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## Plant-induced weathering of a basaltic rock: Experimental evidence

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**Abstract**—The active role of higher plants in the weathering of silicate minerals and rocks is still a question for debate. The present work aimed at providing experimental evidence of the important role of a range of crop plants in such processes. In order to quantitatively assess the possible effect of these diverse plant species on the weathering of a basaltic rock, two laboratory experiments were carried out at room temperature. These compared the amounts of elements released from basalt when leached with a dilute salt solution in the presence or absence of crop plants grown for up to 36 days. For Si, Ca, Mg, and Na, plants resulted in an increase in the release rate by a factor ranging from 1 to 5 in most cases. Ca and Na seemed to be preferentially released relative to other elements, suggesting that plagioclase dissolved faster than the other constituents of the studied basalt. Negligible amounts of Fe were released in the absence of plants as a consequence of the neutral pH and atmospheric pO<sub>2</sub> that were maintained in the leaching solution. However, the amounts of Fe released from basalt in the presence of plants were up to 100- to 500-fold larger than in the absence of plants, for banana and maize. The kinetics of dissolution of basalt in the absence of plants showed a constantly decreasing release rate over the whole duration of the experiment (36 days). No steady state value was reached both in the absence and presence of banana plants. However, in the latter case, the rates remained at a high initial level over a longer period of time (up to 15 days) before starting to decrease. For Fe, the maximum rate of release was reached beyond 4 days and this rate remained high up to 22 days of growth of banana. The possible mechanisms responsible for this enhanced release of elements from basalt in the presence of plants are discussed. Although these mechanisms need to be elucidated, the present results clearly show that higher plants can considerably affect the kinetics of dissolution of basalt rock. Therefore, they need to be taken into account when assessing the biogeochemical cycles of elements that are major nutrients for plants, such as Ca, Mg, and K, but also micronutrients such as Fe and 'nonessential' elements such as Si and Na. Copyright © 2001 Elsevier Science Ltd

### 1. INTRODUCTION

The alteration of rocks at the surface of Earth crust has long been attributed to the sole meteoric processes, as implicitly evidenced by the etymology of the word 'weathering.' While the circulating water is certainly a major weathering agent, investigations on the effects of organic acids on rocks have received great interest in recent years, in the hope of elucidating the possible role of these biochemical agents in the weathering of rocks and minerals, especially in soil environments (e.g., Huang and Keller, 1970; Schnitzer and Kodama, 1976; Razzaghe and Robert, 1979; Tan, 1986; Barman et al., 1992; Eick et al., 1996a and b). In most of these studies organic acids were implicitly assumed to originate from the decomposition of organic matter (i.e., dead parts of living organisms) by microorganisms such as bacteria and fungi. There are also numerous research findings which show that microbes can themselves significantly weather minerals and rocks by excreting organic acids or siderophores (e.g., Banfield et al., 1999; Brantley et al., 1999) and possibly other metabolites which influence pH and redox conditions, as reviewed in details by Robert and Berthelin (1986). Microbiological activity can thereby be responsible

for typical weathering features as evidenced for glass and olivine by Callot et al. (1987), for basalt glass by Thorseth et al. (1992), and for silicates such as feldspars by Jongmans et al. (1997) or olivine by Banfield et al. (1999).

Although land plants are widespread on the whole surface of the Earth, there is much less reported evidence of them being directly responsible for the weathering of rocks (Robert and Berthelin, 1986). Recent papers even showed that whether land plants can effectively play a significant direct role in the weathering of rocks and minerals is still a question for debate (Drever, 1994; Jackson, 1996). This debate, however, focuses on lichens, which are symbiotic associations of algae and fungi characterized by fairly low growth rates and nutrient requirements that enable them to play the role of pioneer vegetation in the colonization of fresh rocks (Chapin, 1980).

Conversely, other land plants such as higher plants can achieve very high growth rates, which are associated with large rates of uptake of water and nutrients. In addition, as their growth relies on photosynthesis they play a major role in CO<sub>2</sub> cycling and contribute to a considerable input of C into the soil since about 25% to 60% of C that is assimilated by the plants is recovered in the below ground parts of the plants during the course of their lives (Lambers et al., 1996; Gobran et al., 1999). About half of this is used for growing roots, the other half being excreted in the soil as various root exudates including respired CO<sub>2</sub> (Lambers et al., 1996). As Berner (1992, 1999) pointed out, higher plants have thereby played a major role in the

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dissolution of Ca and Mg silicates. The C that is released by roots also stimulates the growth of microorganisms in the peculiar volume of soil that is surrounding the roots, i.e., the rhizosphere (Darrah, 1993). In addition to these microbial changes it has been shown in the recent decades that the roots of higher plants can also lead to profound changes of the chemical conditions in the so-called rhizosphere (as reviewed by Darrah, 1993; Marschner, 1995; Hinsinger, 1998).

Uptake of water and inorganic ions (mineral nutrients) at high fluxes by plant roots is responsible for important mass exchanges in the rhizosphere that can drastically modify ionic concentrations in the surrounding liquid phase as reviewed by Hinsinger (1998). Hinsinger and Jaillard (1993) have shown that the considerable decrease in K concentration that occurred around absorbing roots was directly responsible for the weathering of K-bearing phyllosilicates such as trioctahedral micas that had been reported to occur in the rhizosphere by several authors (Mortland et al., 1956; Spyridakis et al., 1967; Hinsinger et al., 1992; Kodama et al., 1994).

The uptake of cations and anions by roots is also directly responsible for substantial changes in rhizosphere pH (Römheld, 1986; Marschner, 1995; Hinsinger, 1998). Indeed when an excess of cations over anions are taken up by roots, they excrete protons so as to maintain their electrical neutrality (Haynes, 1990), thereby resulting in a decrease in pH in the outer medium. Such a root-induced acidification of the rhizosphere has been shown to be responsible for significant dissolution of Ca carbonates (Jaillard et al., 1991) or phosphates (Aguilar and van Dienst, 1981; Hinsinger and Gilkes, 1996; Hinsinger and Gilkes, 1997) and even phyllosilicates (Hinsinger et al., 1993).

Higher plants can also profoundly affect the redox conditions in the rhizosphere, which strongly determine the dynamics of Fe- and Mn-bearing minerals (Uren, 1981; Hinsinger, 1998). Most plants can reduce Fe (Brown and Ambler, 1973; Bienfait et al., 1983; Marschner and Römheld, 1994) and should thereby influence the dissolution of Fe-bearing minerals. Besides, as pointed out earlier, considerable amounts of C are released by roots as various exudates (Darrah, 1993). These not only feed rhizosphere microorganisms. Some of them and particularly organic anions such as citrate for instance (Dinkelaker et al., 1987; Gerke et al., 1994) and nonproteinogenic amino acids called phytosiderophores (Takagi et al., 1984; Römheld, 1991) can complex Fe and numerous other metals. They can thus directly affect the dissolution of the solid phases that contain such metals (Jones et al., 1996; Hiradate and Inoue, 1998). Among higher plants, the various plant species can considerably differ in their ability to alter the chemical conditions of their rhizosphere and, thereby, to adapt to adverse soil conditions (Marschner, 1995): those differences are both qualitative (implied mechanisms) and quantitative (resulting fluxes). Although the direct effect of higher plants on the weathering of minerals and rocks has not been often clearly demonstrated in situ (Gobran et al., 1999), the abovementioned, recent studies showing the diverse chemical changes occurring in the rhizosphere suggest that various mechanisms may be involved.

Evaluating the role of higher plants in the weathering of minerals and rocks is crucial to a better understanding of biogeochemical cycles at the surface of the Earth. These processes are a major source of nutrients for plants and thus need

to be better accounted for in the overall budgets of nutrients in natural ecosystems and, more critically so in the perspective of sustainable production of forests (Marques et al., 1997) and agrosystems. In addition, silicate rocks are now being considered for their potential use in agriculture as alternative slow-release fertilizers (Barak et al., 1983; Coroneos et al., 1996) or amendments (Gillman, 1980). In that respect, too, a better knowledge of how the plants can affect the kinetics of dissolution of silicate rocks and minerals is a prerequisite to the assessment of their potential benefit (Harley and Gilkes, 2000).

The aim of this study was to quantitatively assess the possible effect of higher plants on the weathering of a basaltic rock, for a range of plant species. These were selected among diverse botanical groups. Crop plants were used because of their potentially high growth rates and correspondingly high requirements for nutrients. Two laboratory experiments were carried out to compare the amounts of elements released from basalt when leached with a dilute salt solution at room temperature in the presence or absence of crop plants grown for up to 36 days.

## 2. MATERIAL AND METHODS

### 2.1. Basalt Material

Decimetric sized fragments of a fresh basaltic rock were sampled in a quarry in Londrina Province of Southern Brazil (Carrier Clark, 51°09'18"W et 23°22'33"S). General petrographic (most frequent K-Ar age values in the region are ~130–135 million years) and mineralogic characteristics (dominated by Ca plagioclases with abundant augite and pigeonite and with some Ti magnetite, apatite, quartz, K feldspars, and biotite) of this basalt (Formação Serra Geral) have been described by Piccirillo and Melfi (1988). These rock fragments were carefully crushed in a stainless steel crusher to pass through a 200- $\mu$ m sieve. Particles smaller than 100  $\mu$ m were first discarded by dry sieving. After sonication, the rock powder was wet-sieved at 100  $\mu$ m. After drying at 30°C, the 100- to 200- $\mu$ m particles were stored in a polyethylene bottle. The elemental composition of this size fraction was the following (in mg/g): SiO<sub>2</sub> 449.5, TiO<sub>2</sub> 22.8, Al<sub>2</sub>O<sub>3</sub> 120.1, FeO 180.5, MgO 68.6, CaO 105.2, Na<sub>2</sub>O 20.4, K<sub>2</sub>O 7.9, MnO 2.9, P<sub>2</sub>O<sub>5</sub> 2.0. Ten g of basalt powder were inserted between two pieces of a polyamide net (with a 30- $\mu$ m pore diameter). These were then sealed with a solder-iron, in order to obtain a round bag with a diameter of 60 mm that contained the basalt powder.

### 2.2. Plant Material

The effect of four different plant species from temperate and tropical areas was studied. Plant species widely differ in their nutrient requirements and in their capacity to alter chemical conditions in the rhizosphere (Marschner, 1995): e.g., dicots have larger requirements for divalent cations such as Ca and Mg than monocots. The four species selected in this work were chosen to cover this wide range of behaviors: white lupin and oilseed rape were selected as dicots capable of releasing large amounts of protons and organic anions, such as citrate, in their rhizosphere (Dinkelaker et al., 1987; Hoffland et al., 1989; Hinsinger et al., 1993); banana and maize were selected as monocots, maize being a grass and thus able to release phytosiderophores (Marschner and Römheld, 1994). Three of these species were grown from the seeds, whereas banana seedlings were produced from vitroplantlets (kindly supplied by VITROPIC S.A., Saint-Mathieu-de-Trévières, France). The vitroplantlets of banana (*Musa paradisiaca*, cv Cavendish CV901) were first grown by groups of 10 for 3 weeks in a water-saturated atmosphere on a complete nutrient solution, in order to ensure that the micropropagated sterile plantlets had reached an autotrophic stage of growth. The three other species were grown on the same complete solution for 2 weeks after surface sterilizing the seeds with 2 M H<sub>2</sub>O<sub>2</sub> for 10 min in order to avoid the development of microbial pathogens that might potentially be present at the surface of the seeds. About 3 g

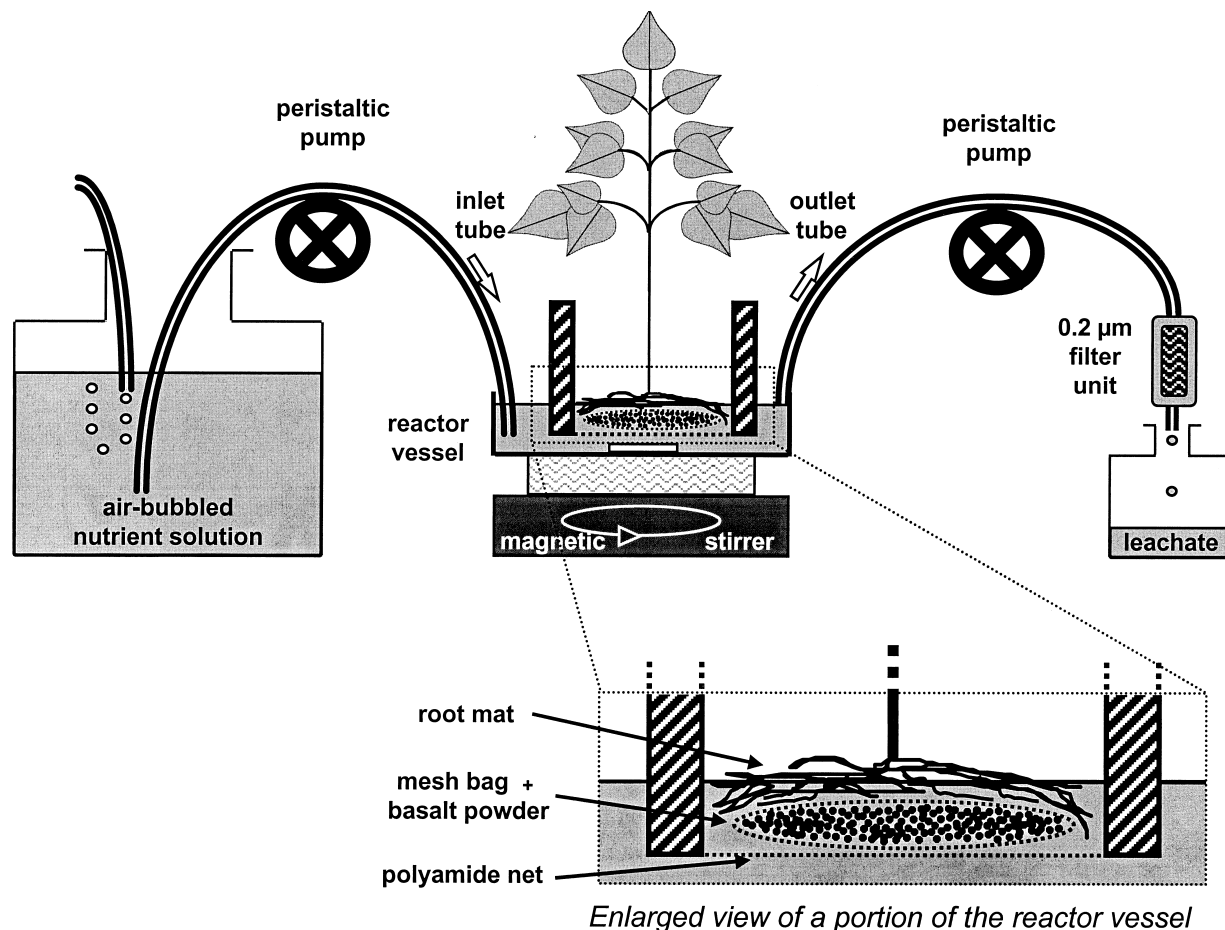


Fig. 1. Schematic diagram of the experimental set-up used for studying the weathering of basalt in the presence of plants. The enlarged view of a portion of the reactor vessel shows the spatial arrangement of roots relative to the mesh bag that contained the ground basalt and the bathing nutrient solution.

of seeds were used for each plant species, i.e., 8 seeds of white lupin (*Lupinus albus* cv Lublanc), 11 seeds of maize (*Zea mays* cv Mona), and 1000 seeds of oilseed rape (*Brassica napus* cv Drakkar). The seedlings were cropped into perspex cylinders (63-mm inner diameter), which were closed at their bottom by a polyamide net (with a 30- $\mu$ m pore diameter, i.e., less than the finer root diameter). Thereby the seedlings developed a dense, planar mat of roots at the surface of the net. It should be kept in mind that no attempt was made to grow the plants under axenic solutions. This means that, in spite of using vitroplantlets and surface sterilized seeds, some microorganisms most certainly contaminated the nutrient solutions during the course of the experiments. However, as plants were not inoculated with mycorrhizal symbionts and although no attempt was made to evaluate the mycorrhizal status of the roots, it is very unlikely that the plants became infected by mycorrhizal fungi during the course of the reported experiments.

### 2.3. Experimental Set-Up and Conditions

An experimental device was designed to maintain the plants in correct growth conditions during the whole experiment and to collect the structural elements released from the basalt powder in the presence or absence of plants (Fig. 1). This device was composed of a reactor vessel made of a polycarbonate Petri dish (90-mm internal diameter). The Petri dish contained a 3-mm-thick PVC grid which supported the abovementioned perspex cylinder with the plants. A control treatment was obtained by using the same perspex cylinder but without plants. A stir bar (1.5-mm thick and 15-mm long) was inserted in a hole in the

middle of the polyvinylchloride grid and the whole reactor vessel was placed on a magnetic stirrer. An extruded polystyrene plate was intercalated to avoid any temperature elevation of the reacting solution. In each reactor vessel, a small bag containing 10 g of basalt powder was inserted between the polyamide net and the root mat inside the perspex cylinder (see enlarged view of this in Fig. 1). For the control treatment without plants, the perspex cylinder was covered with a film of parafilm (Parafilm, American National Can™, Menasha, WI, USA) in order to avoid excessive evaporation. The reactor vessels were connected to a solution reservoir by an inlet Nalgene tubing with a section of nylon manifold tubing (Watson–Marlow, inner diameter = 0.38 mm; Smith and Nephew Watson Marlow, Falmouth, Cornwall, UK). This tubing was attached to the reactor vessel so that the nutrient solution was delivered near the middle of the Petri dish. The reactor vessels were also connected to an outlet tubing that was made of Nalgene tubing with a section of marprene manifold tubing (Watson–Marlow, inner diameter = 0.38 mm). This tube was attached to the Petri dish at 8 mm from its bottom, in order to function as an overflow collector. A Millipore filter unit (Bedford, MA, USA; Sterivex-GS, 0.22- $\mu$ m pore diameter) was inserted between the outlet Nalgene tubing and the manifold outlet tubing in order to avoid any contamination of the leached solution with mineral particles or organic debris. Both inlet and outlet manifold tubing were inserted in a multichannel peristaltic pump (Watson–Marlow 502-AA) for circulating nutrient solution and collecting the leachate at a rate of 14.5 or 21.7 rpm (i.e., 100 or 150 cm<sup>3</sup> per day).

The basic nutrient solution had the following composition: KNO<sub>3</sub> 5 10<sup>-3</sup> M; (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> 10<sup>-3</sup> M; H<sub>3</sub>BO<sub>3</sub> 10<sup>-5</sup> M; MnCl<sub>2</sub> 2 10<sup>-6</sup> M;

$\text{ZnSO}_4$   $2 \cdot 10^{-7}$  M;  $\text{CuSO}_4$   $2 \cdot 10^{-7}$  M;  $(\text{NH}_4)_2\text{MgO}_7\text{O}_{24}$   $3 \cdot 10^{-8}$  M. This nutrient solution was stored in a Nalgene reservoir (10 dm<sup>3</sup> polyethylene carboy) and was bubbled with ambient air during the experiment in order to avoid anoxic conditions around plant roots (Fig. 1).

We performed two different experiments, which are thereafter called A and B. In experiment A, the four plant species were compared over 22 days. The release of the elements in the solution was analysed at a 2 to 7 days time interval but the plant uptake term was only measured at the end of the experiment. Moreover, silicon was accidentally supplied during the first 8 days at a rate of 100 cm<sup>3</sup> per day of 5 ppm Si nutrient solution. Thereafter, the abovementioned Si-free nutrient solution was supplied at a rate of 150 cm<sup>3</sup> per day. In experiment B, only banana was used and a set of six plantlets was harvested at each date of solution collection, in order to assess the kinetic evolution of the plant uptake term. This experiment was performed with the abovementioned Si-free solution supplied at a rate of 150 cm<sup>3</sup> per day for 36 days. Plants and/or solutions were analysed after 2, 4, 6, 8, 15, 22, 29, and 36 days. In both experiments, the same rates of delivery of nutrient solution were applied to the control reactor vessels (without plants) and to the vessels in which plants were growing. The experiments A and B, both in absence (control) and presence of plants, were carried out in a growth chamber providing the following controlled climatic conditions: 16-h-day period at 25°C, relative humidity of 70% and photon flux of 550  $\mu\text{mol}/\text{m}^2/\text{s}$  (in the range 400–700 nm) and 8-h night period at 20°C and relative humidity of 95%.

#### 2.4. Analytical Techniques

At harvest, as pointed out earlier, no attempt was made to evaluate the presence of rhizosphere microorganisms including mycorrhizal symbionts. No mycorrhizal hyphae were found to colonize the mesh bags, which contained the ground basalt and were densely covered by roots (based on visual observation). Microorganisms most certainly developed however as the experimental set-up was not designed to prevent microbial contamination from the environment of the growth chamber. Nevertheless, these microorganisms were most certainly not representative of those commonly found in the rhizosphere.

After harvest, the whole plants were oven-dried at 70°C for 3 days, weighed, and ground to a particle size smaller than 1 mm. For extracting Mg, Ca, Na, and K, 200 mg of dry material were poured in a tube with 30 mL HCl 0.2 M and shaken for 24 h (see Coroneos et al., 1996). The suspension was then filtered on ashless filters (Whatman 541 Tewksbury, MA, USA). After adding  $\text{LaCl}_3$  to the filtered solution to overcome any interferences, Mg and Ca were assayed by flame atomic absorption spectrometry. Potassium and Na were measured by flame emission photometry. For extracting Si, Al, and Fe, the plant material was ashed at 450°C before being digested in hot concentrated  $\text{HNO}_3$ - $\text{HClO}_4$ . These elements were then assayed by inductively coupled plasma emission spectrometry. At each date of solution collection, the outlet bottles were weighed in order to measure the volume of the leachate. A small aliquote was then sampled to measure its pH before acidifying the solution with concentrated HCl for their storage. Their analysis was finally performed with the same techniques as described above for plant digests.

### 3. RESULTS

#### 3.1. Analysis of the Leachates

The cumulated amounts of elements released in the percolating solution in presence or absence of plants in exp. A are given in Figure 2. The Si data are indicated although it was found in the blank solutions that  $\sim 5 \mu\text{g Si}/\text{cm}^3$  was accidentally added during the first 8 days of the experiment. Except for Fe, in most cases, the amounts of elements released in the presence of plants were smaller than in the control without plants. For most elements, the largest amounts released in the presence of plants were found for lupin and the smallest for rape and maize. In the case of Fe, for all species but for rape, the amounts released were smaller without plants than with

plants. Maize led to a considerably larger release of Fe than the other species, which amounted by the end of the experiment (after 22 days) to about 10-fold the amount released without plants. This graph also shows that the shapes of the curves were almost the same with or without plants for most elements and all species but maize. For maize, the kinetics rather exhibited an S-shape, suggesting that the rate of release was not constantly decreasing with time as it was for the other species and for the control treatment without plants.

The cumulated amounts of elements released in the percolating solution in the presence or absence of banana plants in experiment B are given in Figure 3. They were fairly consistent with the results obtained for banana in experiment A (Fig. 2). For Mg, Na, and Si, the amounts released with banana were close to those released without plants. For Ca, the amounts released with banana were smaller and for Fe larger than those released without plants. When comparing the results obtained for the various cropped reactors that might be considered as replicates in this respect, there were fairly large discrepancies for all elements but for Si and, to a lesser extent, for Ca. The amounts found for the plants grown for 29 and 36 days were consistently the largest, whereas those found for plants grown for 15 and 22 days were consistently the smallest. This indicates a large variability among the data obtained in the presence of plants as opposed to the good reproducibility of the results obtained in the two uncropped (control) reactors.

#### 3.2. Plant Growth

The biomass of plants in experiment A are given in Table 1. Although the various plant species had a similar biomass at the beginning of the experiment, their dry weights widely differed by the end of the experiment, with the monocots, and especially maize, achieving a much larger relative growth rate than the dicots (rape and lupin). The growth of banana in experiment B is shown in Figure 4. The shape of the growth curve exhibits some steps suggesting that the rate of growth was not continuously decreasing as one may expect. This irregular shape is most probably due to large variabilities in growth between the various cropped reactors. This is clearly illustrated for the two initial sets of plants that were used as control plants: one of these had a dry wt. 50% larger than the other. Compared with an ideal growth curve, it seems that plants grown for 15 and 22 days had a larger growth and those grown for 29 and 36 days had a smaller growth. This will have to be taken into account when comparing the amounts of elements taken up by the plants among the various cropped reactors.

#### 3.3. Plant Uptake

The elemental contents in the plant tissue before and after the 22 days of growth in experiment A are given in Table 2. The K contents are indicated although K was supplied by the nutrient solution. This explains the considerable increase in plant K contents during the course of the experiment. In addition, among the elements that are considered here, K is the cation for which most plants have the largest requirements, followed by Ca and Mg (Mengel and Kirkby, 1987). There was a systematic increase in cation contents in the plant tissues. However, the increase in Mg content found for all species but for banana was

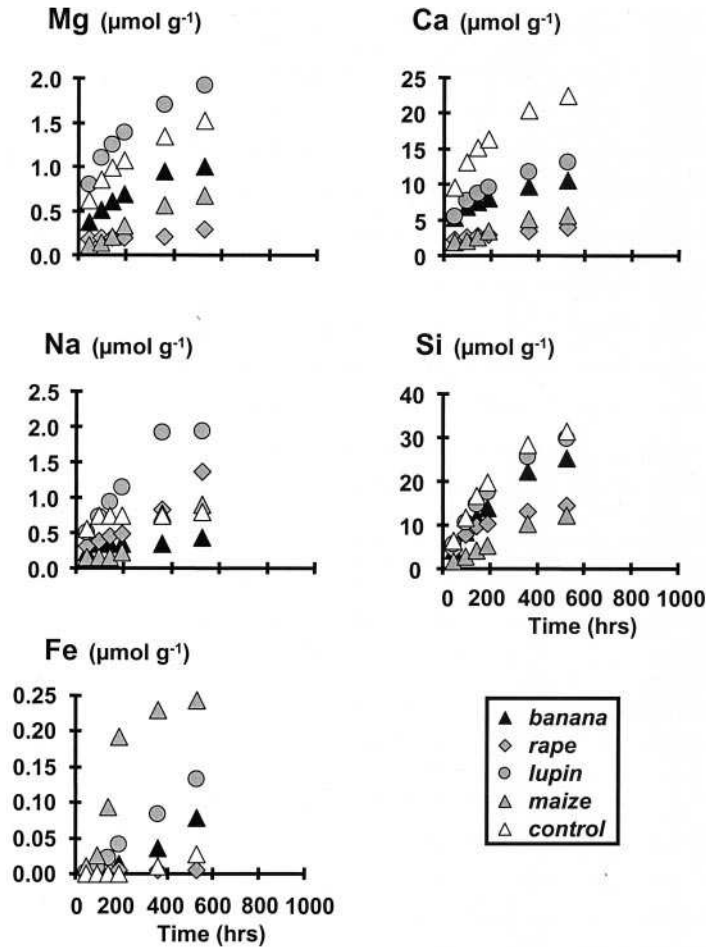


Fig. 2. Cumulated amounts of elements released into the leaching solution in the absence (control) or presence of various plant species in experiment A as a function of time duration.

probably not significant when compared with the standard deviation calculated for control plants. The largest Mg and Ca uptakes were achieved by banana. Silicon is a nonessential element which can however be taken up in large amounts by many species, especially graminaceous species (Epstein, 1999). This explains the fairly large Si contents measured in the plants by the end of the experiment, particularly so for maize. Substantial uptake of Na was found for all four species, and more so for maize. Despite being a nonessential element for plants, Na can be taken up at fairly large rates when it is available for the plants (Mengel and Kirkby, 1987; Marschner, 1995). Iron is a micronutrient which is the reason for the smaller contents of Fe found in the plant tissue, relative to the previous cations. There was, however, a marked increase in Fe content for all plant species, the largest uptake of Fe being achieved by maize and banana. Conversely, aluminium is a toxic element for most plants which explains its small content in the plant tissue. The largest increase in Al content was found for maize. These results clearly show that substantial amounts of elements released from the basalt were taken up by the four species studied in experiment A, banana and maize achieving the largest uptake values. These data thus need to be accounted for in the mass balance of elements released from the basalt (see section below).

The results found for banana in experiment B confirmed the previous ones and provided some kinetical information about plant uptake (Table 3). The elemental contents were almost constantly increasing with time as one would expect. This does not, however, hold true for Ca and Mg for which the contents in plant tissue peaked at 15 to 22 days, in agreement with the biomass that peaked at 15 to 22 days rather than at 36 days (Fig. 4). The kinetics of uptake thus need to be interpreted with caution, taking into account the variability in the amounts, which occurred at least partly as a consequence of the variability in plant biomass.

#### 3.4. Mass Balance of Elements in the Presence or Absence of Plants

The mass balances of the various elements released by basalt in experiment A are given in Figure 5. The total amounts of elements released in the presence of plants were obtained by summing up the amounts found in the leachates and the amounts taken up by the plants (that is the increase in elemental content of plant tissues during the course of the experiment). For Si, its accidental addition in the nutrient solution yielded a contamination of about  $15 \mu\text{mol Si/g}$  basalt (dotted line in Fig. 5). In most instances, the presence of plants resulted in a

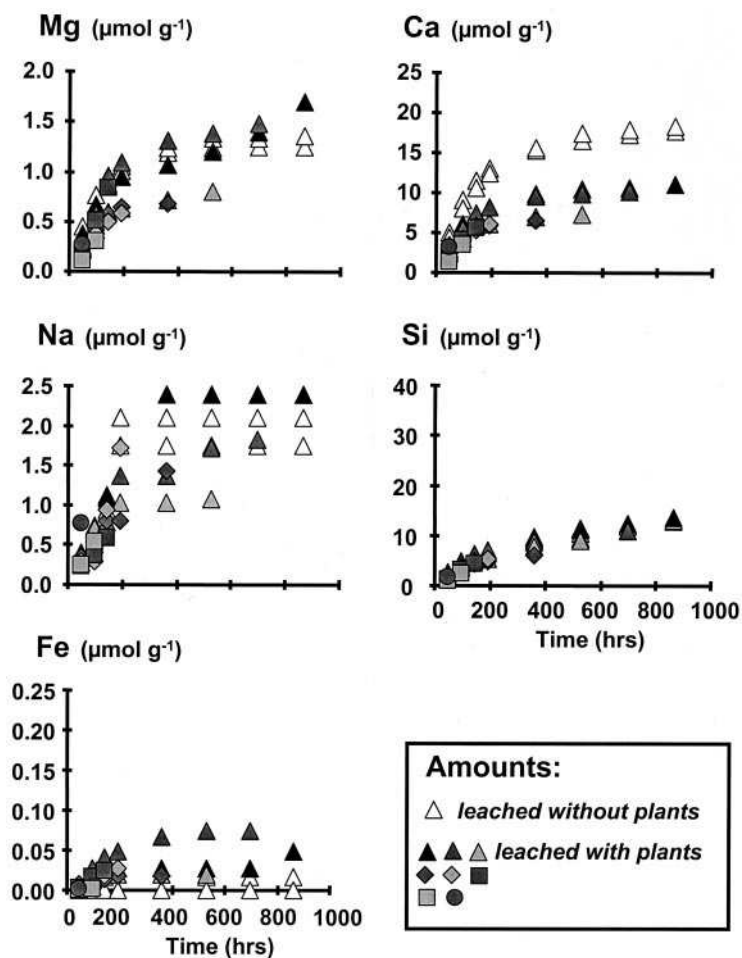


Fig. 3. Cumulated amounts of elements released into the leaching solution in the absence (control,  $\Delta$ ) or presence of banana plants as a function of time duration in experiment B.

substantial increase in the amount of elements released from the basalt, with a major proportion being accumulated in the plant tissue. The amounts of released Ca and Si increased by a factor of up to about two in the presence of plants, with banana and maize having the largest effect. The amount of released Mg increased up to about fivefold in the presence of banana plants. The amount of released Na increased by up to more than one

order of magnitude in the presence of maize. The most dramatic effect of plants was, however, that reported for Fe. The amount of Fe released in the presence of plants increased by orders of magnitude, especially for maize (174-fold) and banana (130-fold), relative to what was found in the absence of plants.

Table 1. Biomass of plants (shoot + root dry weights) and relative growth rates in experiment A.  $DW_0$  represents the dry wt. of control plants (harvested at  $t = 0$ , i.e. at the start of the dissolution experiment),  $DW_{22}$  that of plants supplied with basalt for 22 days, and RGR represents the relative growth rates along the 22 days of the experiment ( $RGR = (DW_{22} - DW_0)/(22 \times DW_0)$ ).

Plant species	$DW_0^a$	$DW_{22}$	RGR $\text{day}^{-1}$
	g per reactor		
Banana	$2.17 \pm 0.04$	7.39	0.11
Rape	$2.38 \pm 0.04$	4.69	0.04
Lupin	$1.96 \pm 0.25$	5.15	0.07
Maize	$3.08 \pm 0.34$	16.31	0.20

<sup>a</sup> Mean  $\pm$  SD (3 replicates).

The kinetics of release of the various elements in the presence or absence of banana plants in experiment B are reported in Figure 6. These results were in fairly good agreement with those obtained in experiment A for banana (Fig. 5). Taking account of the substantial amounts of elements taken up by banana lead to systematic increases in the amounts of elements released from basalt, relative to the uncropped control treatment. The amounts of Mg, Na, and Si released by the end of the experiment increased by a factor of about two in the presence of banana plants. For Ca there was almost no effect of plants at this stage of the experiment, whereas earlier, by 15 days for instance, there was a 50% increase in the release of Ca in the presence of plants. Similarly for Mg, the effect of plants peaked at 15 days of growth, at which stage the release of Mg from basalt had increased by a factor of about eight, compared to that found in the absence of banana plants. As for experiment A, the most striking effect of plants was found for Fe. Indeed, whereas

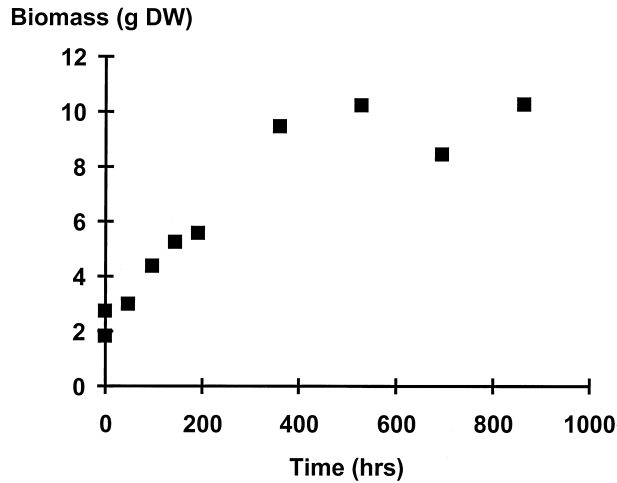


Fig. 4. Biomass of the whole (roots + shoots) banana plants in experiment B as a function of time duration.

the release of Fe remained almost negligible in the absence of plants, the amounts of Fe released in the presence of banana plants reached several  $\mu\text{mol Fe/g}$  basalt, leading to a several hundred-fold increase in Fe release.

#### 4. DISCUSSION

##### 4.1. Order of Release of Elements and Congruence of the Dissolution of Basalt

Compared with their abundance in the basalt, in most cases, both in presence or absence of plants, Ca and Na were preferentially released, whereas Fe was rather retained in the solid. These results suggest that the dissolution of basalt was incongruent in both experiments. For exp. B, this is illustrated by the plots of molar ratios of released elements as a function of time in Figure 7. These molar ratios confirm that Ca and Na were always preferentially released with respect to Si. Whereas Na/Si molar ratio did not exhibit any clear time dependence, for Ca/Si there was a slight decreasing trend with time, more so in the presence than in the absence of plants. However, by the end of the experiment, the Ca/Si molar ratios were still four- to

Table 3. Elemental contents in plant tissues in experiment B (expressed in  $\mu\text{mol}$  per reactor). Potassium was partly supplied by the nutrient, percolating solution. B0, B2, B4, B6, B8, B15, B22, B29, and B36 represent banana plants at the start ( $t = 0$ ) and at the various time steps of the experiment ( $t = 2, 4, 6, 8, 15, 22, 29,$  and  $36$  days), respectively. Data for control plants (harvested at  $t = 0$ ) are those obtained for the highest yielding set of control plants.

	K	Mg	Ca	Na	Si	Fe	Al
B0	4381	249	251	16	10	9.1	1.2
B2	3445	253	261	21	0	6.6	1.5
B4	4670	268	296	21	31	11.2	2.0
B6	5366	298	330	31	37	15.8	3.1
B8	5610	249	262	27	20	12.3	2.8
B15	9249	326	411	45	101	21.6	4.5
B22	11024	307	377	43	109	48.7	6.4
B29	11302	271	324	41	120	42.0	7.5
B36	13771	263	333	37	73	42.9	7.6

sixfold larger than in the basalt. These results suggest that the incongruent dissolution of basalt was partly due to a preferential dissolution of the plagioclase feldspar component, both in presence and absence of banana plants. In experiments A and B, Ca/Na ratios were larger than in the basalt in all cases except maize in experiment A, suggesting that anorthite-type plagioclase was dissolving at a faster rate than albite-type plagioclase.

In the absence of plants in experiment B, the Mg/Si molar ratios remained below its value in the basalt, suggesting that Si was preferentially released relative to Mg. These results do not agree with those reported by Eick et al. (1996a and 1996b) which showed a systematic, preferential release of Mg relative to Si, including the case of experiments conducted at a similar pH (about 7). In the latter case, they obtained the following order of cation release from basalt:  $\text{Ca} > \text{Mg} > \text{Si}$ . In the present experiment, a similar trend was found only in the presence of banana at the beginning of experiment B (Fig. 7). The scattering of the Mg/Si molar ratios over a wide range of values in this experiment, however, restricts the interpretation of the data.

The Fe/Si molar ratios were always below that of the basalt, suggesting a preferential release of Si or a precipitation of secondary phases such as Fe oxides. These results are in agreement with those obtained for basalt at neutral pH (Eick et al.,

Table 2. Elemental contents in plant tissues in experiment A (expressed in  $\mu\text{mol}$  per reactor). Potassium and silicon were partly supplied by the nutrient, percolating solution. B0 and B22 represent banana plants at the start ( $t = 0$ ) and at the end of the experiment ( $t = 22$  days), respectively. R0 and R22 stand for rape, L0 and L22 for lupin, and M0 and M22 for maize. Data for control plants (harvested at  $t = 0$ ) represent mean  $\pm$  SD (3 replicates).

	K	Mg	Ca	Na	Si	Fe	Al
Banana							
B0	4125 $\pm$ 88	298 $\pm$ 12	218 $\pm$ 2	26 $\pm$ 1	63 $\pm$ 19	10.9 $\pm$ 1.2	2.9 $\pm$ 0.2
B22	12412	365	505	50	255	46.6	8.8
Rape							
R0	475 $\pm$ 18	357 $\pm$ 13	345 $\pm$ 5	44 $\pm$ 4	42 $\pm$ 1	3.4 $\pm$ 0.1	4.5 $\pm$ 0.1
R22	10828	376	588	67	255	9.0	7.2
Lupin							
L0	1235 $\pm$ 216	174 $\pm$ 26	116 $\pm$ 26	85 $\pm$ 14	28 $\pm$ 11	5.0 $\pm$ 0.5	2.1 $\pm$ 1.2
L22	5027	207	193	116	112	27.8	3.4
Maize							
M0	1354 $\pm$ 218	361 $\pm$ 90	223 $\pm$ 60	66 $\pm$ 28	66 $\pm$ 16	6.7 $\pm$ 2.0	8.5 $\pm$ 6.2
M22	11744	377	446	183	494	53.0	59.2

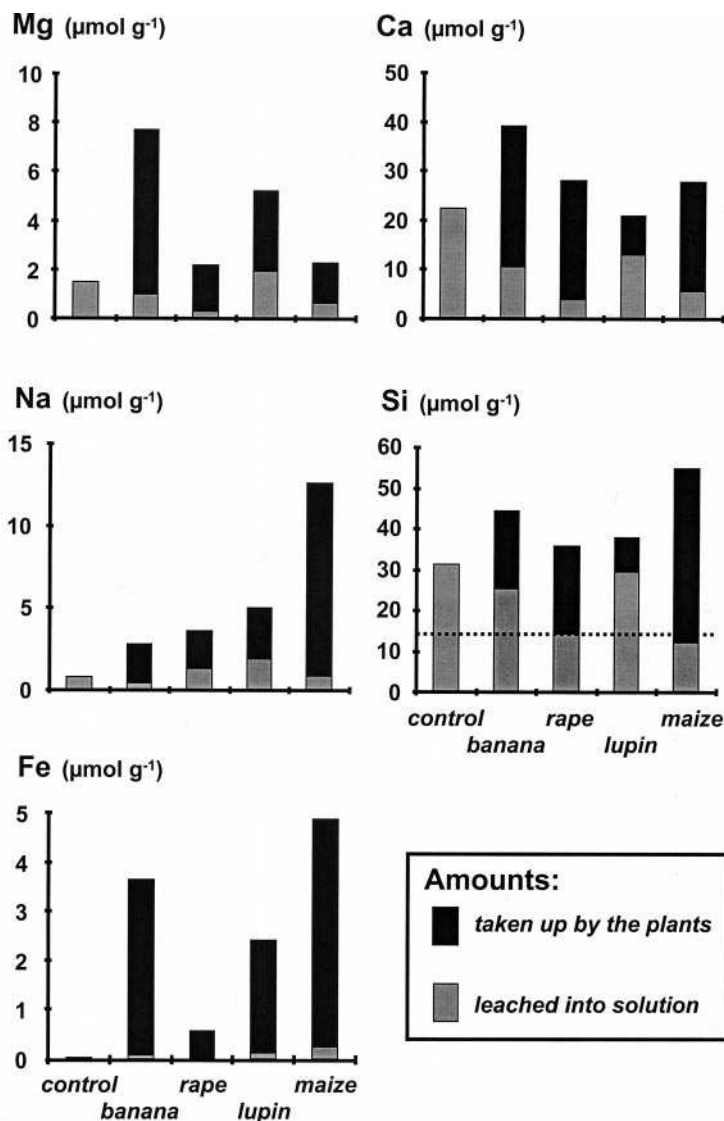


Fig. 5. Mass-balance of elements released into the leaching solution and taken up by plants in the absence (control) or presence of various plant species in experiment A: the bars represent the cumulated amounts of elements over the whole duration of the experiment (22 days). The dotted line represents the level of accidental contamination that took place for silicon.

1996a) and for ferromagnesian silicates (Schott and Berner, 1983; Schott and Petit, 1987). The restricted release of Fe could be expected considering the neutral pH and oxic conditions that were prevailing in the present experiment as the nutrient solution was constantly bubbled with ambient air. Therefore, the low concentrations of Fe found in the leachates both in presence and absence of plants in experiments A and B (Figs. 2 and 3) were most certainly due to the precipitation of Fe oxides in such conditions (Lindsay, 1979; Schott and Berner, 1983; Schott and Petit, 1987). In the presence of plants, however, the Fe/Si molar ratios were much larger than in the absence of plants (Fig. 7). For banana in exp. B there was a trend towards an increase in Fe/Si with time. Nevertheless, even by the end of the experiment, the stoichiometry of Fe and Si in the solid was not attained.

These results thus suggest that ferromagnesian silicates dis-

solved less than plagioclase feldspars contained in the basalt. In all cases, Ca was the most preferentially released cation. However, a major effect of plants, and more critically so of monocot species such as maize and banana, was to dramatically increase the release of Fe which remained almost undetectable in the absence of plants.

#### 4.2. Kinetics of Dissolution

In experiment A, the kinetics of dissolution cannot be analysed in much details because only the release of elements in the leachates was measured at various time intervals along the course of the experiment. As this contributed little to the whole mass balance of released elements (Fig. 5), there is no point to further discuss the results of experiment A.

Conversely, in experiment B, the measurement of the plant



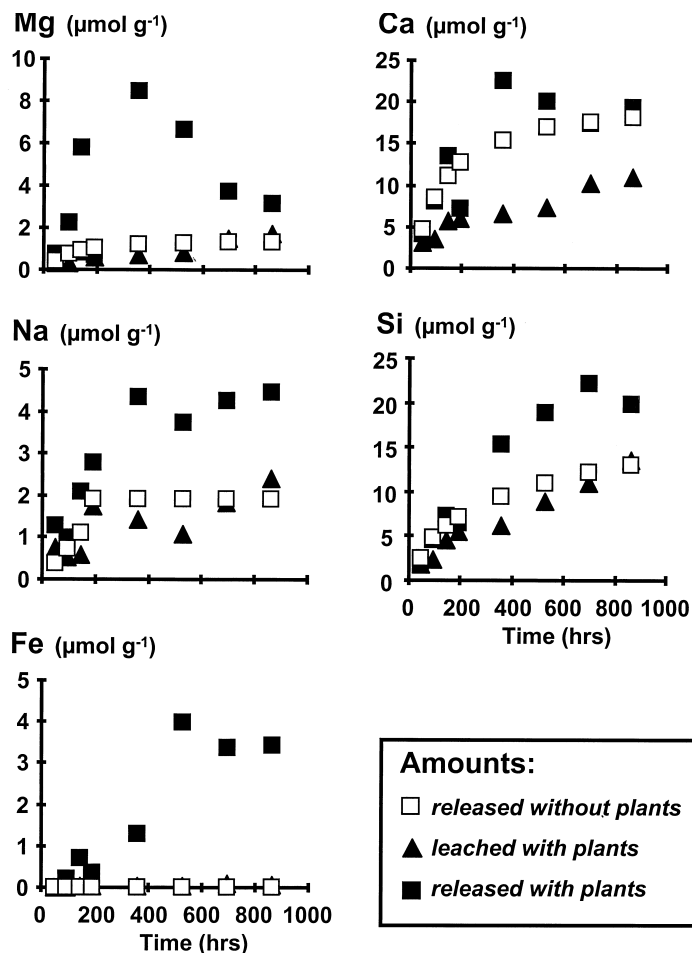


Fig. 6. Kinetics of release of elements in experiment B. In the absence of plants (control) the cumulated amounts of elements released into the leaching solution are plotted as empty squares ( $\square$ ). In the presence of banana plants the cumulated amounts of elements released into the leaching solution are plotted as dark triangles ( $\blacktriangle$ ), and the dark squares ( $\blacksquare$ ) represent the sum of the amount of elements released into solution and taken up by the plants.

uptake term at each step of the kinetics enabled a proper comparison of the kinetics of dissolution in the presence and absence of plants over the whole duration of the experiment. In Figure 8, which draws the evolution of the log values of the dissolution rates as a function of time, the rates were calculated between two consecutive time steps whenever an increase in the amount of element release was found. When this amount was found to decrease with time, no additional dissolution was expected to have occurred and the corresponding points were thus discarded from Figure 8. This is particularly the case for Ca and Mg beyond 15 days in the presence of plants.

Both in presence and absence of plants, no steady state was ever attained during the course of the experiment (Fig. 8). The rapid dissolution that occurred at the early stage of the experiment in the absence of plants was most probably due to the dissolution of the finer particles of basalt which had not been completely removed by ultrasonication (Holdren and Berner, 1979; Helgeson et al., 1984). In most reported experiments on the experimental dissolution of silicates, steady-state dissolution was attained beyond several hundreds of hours, which contrasts with the present results. However, in a recent study of the kinetics of dissolution of basalt, Eick et al. (1996b) reported

that the initial stage of rapid but decreasing release rate lasted up to about 24 days (and 48 days for Si), that is in the order of the whole duration of the present experiment.

In the presence of plants, for all elements but Na, there was an increase in the rate of dissolution at the early stage of the experiment, followed by a plateau up to about 15 days (22 days for Fe) and a decrease towards the end of the experiment (Fig. 8). Noteworthy is the singular shape of the kinetics that were obtained for Ca and more critically so Mg, with rates peaking at 15 days (Fig. 6). Similar results have been described for Ca, Mg, and Fe by Eick et al. (1996a) when studying the kinetics of dissolution of basalt with a solution containing 2 mM oxalate. These authors interpreted such results as the possible consequence of the precipitation of Fe oxides, which subsequently scavenged other elements from the solution as also reported earlier by Siever and Woodford (1979). This might have occurred here as well when considering the shape of the kinetics of release of Fe in the presence of banana plants (Fig. 8), which indeed exhibited a decrease beyond 22 days of experiment. A particular feature of the kinetics of release of Fe is that the rate was minimal at the early stage of the experiment, then drastically increased and remained high up to 22 days (Fig. 8). The

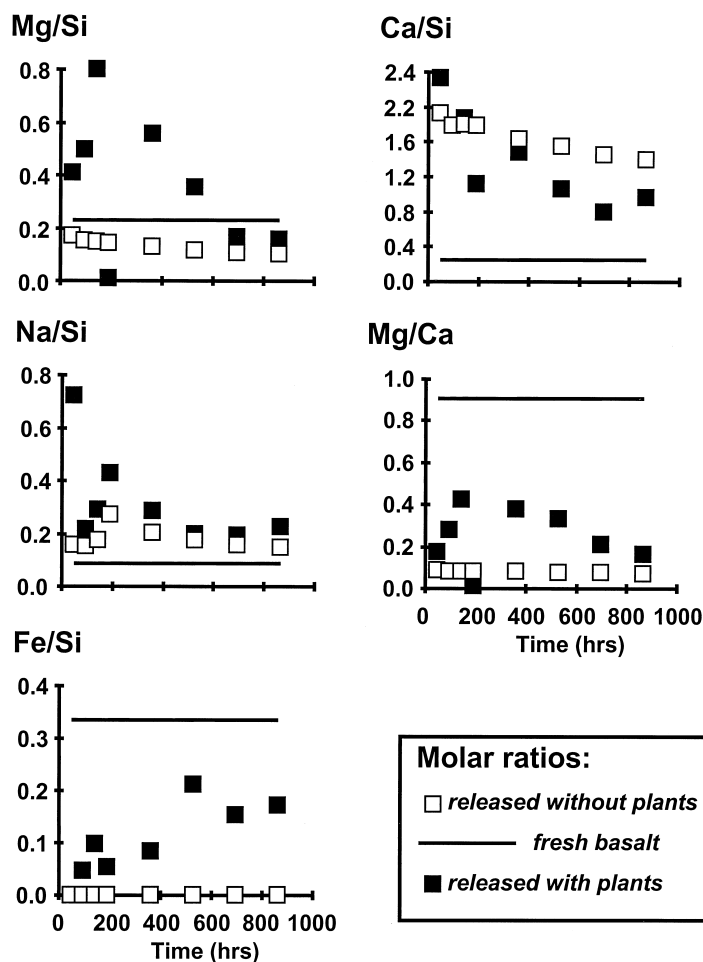


Fig. 7. Time evolution of the molar ratios of elements released in the absence (□) and presence (■) of banana plants in experiment B. The amounts released with plants were deduced from the sum of the amounts leached into the percolating solution and taken up by the plants. The straight line indicates the initial molar ratio in the fresh basalt.

effect of plants on the solubilization of Fe-bearing minerals in the basalt was thus delayed. This will be further discussed later in the section about the possible mechanisms involved.

When investigating the dissolution of basalt in the presence of organic acids, Eick et al. (1996a and 1996b) found that their results were best described by a parabolic kinetic law, suggesting that the dissolution of basalt was a diffusion-controlled process. To test such an hypothesis for our data, the amounts of elements released in experiment B were thus plotted as a function of the square root of time (Fig. 9). The corresponding plots suggests that although reasonably good linear correlations were found (with  $R^2$  ranging from 0.65 to 0.98), the data did not conform to a parabolic law. As for the data of Eick et al. (1996a and 1996b), the curvilinear pattern of the experimental points indicated that a parabolic law was not the best suited law for describing the kinetics. Our results thus suggest: (i) that the kinetics of dissolution of basalt in the absence or presence of plants did not conform to a linear or parabolic rate law and (ii) therefore, that it was neither governed by a surface-controlled nor a diffusion-controlled process. This might be the consequence of either studying a complex solid as a rock rather than an isolated mineral or of an experimental artefact. In addition,

in spite of the vigorous shaking of the solution in the reactor vessels with the magnetic stirrer, it is likely that all basalt particles were not equally affected by the solution or plant roots in the present experiments. Most probably, some gradients of dissolution occurred in the bag that contained the basalt between the outer surface (especially the side that was covered by the root mat in the presence of plants) and the inner core of the bunch of particles.

#### 4.3. Dissolution Rates in the Presence or Absence of Plants

Although no linear rate kinetics was found, we calculated the dissolution rates in order to compare the rates obtained in presence or absence of plants and to compare them with those reported in the literature. The rates that are indicated in Table 4 were deduced from the amounts of elements released between 0 and 22 days in both experiments (so as to compare experiments A and B). There was a fairly good agreement between the rates found in experiments A and B, both in the absence or presence of banana plants. These calculations suggest that the rates of dissolution were fairly low in the absence of plants,

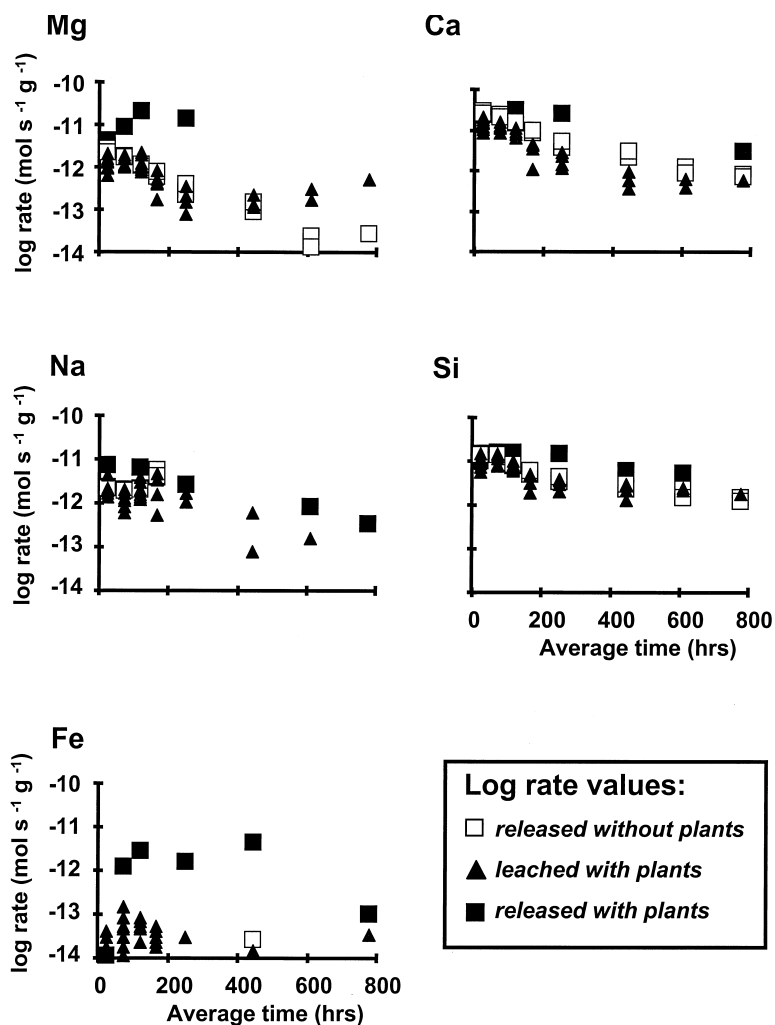


Fig. 8. Log values of the rates of release of elements as calculated between two consecutive time intervals in experiment B. In the absence of plants (control) the cumulated amounts of elements released into the leaching solution are plotted as empty squares ( $\square$ ). In the presence of banana plants the cumulated amounts of elements released into the leaching solution are plotted as dark triangles ( $\blacktriangle$ ), and the dark squares ( $\blacksquare$ ) represent the sum of the amount of elements released into solution and taken up by the plants.

with log values ranging between  $-11$  and about  $-12$  in general, and down to about  $-14$  for Fe. For Mg, Ca, and Si, the rates were lower than those deduced from the batch dissolution experiment that was conducted at neutral pH by Eick et al. (1996a), when calculating the rates in a similar manner, i.e., between 0 and 22 days (Table 4). It is likely that the rates that we calculated underestimated the actual rates, considering that the particles of the inner core of the bag were not as much influenced by the leaching solution as those particles that were close to the surface. Referring the amounts of released element to ten grams of basalt thus probably led to underestimate the actual value.

Compared with the rates obtained in the absence of plants in both experiments A and B, we found that, in the presence of banana, the release rates increased by a factor ranging from 1 to 2 for Na, Ca and Si, by a factor of about 5 for Mg and by a factor of about several hundreds for Fe (Table 4). These results fairly well agree with those found for other plant species in experiment A, except for Mg and Na in the case of maize.

There is thus a consistent, positive effect of plants on the rate of dissolution of basalt. Unexpectedly, in both experiments, the lesser effect was that found for Ca. It is interesting to compare the extent of this effect with what was found with other approaches. Taylor and Velbel (1991) reported that when taking into account what they called the botanical uptake term in the geochemical mass balance of small forested watersheds in North America, the dissolution rates of ferromagnesian silicates such as biotite were increased by a factor of 1 to 4. Benedetti et al. (1994) reported for tropical catchments from Brazil that computed rates of dissolution of basalt were 1.5- to 5-fold larger when incorporating a biomass uptake term in their calculation. Comparing the weathering fluxes of forested lands with adjacent almost bare land in North America and Iceland (i.e., poorly vegetated with bryophytes and lichens), several authors reported an increased release rate of Ca, Mg, Na, and K ranging from 1- to 5-fold (Arthur and Fahey, 1993; Berner, 1999; Moulton and Berner, 1999). In their field experiment at Hubbard Brook (large lysimeters called 'sandboxes'), Bormann

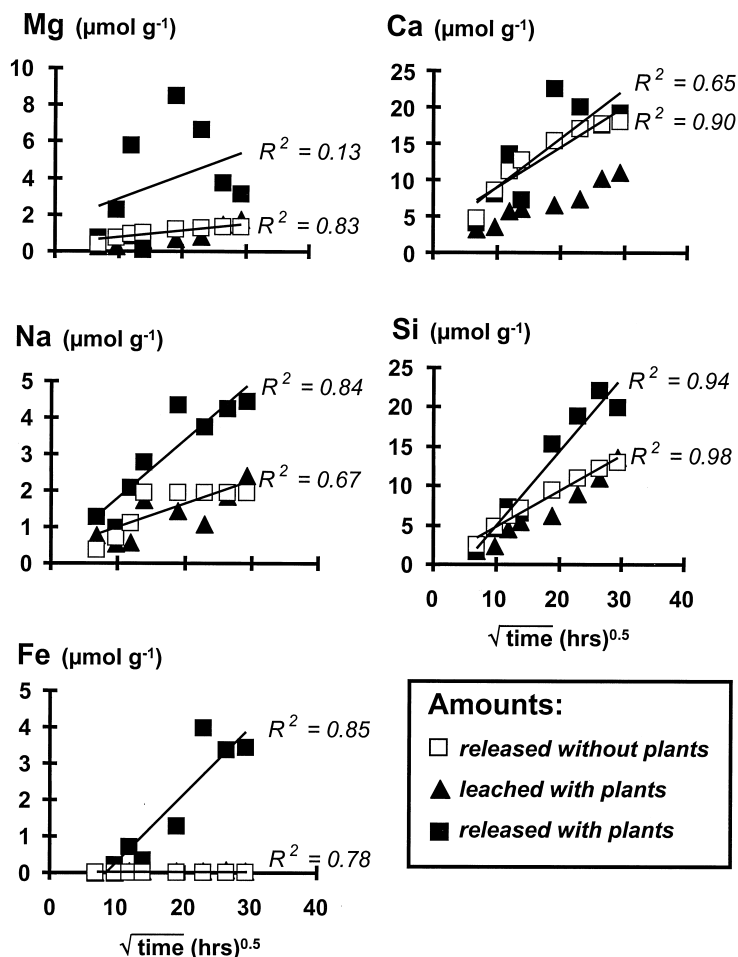


Fig. 9. Parabolic plots of the kinetics of release of elements in experiment B. In the absence of plants (control) the cumulated amounts of elements released into the leaching solution are plotted as empty squares ( $\square$ ). In the presence of banana plants the cumulated amounts of elements released into the leaching solution are plotted as dark triangles ( $\blacktriangle$ ), and the dark squares ( $\blacksquare$ ) represent the sum of the amount of elements released into solution and taken up by the plants. The regression lines and corresponding determination coefficients are given for only for the total amounts of elements released in the presence or absence of plants (squares).

et al. (1998) reported even larger effect for Ca and Mg under young pine trees: relative to the unvegetated 'sandbox,' they measured an increased rate of 2.4 for Ca and 1.8 for Mg in the forested 'sandbox' when taking account of the accumulation of Ca and Mg in the pine trees; when taking also account of the accumulation of secondary products in the 'sandbox' material (as exchangeable cations, organic matter, or secondary minerals), they estimate that pine resulted in 10- and 18-fold increased rates for Ca and Mg, respectively, compared with unvegetated control. Thus, there is a somewhat fairly good agreement between the data computed from field studies and the data measured in the present laboratory experiments. The lesser effect found for Ca than for Na in our experiment in contrast with these other authors might be the consequence of lower requirements for Ca of the crop species studied in the present work compared with those of trees. In addition, the present experiment points to the case of Fe for which the most dramatic effect of plants was reported. Unfortunately, none of the abovementioned works reported on the mass balance of Fe. There is thus no doubt that plants need to be taken into account

in the geochemical budgets. The question that now arises is: how do plants enhance the dissolution rates to such an extent?

#### 4.4. Possible Mechanisms of Plant-Induced Dissolution of Basalt

The first and most immediate hypothesis that can account for the reported stimulation of the dissolution of basalt in the presence of plants is based on the uptake activity of plant roots (Hinsinger, 1998). By taking up, at fairly high rates, major nutrients such as K, Ca, and Mg and also nonessential elements such as Si, plant roots constantly depleted the solution. This removal of the dissolution products can thus have shifted the dissolution equilibrium according to Le Chatelier's principle, thereby resulting in an increased dissolution of the rock. This has been shown to occur for the root-induced dissolution of K-bearing silicates such as trioctahedral micas (Hinsinger and Jaillard, 1993; Hinsinger et al., 1993). Also, the uptake of Ca by plants has been reported to enhance the dissolution of phosphate rocks (apatite) in a similar manner (Johnston and Olsen,

Table 4. Log values of the dissolution rates (rates expressed as mol/g/s basalt) in experiments A and B and in the data obtained for a different basalt by Eick et al. (1996a). In the latter experiment, the authors did not supply data about Na and mentioned that the release of Fe remained undetectable at pH 7. In all three experiments, the rates were deduced from the total amount of elements dissolved between 0 and 22 days. The resulting log values thus do not correspond to linear rate dissolution.

	Mg	Ca	Na	Si	Fe
<i>Experiment A</i>					
Control	-12.10	-10.93	-12.38	—	-13.83
Banana	-11.39	-10.69	-11.83	—	-11.72
Rape	-11.94	-10.83	-11.72	—	-12.53
Lupin	-11.56	-10.96	-11.58	—	-11.90
Maize	-11.92	-10.83	-11.18	—	-11.59
<i>Experiment B</i>					
Control	-12.17	-11.05	-12.00	-11.24	-14.38
Banana	-11.46	-10.98	-11.71	-11.00	-11.68
<i>Data from Eick et al. (1996a)</i>					
pH 7	-10.50	-10.49	—	-10.64	—
pH 5	-10.05	-10.37	—	-10.25	-10.06

1972; Hinsinger and Gilkes, 1997). The uptake of elements by higher plants can represent a substantial sink that needs to be taken into account at field scale as shown by the calculations and experiments of, e.g., Taylor and Velbel (1991), Benedetti et al. (1994), and Bormann et al. (1998).

In addition, plants can significantly alter the pH in the surrounding environment of their roots, the so-called rhizosphere (Römheld, 1986; Hinsinger, 1998). This effect is partly accounted for by the production of CO<sub>2</sub> by root respiration (Nye, 1981). More critically so, the decrease in rhizosphere pH is largely due to the release of H-ions to compensate for an excess of cations over anions being taken up by the plants and the maintenance of the electrical neutrality of the plant root tissues (Haynes, 1990). The root-induced release of Mg from a Mg-bearing phyllosilicate has been shown to be the consequence of the release of H-ions by rape roots (Hinsinger et al., 1993). The enhanced dissolution of apatite in the rhizosphere of diverse plant species has also been attributed to the release of H-ions by their roots (Aguilar and van Diest, 1981; Hinsinger and Gilkes, 1996 and 1997).

In the present experiments, we measured the pH of leachates (Table 5 and Fig. 10). There was indeed a general trend towards a decrease in pH in the presence of plants relative to the control without plants. At the early stage of experiment B, the pH measured for cropped reactor vessels was 1 to 2 pH units lower than in the uncropped, control vessels (Fig. 10). Then, between 4 and 8 days, the pH increased in the cropped reactor vessels, remaining however about 0.5 pH unit below the control pH. The peak of pH decrease at the early stage of the experiment coincides fairly well with the period of maximum uptake rate of major cations such as Ca and Mg (Fig. 6) and resulting maximum rate of dissolution of basalt (Fig. 8). This suggests a possible role of the release of H-ions by plant roots in the plant-induced dissolution of basalt. Later in the course of

experiment B, the release of H-ions decreased (Fig. 10), possibly as a consequence of a restricted plant growth (Fig. 4) that occurred because of likely nutritional disorders (nutrient deficiencies or metal toxicities). In experiment A, the smallest pH values were found for maize and banana, followed by lupin (Table 5). Rape almost did not alter or slightly increased the pH compared with control pH. The ranking of the pH values found for the various species was in good agreement with their ability to enhance the release of elements from basalt (Fig. 4). This further suggests that the release of H-ions by plant roots might have played some significant role in the root-induced dissolution of basalt. This effect is, however, quite difficult to assess quantitatively because the dissolution of basalt itself consumes H-ions and thereby buffer the pH of the leaching solution.

For the considerable enhancement of Fe release that occurred in the presence of plants, other processes might be invoked in addition to the previous ones. Indeed, higher plants are known to mobilize Fe mainly through two different pathways (Marschner and Römheld, 1994): (i) complexation of Fe by phytosiderophores produced by graminaceous species (grasses) or (ii) reduction of Fe for the other species. In addition, these processes are known to be induced as a response to Fe-deficiency. Under such circumstances, both the synthesis and release of phytosiderophores by grasses and the reduction activity of other species are known to be dramatically increased (Marschner and Römheld, 1994). At the early stage of this experiment, the concentration of Fe was minimal in the leachate, even in the presence of plants (Figs. 2 and 3). It is thus possible that plants had inadequate supply of Fe at that stage. Such an Fe deficiency might have then induced an increase in the release of phytosiderophores by maize and in the reduction activity of the roots of other species. Such a phenomenon would explain the delay that was found in the kinetic of release of Fe, compared with other elements (Fig. 6). In experiment B, it was found that

Table 5. pH values measured in the leachates in experiment A.

	Control	Banana	Rape	Lupin	Maize
After 15 days	7.09	6.52	7.05	6.86	6.44
After 22 days	7.10	6.54	7.25	6.48	6.59

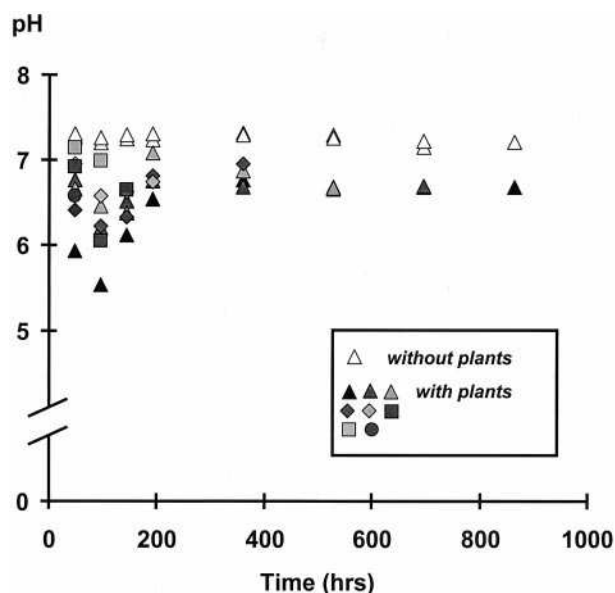


Fig. 10. Values of pH of the leaching solution in the absence (control,  $\Delta$ ) or presence of banana plants as a function of time duration in experiment B.

the rate of release of Fe in the presence of banana increased by about two orders of magnitude between Day 2 and Days 4 to 22 (Fig. 8). This delay might be the time required for the induction of an enhanced reduction activity in banana roots. Among the four species studied in experiment A, the graminaceous species (maize) was found as the most efficient species at solubilizing Fe from basalt (Table 4). This is in agreement with the widely admitted idea that due to the production of phytosiderophores, grasses have evolved a very efficient strategy to mobilize Fe (Römheld, 1991). Lastly, many plants have been reported to release other exudates that can potentially complex Fe, such as citrate and malate (e.g. Jones et al., 1996). This rhizosphere process might thus have contributed some portion of the much increased release of Fe that was reported here in the presence of plants. Indeed, in their experiments conducted at neutral pH, Eick et al. (1996a) reported a considerable increase in the release of Fe from basalt in the presence of 2 mM citrate, that is at concentration in the order of what might occur in the rhizosphere (Jones et al., 1996). To verify whether this rhizosphere process played some role in the plant-induced weathering of basalt, future works should therefore attempt to simultaneously determine the concentrations of root exudates.

The present experiments were not designed for distinguishing between the effects of higher plants and those of associated microorganisms that possibly developed in the rhizosphere. Future works should, therefore, be conducted: (i) under axenic conditions to evaluate the direct effect of higher plants per se and (ii) with plants inoculated with soil microflora (both symbiotic and non symbiotic) to evaluate the additional effect of rhizosphere microorganisms. In a former work of this kind, it is interesting to point out that Leyval et al. (1990) showed that maize plants which had been inoculated by either mycorrhizal symbionts or non symbiotic bacteria (or both of them) did not achieve significantly larger release of K, Fe, and Mg from a phlogopite-type phyllosilicate, compared with maize grown

under axenic conditions (without any rhizosphere microorganisms). This demonstrates that the direct effects of higher plants on the weathering of silicates are substantial and can possibly be more important than the effects of rhizosphere microflora. This needs to be further substantiated in future works.

## 5. CONCLUSIONS

The amounts of Si, Fe, Ca, Mg, and Na released from a basalt under leaching conditions in the presence or absence of plants have been measured in laboratory conditions. This study shows that for all elements but Fe, the action of various plant species resulted in an increase in the release rate by a factor ranging from 1 to 5 in most cases. Ca and Na seemed to be preferentially released relative to other elements, suggesting that plagioclase dissolved faster than the other basalt constituents. For Fe, only a negligible amount was released in the absence of plants as a consequence of the neutral pH and atmospheric  $pO_2$  that were maintained in the percolating solution. However, in the presence of plants, the amount of Fe released from basalt reached a maximum increase of about 100- to 500-fold for banana and maize. The kinetics of dissolution was followed in an experiment with banana. In the absence of plants, the rate of release was maximum in the early days of the experiment and then constantly decreased until the end of the experiment (36 days) without reaching any steady-state value. In the presence of plants, a similar trend was found but with rates remaining at a high initial level over a longer period of time (up to 15 days) before to decrease. It was also found that the pH decrease that occurred throughout the experiment as a consequence of the release of H-ions by plant roots also reached a maximum at the early stage of the experiment (especially between 2 and 8 days). This suggested that besides the stimulating effect of the uptake of elements by plants, the release of H-ions by the roots also enhanced the rate of dissolution of basalt. For Fe, the initial rate measured after 2 days was about two orders of magnitude below the maximum value that was reached beyond 4 days of growth. This delay might indicate an induction period during which Fe deficiency that the plants experienced because of the extremely low, initial rate of release of Fe resulted in a response commonly found in Fe-deficient plants: for most plants, this response is an enhancement of the reduction activity of the roots, which might well explain the subsequent increase in the rate of release of Fe. For graminaceous species such as maize, the response to Fe-deficiency consists of an enhanced synthesis and release of strong Fe chelators called phytosiderophores, which render these species very efficient at mobilizing Fe. Indeed, maize induced the largest increase in the rate of release of Fe from basalt, relative to the control without plants.

Although the mechanisms of action of the plants were not fully elucidated in the present experiment, the results reported here definitely support the conclusion that higher plants can play a very significant role in the weathering of rocks. They thus show that land plants need to be taken into account in the geochemical mass balance of elements, particularly for those elements that are taken up by the plants, as had been suggested earlier by the models of Taylor and Velbel (1991) and the experiments conducted for young forest trees by Bormann et al. (1998). In addition to the effect of plants that is simply due to

the removal of dissolution products which can be considerable in the mass balance for those elements that are taken up at high rates (Si and major nutrients such as K, Ca, and Mg), higher plants can affect the dissolution of basalt by several other mechanisms (exudation of H<sup>+</sup>-ions or chelatants, reduction of Fe). Further studies are thus needed for determining the respective influence of these various mechanisms. To proceed further, future investigations would advantageously focus on isolated silicate minerals rather than a complex rock such as basalt for which the stoichiometry and the kinetics of dissolution are too complicated to be fully understood. It should also be pointed out that the present experiments were not carried out under axenic conditions. Therefore, they did not enable to distinguish between the direct effects of plant roots and the effects of associated microorganisms that were potentially present. In order to address this question, future works should thus try to quantitatively evaluate the contribution of each by comparing axenically grown plants with plants inoculated with soil microflora.

The present results suggest that weathering processes have been largely underestimated in many earlier works which, most often, did not take account of the potential roles of higher plants. As stressed by Bormann et al. (1998) weathering is thus wrongly seen as a rather slow process. It might occur much faster in the rhizosphere of higher plants and would therefore deserve to be seen as a short term process. There is thus a need to reassess biogeochemical budgets, especially so in the perspective of better evaluating the potential contribution of weathering (including plant-induced processes) to plant nutrition (Gobran et al., 1999). This is particularly needed for achieving low-input, sustainable production of forests and agrosystems. These results also suggest that there is a need to reassess our views of concepts such as ecosystem and soil fertility: contrary to what as long been assumed, rock fragments and parent rock materials rich in primary minerals should be considered as potential sources of nutrients that potentially contribute a substantial proportion of soil fertility (Corti et al., 1998; Gras, 1994). In addition, crushed silicate rocks may also be considered as potential fertilizers that would deserve to be further studied in that respect (Coroneos et al., 1996; Harley and Gilkes, 2000). It is interesting to point out that ground basalt has been previously reported as a very efficient source of Fe to alleviate Fe-deficiency (chlorosis) in calcareous soils (Barak et al., 1983), although restricted release of Fe from basalt would be expected considering the slightly alkaline bulk soil pH of those soils. The much increased release of Fe that took place in the presence of plants in the present work provides a possible explanation for this apparent contradiction. The biogeochemical cycles of elements such as Fe and other elements such as Si and major nutrients for higher plants (Ca, Mg, K) need therefore to be reassessed in the light of the present results.

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## REFERENCES

- Aguilar S. A. and van Diest A. (1981) Rock phosphate mobilization induced by the alkaline pattern of legumes utilizing symbiotically fixed nitrogen. *Plant Soil* **61**, 27–42.
- Arthur M. A. and Fahey T. J. (1993) Controls on soil solution chemistry in a subalpine forest in north-central Colorado. *Soil Sci. Soc. Am. J.* **57**, 1123–1130.
- Banfield J. F., Welch S. A., Taunton A. E., Santelli C. M., and Barker W. W. (1999) Exploring microbial controls on mineral weathering. In *Geochemistry of the Earth's Surface* (ed. Ármannsson). pp. 353–356. Balkema.
- Barak P., Chen Y., and Singer A. (1983) Ground basalt and tuff as iron fertilizer for calcareous soils. *Plant Soil* **73**, 155–158.
- Barman A. K., Varadachari C., and Ghosh K. (1992) Weathering of silicate minerals by organic acids. I. Nature of cation solubilisation. *Geoderma* **53**, 45–63.
- Benedetti M. F., Menard O., Noack Y., Carvalho A., and Nahon D. (1994) Water-rock interactions in tropical catchments: Field rates of weathering and biomass impact. *Chem. Geol.* **118**, 203–220.
- Berner R. A. (1992) Weathering, plants, and the long-term carbon cycle. *Geochim. Cosmochim. Acta* **56**, 3225–3231.
- Berner R. A. (1999) Plants, weathering and the evolution of atmospheric CO<sub>2</sub>. In *Geochemistry of the Earth's Surface* (ed. Ármannsson). pp. 3–5. Balkema.
- Bienfait H. F., Bino R. J., van der Blik A. M., Duivenvoorden J. F., and Fontaine J. M. (1983) Characterization of ferric reducing activity in roots of Fe-deficient *Phaseolus vulgaris*. *Physiol. Plant* **59**, 196–202.
- Bormann B. T., Wang D., Bormann F. H., Benoit R., April D., and Snyder M. C. (1998) Rapid plant induced weathering in an aggrading experimental ecosystem. *Biogeochem.* **43**, 129–155.
- Brantley S. L., Liermann L., Kalinowski B., Givens S., Pantano C. G., and Barnes A. (1999) Abiotic vs. Biotic dissolution of hornblende. In *Geochemistry of the Earth's Surface* (ed. Ármannsson). pp. 357–359. Balkema.
- Brown J. C. and Ambler J. E. (1973) "Reductants" released by roots of Fe-deficient soybeans. *Agron. J.* **65**, 311–314.
- Callot G., Maurette M., Pottier L., and Dubois A. (1987) Biogenic etching of microfractures in amorphous and crystalline silicates. *Nature* **328**, 147–149.
- Chapin F. S. III (1980) The mineral nutrition of wild plants. *Ann. Rev. Ecol. Syst.* **11**, 233–260.
- Coroneos C., Hinsinger P., and Gilkes R. J. (1996) Granite powder as a source of potassium for plants: A glasshouse bioassay comparing two pasture species. *Fert. Res.* **45**, 143–152.
- Corti G., Ugolini F. C., and Agnelli A. (1998) Classing soil skeleton (greater than two millimeters): Proposed approach and procedure. *Soil Sci. Soc. Am. J.* **62**, 1620–1629.
- Darrah P. R. (1993) The rhizosphere and plant nutrition: A quantitative approach. *Plant Soil* **155/156**, 1–20.
- Drever J. I. (1994) The effect of land plants on weathering rates of silicate minerals. *Geochim. Cosmochim. Acta* **58**, 2325–2332.
- Dinkelaker B., Römheld V., and Marschner H. (1989) Citric acid excretion and precipitation of calcium citrate in the rhizosphere of white lupin (*Lupinus albus* L.). *Plant Cell Envir.* **12**, 285–292.
- Eick M. J., Grossl P. R., Golden D. C., Sparks D. L., and Ming D. W. (1996a) Dissolution of a lunar basalt simulant as affected by pH and organic anions. *Geoderma* **74**, 139–160.
- Eick M. J., Grossl P. R., Golden D. C., Sparks D. L., and Ming D. W. (1996b) Dissolution kinetics of a lunar basalt simulant at 298 K. The effect of pH and organic acids. *Geochim. Cosmochim. Acta* **56**, 157–170.
- Epstein E. (1999) Silicon. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **50**, 641–664.
- Gerke J., Römer W., and Jungk A. (1994) The excretion of citric and malic acid by proteoid roots of *Lupinus albus* L.: Effects on solubility of phosphate, iron and aluminum in the proteoid rhizosphere in samples of an oxisol and a luvisol. *Z. Pflanzenernaehr. Bodenkd.* **157**, 289–294.
- Gillman G. P. (1980) The effect of crushed basalt scoria on the cation exchange properties of a highly weathered soil. *Soil Sci. Soc. Am. J.* **44**, 465–468.

- Gobran G. R., Clegg S., and Courchesne F. (1999) The rhizosphere and trace element acquisition in soils. In *Fate and Transport of Heavy Metals in the Vadose Zone* (eds. H. M. Selim and A. Iskander), pp. 225–250. CRC Press.
- Gras R. (1994) *Sols Caillouteux et Production Végétale*. Institut National de la Recherche Agronomique.
- Harley A. D. and Gilkes R. J. (2000) Factors influencing the release of plant nutrient elements from silicate rock powders: A geochemical overview. *Nutr. Cycling. Agroecosyst.* **56**, 11–36.
- Haynes R. J. (1990) Active ion uptake and maintenance of cation-anion balance: A critical examination of their role in regulating rhizosphere pH. *Plant Soil* **126**, 247–264.
- Helgeson H. C., Murphy W. M., and Aagaard P. (1984) Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions. II. Rate constants, effective surface area and the hydrolysis of feldspar. *Geochim. Cosmochim. Acta* **48**, 2405–2432.
- Hinsinger P. (1998) How do plant roots acquire minerals nutrients? Chemical processes involved in the rhizosphere. *Adv. Agron.* **64**, 225–265.
- Hinsinger P. and Gilkes R. J. (1996) Mobilization of phosphate from phosphate rock and alumina-sorbed phosphate by the roots of ryegrass and clover as related to rhizosphere pH. *Eur. J. Soil Sci.* **47**, 533–544.
- Hinsinger P. and Gilkes R. J. (1997) Dissolution of phosphate rock in the rhizosphere of five plant species grown in an acid, P-fixing mineral substrate. *Geoderma* **75**, 231–249.
- Hinsinger P. and Jaillard B. (1993) Root-induced release of interlayer potassium and vermiculitization of phlogopite as related to potassium depletion in the rhizosphere of ryegrass. *J. Soil Sci.* **44**, 525–534.
- Hinsinger P., Jaillard B., and Dufey J. E. (1992) Rapid weathering of a trioctahedral mica by the roots of ryegrass. *Soil Sci. Soc. Am. J.* **56**, 977–982.
- Hinsinger P., Elsass F., Jaillard B., and Robert M. (1993) Root-induced irreversible transformation of a trioctahedral mica in the rhizosphere of rape. *J. Soil Sci.* **44**, 535–545.
- Hiradate S. and Inoue K. (1998) Interaction of mugineic acid with iron (Hyd)oxides: Sulfate and phosphate influences. *Soil Sci. Soc. Am. J.* **62**, 159–165.
- Hoffland E., Findenegg G. R., and Nelemans J. A. (1989) Solubilization of rock phosphate by rape. II. Local root exudation of organic acids as a response to P-starvation. *Plant Soil* **113**, 161–165.
- Holdren G. R. Jr. and Berner R. A. (1979) Mechanism of feldspar weathering. I. Experimental studies. *Geochim. Cosmochim. Acta* **43**, 1161–1171.
- Huang W. H. and Keller W. D. (1970) Dissolution of rock-forming silicate minerals in organic acids: Simulated first-stage weathering of fresh mineral surfaces. *Am. Mineral.* **57**, 2076–2094.
- Jackson T. A. (1996) Comment on “The effect of land plants on weathering rates of silicate minerals” by James I. Drever. *Geochim. Cosmochim. Acta* **60**, 723–724.
- Jongmans A. G., van Breemen N., Lundström U., van Hees P. A. W., Finlay R. D., Srinivasan M., Unestam T., Giesler R., Melkerud P.-A., and Olsson M. (1997) Rock-eating fungi. *Nature* **389**, 682–683.
- Jaillard B., Guyon A., and Maurin A. F. (1991) Structure and composition of calcified roots, and their identification in calcareous soils. *Geoderma* **50**, 197–210.
- Johnston W. B. and Olsen R. A. (1972) Dissolution of fluorapatite by plant roots. *Soil Sci.* **114**, 29–36.
- Jones D. L., Darrah P. R., and Kochian L. V. (1996) Critical evaluation of organic acid mediated dissolution in the rhizosphere and its potential role in root iron uptake. *Plant Soil* **180**, 57–66.
- Kodama H., Nelson S., Yang F., and Kohyama N. (1994) Mineralogy of rhizospheric and non-rhizospheric soils in corn fields. *Clays Clay Min.* **42**, 755–763.
- Lambers H., Scheurwater I., and Atkin O. K. (1996) Respiratory patterns in roots in relation to their functioning. In *Plant Roots. The Hidden Half*, 2nd Ed. (eds. Y. Waisel, A. Eshel and U. Kafkafi), pp. 529–556. Marcel Dekker.
- Leyval C., Laheurte F., Belgy G., and Berthelin J. (1990) Weathering of micas in the rhizospheres of maize, pine and beech seedlings influenced by mycorrhizal and bacterial inoculation. *Symbiosis* **9**, 105–109.
- Lindsay W. L. (1979) *Chemical equilibria in soils*. John Wiley and Sons.
- Marques R., Ranger J., Villette S., and Granier A. (1997) Nutrient dynamics in a chronosequence of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) stands on the Beaujolais Mounts (France). 2—Quantitative approach. *Forest Ecol. Management* **92**, 167–197.
- Marschner H. (1995) *Mineral Nutrition of Higher Plants*, 2nd ed. Academic Press.
- Marschner H. and Römheld V. (1994) Strategies of plants for acquisition of iron. *Plant Soil* **165**, 261–274.
- Mengel K. and Kirkby E. A. (1987) *Principles of Plant Nutrition*, 4th ed. International Potash Institute.
- Mortland M. M., Lawton K., and Uehara G. (1956) Alteration of biotite to vermiculite by plant growth. *Soil Sci.* **82**, 477–481.
- Moulton K. L. and Berner R. A. (1999) Quantitative effects of plants on weathering: Forest sinks for carbon. In *Geochemistry of the Earth's Surface* (ed. Ármannsson), pp. 57–60. Balkema.
- Nye P. H. (1981) Changes of pH across the rhizosphere induced by roots. *Plant Soil* **61**, 7–26.
- Piccirillo E. M. and Melfi A. J. (1988) *The mesozoic flood volcanism of the Paraná Basin—Petrogenetic and geophysical aspects*. Universidade De São Paulo, Instituto Astronômico e Geofísico.
- Razzaghe M. K. and Robert M. (1979) Géochimie des éléments majeurs des micas en milieu organique: mécanismes de l'altération des silicates. *Ann. Agron.* **30**, 493–512.
- Robert M. and Berthelin J. (1986) Role of biological and biochemical factors in soil mineral weathering. In *Interactions of soil minerals with natural organics and microbes* (eds. P. M. Huang and M. Schnitzer), Special Publication No. 17, pp. 453–495. Soil Science Society of America.
- Römheld V. (1986) pH-Veränderungen in der Rhizosphäre verschiedener Kulturpflanzenarten in Abhängigkeit vom Nährstoffangebot. *Potash Rev.* **55**, 1–8.
- Römheld V. (1991) The role of phytosiderophores in acquisition of iron and other micronutrients in graminaceous species: An ecological approach. *Plant Soil* **130**, 127–134.
- Schott J. and Berner R. A. (1983) X-ray photoelectron studies of the mechanism of iron silicate dissolution during weathering. *Geochim. Cosmochim. Acta* **47**, 2233–2240.
- Schott J. and Petit J. C. (1987) New evidence for the mechanisms of dissolution of silicate minerals. In *Aquatic Surface Chemistry* (ed. W. Stumm), pp. 293–315. Wiley.
- Schott J., Berner R. A., and Sjöberg E. L. (1981) Mechanisms of pyroxene and amphibole weathering. I. Experimental studies of iron-free minerals. *Geochim. Cosmochim. Acta* **45**, 2123–2135.
- Schnitzer M. and Kodama H. (1976) The dissolution of micas by fulvic acid. *Geoderma* **15**, 381–391.
- Siever R. and Woodford N. (1979) Dissolution kinetics and weathering of mafic minerals. *Geochim. Cosmochim. Acta* **43**, 717–724.
- Spyridakis D. E., Chester S. G., and Wilde S. A. (1967) Kaolinitization, of biotite as a result of coniferous and deciduous seedling growth. *Soil Sci. Soc. Am. Proc.* **31**, 203–210.
- Takagi S., Nomoto K., and Takemoto T. (1984) Physiological aspects of mugineic acid, a possible phytosiderophore of graminaceous plants. *J. Plant Nutr.* **7**, 469–477.
- Tan K. H. (1986) Degradation of soil minerals by organic acids. In: *Interactions of soil minerals with natural organics and microbes*, (ed. P. M. Huang and M. Schnitzer), Special Publication No. 17, pp. 1–27. Soil Sci. Soc. Am.
- Taylor A. B. and Velbel M. A. (1991) Geochemical mass balances and weathering rates in forested watersheds of the Southern Blue Ridge II. Effects of botanical uptake terms. *Geoderma* **51**, 29–50.
- Thorseth I. H., Furnes H., and Heldal M. (1992) The importance of microbiological activity in the alteration of natural basaltic glass. *Geochim. Cosmochim. Acta* **56**, 845–850.
- Uren N. C. (1981) Chemical reduction of an insoluble higher oxide of manganese by plant roots. *J. Plant Nutr.* **4**, 65–71.