming material differs from crop to crop and from soil to soil. Successful applications of basic slag are reported from fertilizing potatoes, sugar beet, fodder beet and various cereals (ryegrass, rape, maize) in temperate climates. In comparison to water-soluble phosphate fertilizer, the effectiveness of basic slag was inferior in crops that need readily available P like carrots, lettuce or broccoli (Mattingley 1968). Basic slag has also been used as P-fertilizer and liming material for grassland on acid soils in many countries, including New Zealand (Lynch and Davies 1964), Germany (Fleischel 1972) and Brazil (Sanchez and Uehara 1980). Basic slag is also used as effective liming material and fertilizer for tree crops, providing P, Ca and Mg (Mayer-Krapoll 1969; Vandre *et al.* 1991; Belcacem *et al.* 1992), especially on poor, sandy soils.

In the past, ‘waste utilization’ practices used single ‘waste-products’. New concepts stress the potential of combining or co-utilizing by-products, for example coal fly ash in combination with biosolids, such as sewage sludge and poultry manure (Schumann and Sumner 2000). This concept of blending and co-utilization could be extended to other areas of ‘waste’ and rock utilization, such as blending selected non-contaminated mine wastes or suitable volcanic rocks with sewage sludge or other organic ‘wastes’ for selected agricultural and forestry operations.

10.4 Water conservation with rock mulch

Rock-mulch systems are long-term, irrigation-free, soil and water conservation farming practices known mainly from arid and semi-arid environments. Rock-mulch systems use rocks and minerals to cover soil and in some cases water surfaces. Rock-mulching may sound strange for modern day farmers, but historically it has proved to be an effective and sustainable technique in drought prone arid to semi-arid areas.

Rock-mulch practices are very old soil and water conservation techniques. Lightfoot (1994) discussed early evidence of this technique in the Atacama Desert of South America, the Negev desert region of Israel, and the Southwestern United States (Doolittle 1998; White *et al.* 1998). In Peru and Israel, stone mounds constructed hundreds of years ago by the Lapa Lapa and the Nabatean people respectively, are thought to have been built in order to retain scant rainfall, collect dew, and transfer it to the soil, while coarse grained 'cobble' mulch was used by the Anasazi people in the United States for similar purposes (Lightfoot 1994).

Gale *et al.* (1993) document a four-centuries old rock-mulching technique that is still used today in northwest China. The technique is designed to conserve sporadic and limited precipitation and to reduce soil losses from the loess soils of this region. In dry parts of southern Switzerland, rock-mulches are widely used in vineyards (Nachtergaele *et al.* 1998). Scoria is also used in Saudi Arabia as a support and mulch medium for trees outside the Geological Survey headquarters. Combined with an innovative subsurface drip irrigation system, the use of scoria has proved to be a highly effective water conserving technique using only about 10% of the water used with normal soils (Habib *et al.* 2001).

Early application of rock-mulching techniques may have been triggered in some areas by external events, such as volcanic eruptions and the subsequent covering of fields with thin veneers of volcanic pyro-clastic materials in some arid and semi-arid areas, for example in the Canary Islands (Fernández and Tejedor 1987; Tejedor *et al.* 2003) and in the southwestern United States (Doolittle 1998). In other areas, the use of rocks as mulching material is not thought to have been event-driven but instead based on observations that soils under rocks are often moist (Kamar 1994).

In arid and semi-arid areas the amount of moisture stored in soils is low because of low precipitation and high evaporation rates. Typically, the productivity of soils in these areas is limited by the lack of soil moisture. When there is not sufficient precipitation and infiltration into the soils during the growing season, agricultural production relies on water harvesting techniques, irrigation, or depends on moisture reserves stored before the time of planting. In these situations mulching can increase the yield of crops.

In general, mulching practices have many positive effects on soil productivity, including:

- reduction of evaporative loss of soil moisture,
- increase in water infiltration,
- reduction of the mechanical impact of rain, hail and wind,
- reduction of run-off water and erosion,
- moderation of soil temperature fluctuations,
- reduction of weed growth,
- extension of growing period.

Many of the mulching materials currently in use are organic materials or plastic films. Rock- and mineral-mulches offer several advantages over these organic mulches. The main advantage of mineral- and rock-mulch over plant residue-mulch is that pebble size rocks are often easily available, in addition they do not decompose and typically do not attract insects and pests. Another reported potential advantage of rock- or gravel-mulches is their ability to act as a heat sink in areas with short growing seasons. Gravel-mulches, especially those with dark rocks that absorb solar radiation, then dissipate heat to the soil and thus hasten germination. The seeds or seedlings planted in gravel mulches get a head start over those planted in colder soils.

Over the last few decades, considerable amounts of field and laboratory work has been carried out on the principles of rock-mulching and on factors such as the most effective thickness of the mulch layer and the size of the rock or gravel mulch materials (Corey and Kemper 1968; Fairbourne 1973; Modaihsh *et al*. 1985; Groenevelt *et al*. 1989; Valentin and Casenave 1992; Kemper *et al*. 1994; Poesen and Lavee 1994).

The principal behind using mulching materials such as rock/gravel/sand to reduce soil moisture losses is the disruption of the capillary flow of water at the soil-air boundary. Rock-mulches have extremely low abilities of transmitting water and will not transmit capillary water. Capillary flow is interrupted when the soil pores are smaller than the mulch pores (Pérez 1998). Consequently, water must evaporate at the soil-mulch boundary and will then slowly diffuse through the rock-mulch layer (Pérez 1998). Rock-mulches have been compared to one-way moisture valves. Coarse rock fragments on the soil surface allow water to infiltrate the soil easily, but greatly reduce water movement out of the soil (Fairbourne 1973).

Fernández and Tejedor (1987) and Tejedor *et al*. (2003) demonstrated the positive effects of rock mulching in the Canary Islands, where rock-mulching methods have been practiced for more than 200 years. The climate on the Canary Islands of Spain is very dry, with precipitation rates of less than 150 mm annually and potential evapo-transpiration rates in excess of 2000 mm. The traditional method involves covering the naturally fertile volcanic soils with several centrimeters of volcanic rock (both scoria and pumice) (Figure 10.16), then transplanting seedlings into the mulch.

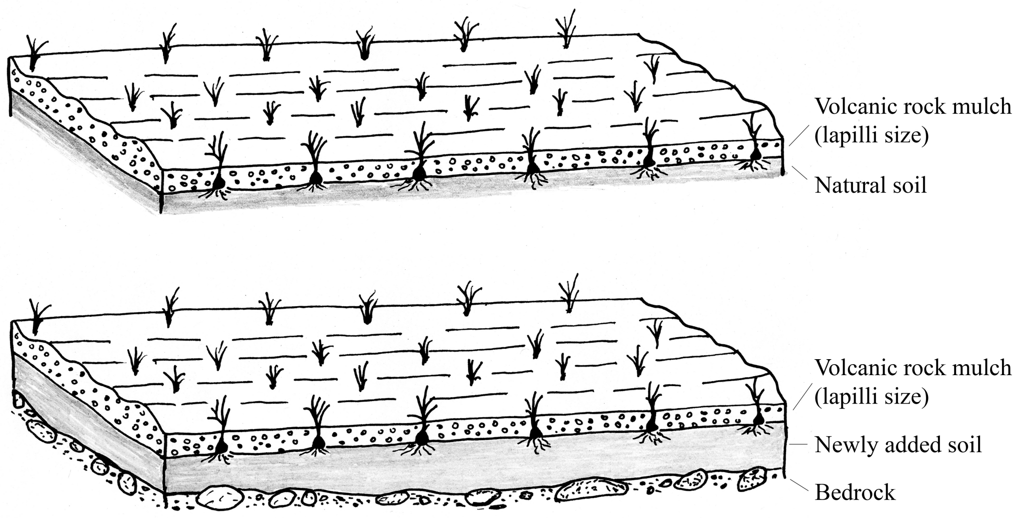


Figure 10.16. *Illustration of the two systems of rock mulch in the Canary Islands: a) rock mulch with volcanic rock, lapilli size, on natural soil, b) rock mulch with volcanic rock, lapilli size, on artificially constructed soil. Note that the roots of the onions are anchored in the soil.*

Crops grown in this system include onions, beans, lentils, barley, maize/corn, grapes, and others. Figure 10.17 illustrates a rock mulched field with onions. Care is taken not to mix the rock mulching material with the underlying soil in order to retain its most effective moisture conserving properties (Groenevelt *et al.* 1989). The crops are carefully harvested, again with as little mixing as possible of the underlying soils with the coarser mulching material. Typically, rock mulched fields are not ploughed. The mulching material is renewed after 20-30 years. This farming practice requires minimal work (small amounts of weeding) and is in fact a minimum tillage practice. This soil and water conservation technique is described by Tejedor *et al.* (2003) as ‘a sustainable agricultural model’, an irrigation-free agriculture in arid environments with fertile soils underlying the mulch.

Tejedor *et al.* (2003) monitored physical soils data of 30 year old mulched and unmulched fields at three separate sites on the Canary Islands over a period of three years. The mulching material applied were two types of locally available basaltic tephra with different grain sizes, mainly sand size. They found that the soil moisture content at 1m depth was 13% higher in mulched soils as compared to unmulched soils. In comparison to unmulched soils, the tephra covered soils retained eight times more water in the surface layer during the driest months. Infiltration measurements in the field reveal that the basic infiltration velocity was approximately double in the mulched soils as compared to the unmulched soils.

Figure 10.17. *Rock mulch field with onions (left); Onion farmer (right), Tenerife, Canary Island, Spain.*

In laboratory experiments with rainfall simulators, Tejedor *et al*. (2003) showed that runoff started on unmulched soils 3 minutes after the beginning of the rain and on mulched soils 26-31 minutes after the onset of rain. These quantitative data illustrate that rock mulches conserve water, protect soils from impacts of rain drops and reduce runoff and soil erosion. Tejedor *et al*. (2003) suggest that the irrigation-free agricultural practice of rock mulching may be one of the more sustainable strategies to reduce the risks of crop failure in drought prone environments. It is most suitable in areas with good quality soils, commonly of volcanic origin, as a base under the rock mulch in climates with growth-limiting low and irregular rainfall.

Two recent research projects on rock mulch have been carried out in the semi-arid Rift Valley of East Africa. In the first, Kamar (1994) describes the greater effectiveness of rock mulches with regards to reduction of runoff and evaporation in comparison to organic mulches in the Rift Valley area of Kenya. In the second, the Ethiopia-Canada agrogeology rock mulch project, Woldeab *et al*. (1994) quantified the effects of rock mulch practices in parts of the semi-arid Rift Valley of Ethiopia over a period of three years. Mulched fields received 3 cm and 6 cm thick layers of black scoria and white pumice respectively. The result of this work showed that the soil moisture content in mulched soils was on average 10% higher than in the adjacent unmulched soils. Temperature variations were less pronounced in mulched soils than in control fields. Maize/corn seed germination was considerably higher in mulched soils than in unmulched soils. In all mulched fields the seeds germinated 8-10 days earlier than in the bare, unmulched fields. Weed suppression was highest in mulched fields. The unmulched fields remained termite-free, in contrast to the control fields. The yield increase of maize/corn in these trials varied between 95% and 119%. In two of the three years, maize/corn yields from the 3 cm scoria mulch fields were generally higher than on fields with 6 cm thick mulch covers. There were only slight differences in soil moisture, temperature and yield responses between the two different rock types. The experiments in Ethiopia illustrated the effectiveness of the rock mulch technique as the soil moisture gap between the irregularly occurring rains was bridged (Woldeab *et al.* 1994).

The composition of rock-mulch material is not of great importance as the effectiveness of a mulching-media is based on its physical nature and not its chemical-mineralogical characteristics. However, the optimal thickness of rock-mulch applications on soils varies from site to site. A review of the size of optimal rock mulch particles shows a great spread of data. Optimal thickness of mulch layers seems to vary between 2 and 6 cm, although thicker layers are also reported. When the mulch layer is too thin, wind erosion can reduce its effectiveness and weeds can grow through the mulch easier. Particle size also varies from site to site. The grain size of commonly used rocks as mulching material varies but is generally in the 2-3 mm to 2-3 cm range, from sand to gravel size. It is generally agreed that particle size <0.1 mm in diameter are unsuitable as they provide sufficient capillary action to maintain liquid-phase continuity and thus evaporative losses (Modaihsh *et al*. 1985). Fine-grained sand mulches are also more susceptible to wind erosion.

An interesting new system that combines in-situ rainwater harvesting methods with gravel mulch techniques has been described from China by Li *et al*. (2000). The technique uses plastic covered ridges and gravel mulched furrows and was effective in conserving moisture in soils and increased yield and water use efficiency. Other potential uses of rock-mulch with light-weight, light-coloured rocks (e.g. pumice) include ‘floating pumice mulch’ applications, and the use of light-weight pumice rock mulches on rooftop gardens.

An innovative ‘floating pumice mulch’ technique was tested in the semi-arid areas of the Rift Valley in Ethiopia, where farmers grow beans on ridges supplied by intermittent irrigation water in furrows (ridge and furrow system). Locally available, light-weight white pumice, which floats on water, was applied in furrows with irrigation water (see Figure 10.18).

Due to its whitish colour the pumice reflected light and reduced evaporation. When the flow of irrigation water stopped, the light pumice settled on the floor of the furrow and acted as mulch, further reducing evaporation. The pumice started to float again with the next flow of irrigation water. Initial data suggest that the ‘floating pumice mulch’ reduced evaporation from the irrigated furrows and increased the irrigation water use efficiency (van Straaten, unpublished). Further research is needed to evaluate the effectiveness of floating pumice mulch in furrow mulch irrigation systems in arid and semi-arid areas, located near substantial pumice deposits.

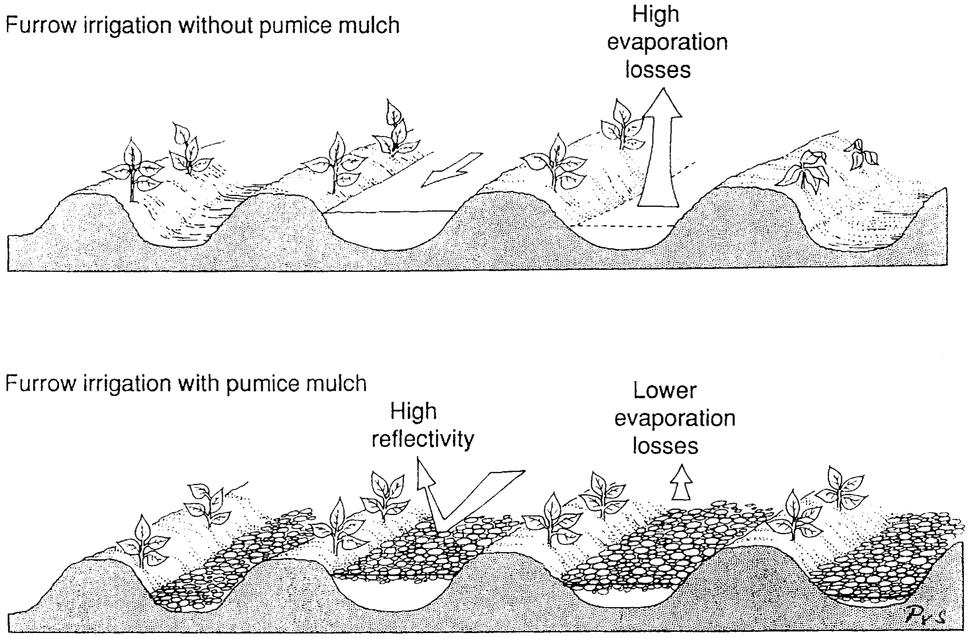


Figure 10.18. *Schematic representation of floating pumice mulch in furrow irrigation system in semi-arid Ethiopia.*

Economic factors and site-specific parameters must be considered before starting a rock-mulch operation. Among the constraints of the agricultural application of rock mulches are the high initial costs, the high labour requirements at the set-up stage, the long adoption time required by farmers unacquainted with this rock-based technique, and the large amounts of rock or gravel needed at the start of the operation. Rock-mulch systems require a high capital investment at the set-up stage to transport of sand and gravel size rock materials from quarries or gravel pits to the fields, and spread of rock mulch material onto the fields. At the beginning of the cropping season there are also high labour costs for seeding or transplanting seedlings into the mulch. From a technical point of view, rock-mulch techniques can be applied in a variety of environments, and for a number of crops, but are probably best suited for perennial crops, fruit tree and tree growing operations in arid and semi-arid environments or for a variety of crops in areas with short growing seasons. Cultural sensitivities, and information exchange are also important factors in the participation of potential users necessary for technique to be successfully adopted. With good management, rock mulch systems have low maintenance cost and low ongoing labour requirements, (minimum tillage and weed removal). With proper management rock mulches do not have to be replaced for 20-30 years and thus can function as long-term agricultural investments and long-term natural resource management systems.

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