



A preliminary evaluation of volcanic rock powder for application in agriculture as soil a remineralizer



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HIGHLIGHTS

- Volcanic rock powder as fertilizer in agriculture
- Volcanic rock powder as a source of nutrients to plants
- This technology may favor the use of volcanic rock in agriculture.

GRAPHICAL ABSTRACT



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ABSTRACT

Mineralogical and geochemical characteristics of volcanic rock residue, from a crushing plant in the Nova Prata Mining District, State of Rio Grande do Sul (RS), Brazil, in this work named rock powder, were investigated in view of its potential application as soil amendment in agriculture. About 52,400 m³ of mining waste is generated annually in the city of Nova Prata without a proper disposal. The nutrients potentially available to plants were evaluated through leaching laboratory tests.

Nutrient leaching tests were performed in Milli-Q water; citric acid solution 1% and 2% (AC); and oxalic acid solution 1% and 5% (AO). The bulk and leachable contents of 57 elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Mining waste were made up by CaO, K₂O, SiO₂, Al₂O₃, Fe₂O₃, and P₂O₅. The analysis by X-ray diffraction (XRD) showed the major occurrence of quartz, anorthite, cristobalite, sanidine, and augite. The water leachable concentrations of all elements studied were lower than 1.0 mg/kg, indicating their low solubility. Leaching tests in acidic media yield larger leachable fractions for all elements being studied are in the leachate of the AO 1%.

These date usefulness of volcanic rock powder as potential natural fertilizer in agriculture in the mining district in Nova Prata, Rio Grande do Sul, Brazil to reduce the use of chemical fertilizers.

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1. Introduction

Brazil has an important role in the world mineral industry. However, as regards agro-minerals, minerals used in agriculture, the country has not been able to meet the internal needs, making it dependent on the import of some minerals. Brazil is the fourth largest consumer of fertilizers in the world but is responsible for only 2% of world production of fertilizers (IBRAM, 2012). The country imports 91% of potassium and 51% of phosphate required, both essential for the fertilizer industry (IBRAM, 2012).

As Brazil is one the leading agricultural producers in the world, and has been showing a growing demand in recent years, the use of fertilizers has intensified with the purpose of increasing productivity. A consequence of this is the trade deficit in the sector of industrial minerals, due to the large volume of imports of phosphate, potassic, and sulphuric fertilizers (Oliveira and Ferreira, 2007). The main phosphate national reserve is located in the municipality of Tapira in the State of Minas Gerais, Brazil with approximately 1 Gt of ore (Souza and Cardoso, 2008). In Brazil, the potassium fertilizer production restricted to mine/mill complex of Taquari-Vassouras, in Sergipe, leased to the Companhia Vale, which produced 383 kt of K_2O in 2008 (MME, 2009). The potassium produced in Brazil is almost entirely used as fertilizer, around 95%, with 90% in the form of potassium chloride (Oliveira and Ferreira, 2007).

One of the main factors justifying the use of volcanic rock powder in agriculture refers to the possibility of reducing the use of chemical fertilizers. Studies report that the economy in the cost of production can reach up to 50% with the use of this technique (Theodoro, 2000). Most Brazilian regions have reserves of volcanic rock, rich in elements such as phosphorus, calcium, and magnesium. The effects generated by fertilization using rock powder may extend by up to four or five consecutive years because of the slow release of nutrients (Theodoro, 2000). With that, the study and development of new fertilizers have grown in recent years and the use of rock powder in agriculture (stonemeal) has presented advantages, mainly to costs, transformation of waste in products, and market expansion for new products of quarries (Loureiro et al., 2009). The application of rock powder for remineralizing of soil is related to its mineral characteristics and its interaction with the environment in which it will be applied, in order to improve the conditions of soil fertility (Theodoro, 2000).

Around 52,400 m³/a of waste of mining are generated in the city of Nova Prata. However, only a fraction of this waste is intended for the production of gravel and the rest remains in the quarry without a proper disposition (Toscan et al., 2007). In this region, only one gravel mining company sells the powder in particle size fraction <0.1-mm.

The volcanic rock is composed mainly of SiO_2 , Al_2O_3 , Fe_2O_3 , MnO, MgO , Na_2O , K_2O , and CaO (Ramos et al., 2014; NuneS et al., 2014).

Given that Brazil is one of the largest suppliers of food in the world, the study of volcanic rock powder as a potential fertilizer with respect to the content and release of nutrients and to the economics and market viability is still required to provide the development of sustainability policies for the mining activity and food production. Thus, the main objectives of this study are: 1) characterize a residue of volcanic rock from the city of Nova Prata, RS; 2) evaluate the leaching tests of rock powder, through laboratory simulations, its potential to provide macro- and micro-nutrients that contribute to soil fertility; 3) support future studies of rock powder used in the replacement of chemical fertilizers.

Brazil is also one of the few countries in the world with the potential to expand its agricultural production, whether by increased productivity, or the expansion of cultivable area (Scolari, 2006). With this, the present study may contribute, not only to meet the growing intern of its population, but also for a greater food supply in the world context. Additionally, the Brazilian Government is stimulating the search for alternative routes for the production of fertilizers.

2. Material, methods and analytical procedures

2.1. Study area

In the mining district located in Nova Prata, Rio Grande do Sul (Fig. 1), there are basic, intermediate, and acidic igneous rocks. At the top of the plateau, acidic rocks are interspersed with basic and intermediate rocks. At the base of the plateau, there are only basic and intermediate rocks (Prates et al., 1998). A large (20 kg) mining waste sample was obtained from the Sindicato da Indústria de Extração de Pedreiras de Nova Prata (latitude: 28°46'27,37" S and longitude: 51°38'16,61" W).

The residue of volcanic rock belongs to the Caxias facies, and corresponds to the volcanic lava flows, which are acid in the upper position of the volcanic eruption, in general. This lithology was described by Nardy et al. (2008) as belonging to the Palmas Group of Serra Geral Formation, which was generated by intense volcanism during the transition between the Jurassic and Cretaceous periods, where the division of Gondwana and the separation of the South American continent from Africa formed the South Atlantic Ocean. These rocks have only a slight variation in composition and a continuity of mineralogical characteristics (Juchem et al., 2007).

For this study five random samples (each 4 kg) of volcanic rock powder were collected from each ore deposit using a polypropylene shovel and were subsequently transferred to clean polypropylene bags. These samples were then mixed, resulting in a primary sample of 20 kg that was then submitted to homogenization and subsequent quartering procedures according to the standard methods for mineral particles (Oliveira and Aquino, 2007), resulting in two parts of 10 kg each. One portion (10 kg) was reprocessed by quartering, resulting in ten samples of approximately 1 kg that were stored in plastic bags and randomly selected to use in this work.

2.2. Mineralogy

The mineral composition of the mining waste major crystalline mineralogy of volcanic rock powder was evaluated by X-ray powder diffraction (XRD) at the Unidade de Raios X – RIAIDT of University of Santiago de Compostela (Spain). The sample was homogenized and compacted on the sample holder to obtain a uniform surface, required for this technique (Oliveira et al., 2012a, 2012b). The sample was spun during the data collection in order to get the best peak profile and to minimize the preferred orientation effect. The sample was analyzed with a Philips powder diffractometer fitted with a Philips “PW1710” control unit, Vertical Philips “PW1820/00” goniometer and FR590 EnrafNonius generator. The instrument was equipped with a graphite diffracted-beam monochromator and Cu-radiation source $\lambda(K\alpha_1) = 1.5406 \text{ \AA}$, operating at 40 kV and 30 mA. The XRD pattern has been collected by measuring the scintillation response to Cu $K\alpha$ radiation versus the 2θ value over a 2θ range of 2–65, with a step size of 0.02° and counting time of 3 s per step. The semi-quantification of the individual crystalline phase (minerals) of sample was determined using the program Match! (©2003–2011 CRYSTAL IMPACT, Bonn, Germany).

Field emission scanning electron microscope (FE-SEM) and high-resolution transmission electron microscope (HR-TEM) allow the direct (real space) visualization of minerals. The morphology, structure, and chemical composition of minerals were investigated using a FE-SEM Zeiss Model ULTRA (with charge compensation for all applications on conductive as well as non-conductive samples). The FE-SEM was equipped with an energy-dispersive X-ray spectrometer (EDS). The working distance of the FE-SEM/EDS was 5–10-mm, beam voltage 5–20.0 kV, aperture 6, and micron spot size 5 or 5.5. The mineral identifications were made on the basis of morphology and grain composition using both secondary electron and back-scattered electron modes. EDS spectra were recorded in FE-SEM and image mode and then quantified

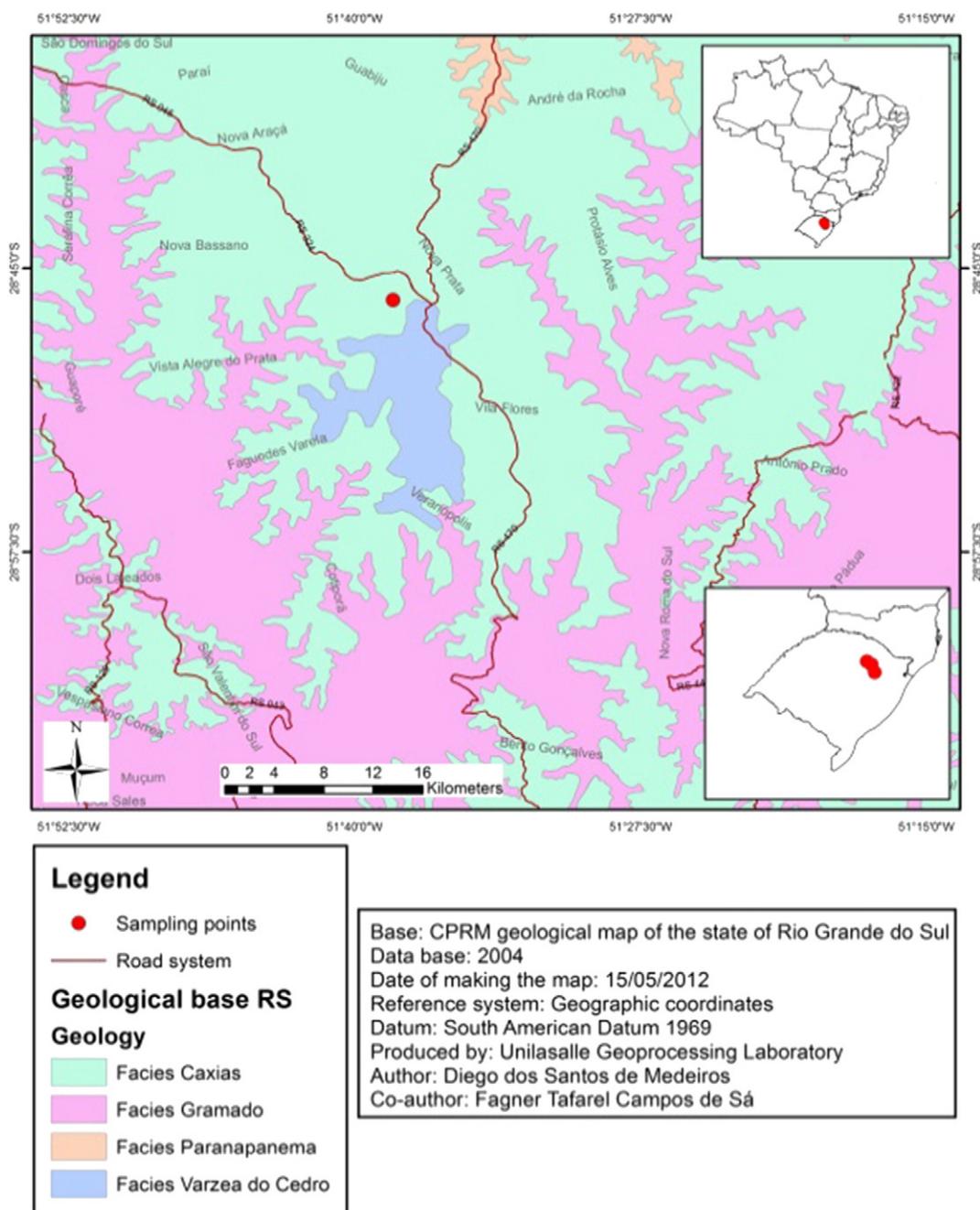


Fig. 1. Location and sampling point of rock powder in the city of Nova Prata.

using ES Vision software that uses the thin-foil method to convert X-ray counts of each element into atomic or weight percentages.

Petrographic analyses were performed in transmitted light microscope, Nikon, model Eclipse – 50iPOL with five objectives with correction to infinity, with total magnification of 25; 40; 100; 200; and 400 times.

2.3. Chemical characterization and mobility of the elements

The Si concentration was determined by fusion with LiBO_2 followed by analysis of X-ray fluorescence spectrometer on a Philips model PW1480. The rock dust sample was acid digested following a two-step

Table 1

Composition of the solution extractors, processes and methodologies used in the leaching of nutrients.

Extractor	Extracting solution	Conc. ($\text{mol} \cdot \text{L}^{-1}$)	Amount of sample (g)	Amount of solution (mL)	Agitation (rpm)	Period of agitation (min)	Methodology
1	Milli-Q water		1	10	60	1440	EN 12457-2 (2002)
2	AC ($\text{C}_6\text{H}_8\text{O}_7$)	0.02	5	500	40	30	MAPA-Brasil (2007)
3	AC ($\text{C}_6\text{H}_8\text{O}_7$)	0.02	5	100	40	1440	Adapted from MAPA-Brasil (2007)
4	AC ($\text{C}_6\text{H}_8\text{O}_7$)	0.01	5	50	300	1440	Silva (2009)
5	AO ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)	0.05	5	50	300	1440	Adapted from Silva (2009)
6	AO ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)	0.01	5	100	300	1440	Silva (2009)

Table 2
Semi-quantitative mineralogical characterization by X-ray diffraction.

Mineral phase	(%)
Quartz	15
Anorthite	54
Sanidine	19
Cristobalite	1
Augite	10

digestion method (Querol et al., 1997); this consisted of a HNO₃ hot extract followed by HF:HNO₃:HClO₄ acid digestion of the residue. The resulting solution was then analyzed at the Institute of Environmental Assessment and Water Research (Spain) by inductively coupled plasma atomic emission spectrometry (ICP-AES) for major and selected trace elements and by inductively coupled plasma mass spectrometry (ICP-MS) for additional trace elements.

Leaching tests of the elements present in the sample were performed in Milli-Q water and five acidic solutions in particle size range

<0.1-mm. Concentrations of major elements and trace elements in the leachate were determined by ICP-MS and ICP-AES.

In order to study the leaching of elements, the compliance leaching test EN 12457-2 (2002) was applied at the Institute of Environmental Assessment and Water Research (Spain). This is a single batch leaching test performed at a liquid to solid ratio (L/S) of 10 L/kg with 24 h of agitation time and deionized water as leachant. In all cases, analyses were performed in duplicate. Major, minor, and trace element concentrations in solid sample and leachates were determined by means of ICP-MS and ICP-AES, respectively.

2.4. Leaching tests

The leaching tests are used to determine or evaluate the chemical stability of the waste when in contact with aqueous solutions, thus verifying the degree of mobilization of its nutrients. Thus, this assay seeks to reproduce in the laboratory the phenomena of drag, dilution, and desorption occurring by passing water through a waste when disposed in the environment. Such a test may represent several years of natural

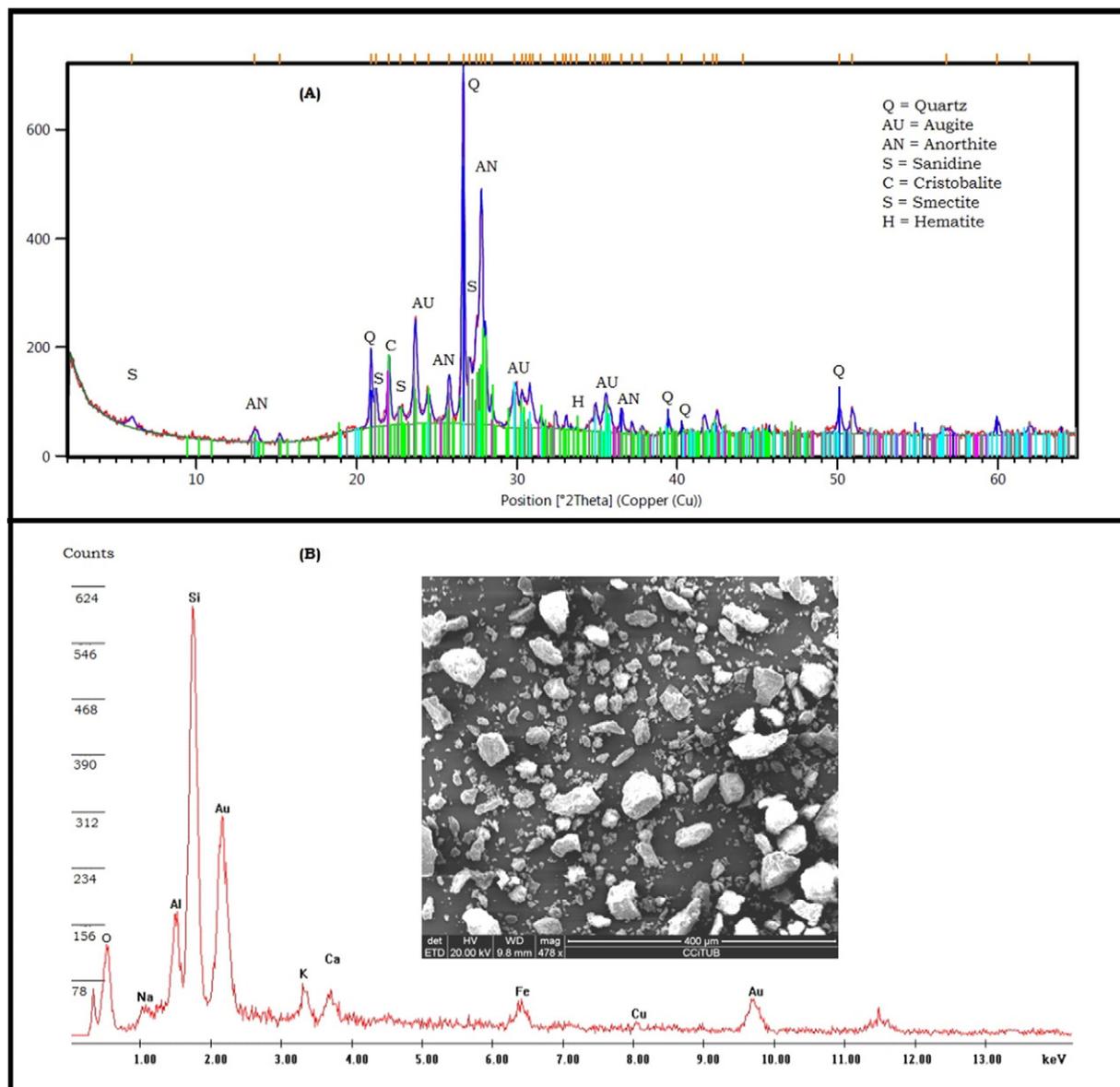


Fig. 2. (A) Diffractogram of X-rays from the sample of rock powder detailed in Table 2, (B) elements detected by FE-SEM/EDS in the studied rock powder.

phenomena leaching (Arroio and Higa, 1984). The leaching tests with acidic solutions are meant to reproduce the soil environment during the assimilation of nutrients by plant roots.

In evaluating the leachability of the material, a comparison is made between the concentration of the nutrient in the leachate and the crude residue. These values indicate the portion of waste released to the environment. The leaching test is influenced by the temperature, the type of leaching solution of the residue/leaching ratio of the number of extractions, the specific surface area of the waste, and the degree of agitation used in the assay (Chamie, 1994). Assays leaching of nutrients present in the sample were performed in Milli-Q water and five acidic solutions in particle size range <0.1-mm. The pH of each leachate was also measured (with a pH meter DM-2P Digimed) to trace the relationship between this parameter and leachables elements. All analyses were performed in duplicate. The development of this research was based on six leaching methods (Table 1).

According to Castilhos and Meurer (2001), studies were been conducted for quantify the nutrient release rates of mineral sources for

the nutrition of plants. In these studies, ion-exchange resins were used, saline solutions at sodium tetraphenylborate dilute, and low molecular weight organic acids such as citric and oxalic acids. These acids can facilitate rock weathering of minerals through formation on metalorganic complexes and are naturally produced by plants in the rhizosphere (root zone). Given this, these acids were used in this study as solution extractors.

Although a mineral may have a high content of nutrients and, consequently, it can be considered as alternative fertilizer in potential, these nutrients may not be fully available to the extractors. Therefore, the extractors will define the element "available" that is a partial indication (or proportion) of the amount that the plant could absorb. In this way, one can deem it necessary to employ some sort of structural modification of this mineral in order to make the nutrient more accessible to the extraction process.

According to Bigham et al. (2001), some organisms are able to promote weathering in rocks through the secretion of low molecular weight organic acids. Oxalic acid, for example, is an agent for the

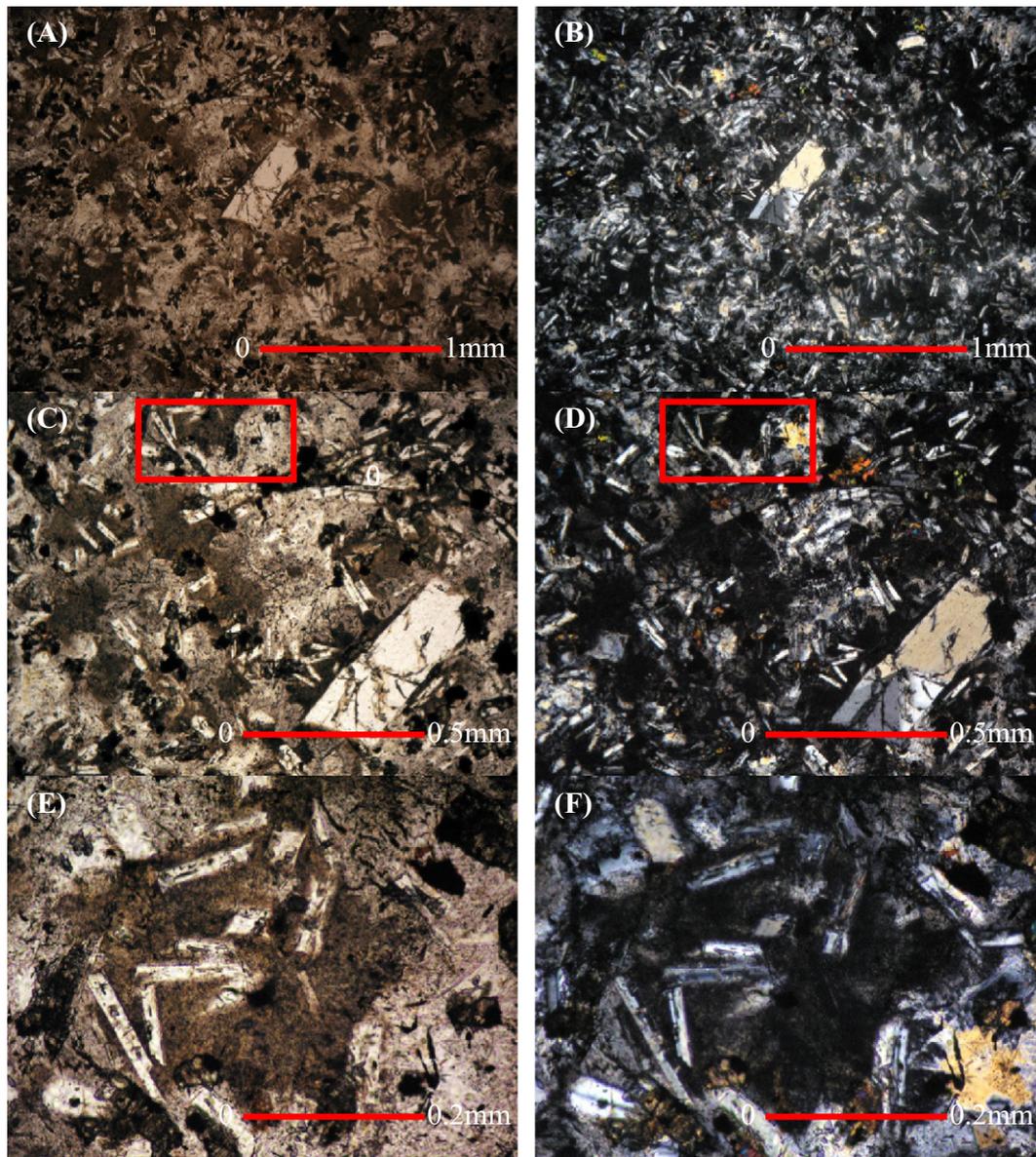


Fig. 3. A and B: Phenocrysts of plagioclase in microcrystalline array composed of crystallites of plagioclase and pyroxene in spherulitic intergrowth (Natural Light (LN) and polarized light (PL)/increase of 25 \times /graphic scale 1.0 mm); C and D: showing in detail the previous photomicrography the aggregates with spherulitic texture in the array (LN and LP/increase of 40 \times /graphic scale 0.5 mm); E and F: detail of the area bounded in red (LN and LP/increase of 100 \times /graphic scale 0.2 mm), characterizing the occurrence of crystallites of plagioclase in association with mafic minerals and incipient micrographic texture.

efficient extraction of octahedral cations of rocks by combining protonic attack and complexation reactions (Girgin and Obut, 2002).

3. Results and discussions

3.1. Mineralogy

The results of the semiquantitative analysis of the minerals of the sample by X-ray diffraction are given in Table 2 and Fig. 2A.

According to these, the crystalline mineral assemblage is made of 54% anorthite, a Ca-plagioclase, feldspar with low resistance to weathering (Alleoni and Melo, 2009). Therefore, it can release nutrients more easily to the environment. Sanidine contains high proportion of K. This mineral presents average resistance to weathering (Alleoni and Melo, 2009). Augite, which composes 10% of the sample, a Fe–Mg–pyroxene, can release Si, Mg, Fe, and Ca and form new minerals (Song and Huang, 1988). Furthermore, the mining waste contains

an undetermined proportion of glassy, non X-ray detectable mass that may supply also a number of elements to the soil.

The analysis by FE-SEM/EDS proved to be a satisfactory technique that can be used for chemical characterization of volcanic rock dust sample, containing Al, Si, K, Ca, Fe, Cu, and Na most of the particles that were evaluated and later analyzed with EDS (Fig. 2B). The sample shows the irregular and angular morphology of particles (Fig. 2B).

Petrographic results demonstrated that the rock consists predominantly of microphenocryst of plagioclase (anorthite), which occur as spherulitic aggregates, and smaller amounts of alkali feldspar (sanidine) and pyroxene (augite), which represent approximately 35% of the mineral phases present in the sample. Many of the microphenocryst of plagioclase anorthite and alkali feldspar have stains of oxidation along of microfractures. The microphenocrysts of pyroxene (likely clinopyroxene (augite)) were very oxidized and replaced with opaque minerals, also occurring in a small fragments (Fig. 3A and B). Some pyroxene crystals are more preserved, but the small size of the grains does not permit the determination of the optical properties to determine the existence of two pyroxenes. Opaque minerals likely comprise titanomagnetite, which occur as microphenocryst and aggregated with skeletal shapes, often replacing the pyroxene. Apatites occur with relative abundance, constituting an accessory mineral phase.

3.2. Chemical characterization and mobility of the elements

Besides the SiO₂ that accounts for 64.8% of the whole rock, the main elements that make up the rock powder sample are shown in Table 3. According to these results, the Si comes from quartz, anorthite, cristobalite, sanidine, and augite, detected in the sample by mineralogical analyses, but also for the amorphous glassy matrix.

Aluminum is the second most abundant element in the sample (Table 3). Studies by Kautzmann (2011) and Nunes (2012) showed that basalt rock powder samples from the same region did not provide Al to the environment. This fact is important since Al³⁺ is toxic to plants and inhibits the growth and development of roots because it changes the adsorption of water and nutrients (Malavolta, 2006). At pH values greater than 5.8, practically the entire Al appears as insoluble Al(OH)₃, therefore, non-toxic to plants (Faquin, 2005).

The presence of opaque minerals, probably titanomagnetite may be related to high content of iron and titanium. Iron is insoluble in aqueous medium, at pH > 4 which is fundamental, because the excess iron can cause growth problems in plants and the necrosis in leaves (Malavolta, 2006).

Both sodium and potassium appeared in the sample with levels close to 0.6–1.5% of its composition probably due to the presence of sanidine.

Other inorganic chemical elements analyzed represent less than 1.5% of the total composition of the sample. Of note was the abundance of elements such as Ca, P, and S, which with the weathering via hydrolysis is easily available to the soil (Alleoni and Melo, 2009), thus providing macro- and micronutrients essential for plant growth. The results of chemical composition by ICP-MS, ICP-AES, and EDS (Fig. 2B) confirm that the sample under study is coming from minerals typical of volcanic rocks but specially for the amorphous glassy matrix.

Therefore, the methodology used has proved to be effective for analyses of rock powder with applicability in agriculture.

ICP-MS analysis verifies that the concentrations of potentially toxic elements such as As, Pb, and Li, among others, do not represent environmental risk (Table 3).

3.3. Leaching tests

The concentrations of the fractions of the elements leached during standardized test of the European Union EN 12457-2 (EN 2002) and other methodologies along with pH are expressed in Table 4. The latter was a factor of great importance in geochemical mobility of the

Table 3
Chemical composition of major elements and trace elements of rock powder.

Element	mg/kg
Al	43,769
Ca	16,536
Fe	28,398
K	16,054
Mg	5047
Na	14,029
P	691
S	449
Mn	863
Li	17
Be	3
B	31
Sc	19
V	84
Cr	7
Co	14
Ni	3
Cu	66
Zn	116
Ga	21
Ge	1
As	3
Tb	1
Rb	116
Sr	170
Y	45
Mo	1
Pb	19
Sn	5
Nb	44
Cs	7
Ba	647
La	42
Ce	81
Pr	12
Nd	35
Sm	8
Eu	2
Gd	8
Ho	2
Er	4
Dy	7
Yb	4
Th	13
Hf	6
Ta	3
W	1
Tl	1
Zr	243
U	4

Table 4
pH, concentration of elements in leachate rock powder and nutrient release potential of rock powder through the solution extractors (percent).

pH	7.55		2.89		2.89		3.04		2.99		1.91	
	Extractor 1		Extractor 2		Extractor 3		Extractor 4		Extractor 5		Extractor 6	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Al	<1	0	651	2	602	1	700	2	717	2	4078	9
Ca	1	0	751	5	1132	13	1631	10	129	1	2690	16
Fe	<1	0	1119	4	947	3	1118	4	1796	6	9725	34
K	<1	0	320	2	201	1	177	1	135	1	506	3
Mg	<1	0	294	6	272	5	303	6	302	6	1541	30
Na	<1	0	403	3	202	1	232	2	130	1	632	4
P	0	0	592	85	527	76	243	35	555	80	644	93
S	<1	0	28	6	13	3	8	2	8	2	4	1
Si	<1	0	449	0	415	0	475	0	414	0	2341	0
Mn	0	0	178	21	222	26	236	27	160	18	603	70
Li	0	0	<1	1	<1	1	<1	2	<1	2.0	2	14
Be	0	0	<1	7	<1	6	<1	8	<1	6	<1	23
B	0	0	1	4	1	3	1	4	1	2	2	8
Sc	0	0	<1	3	<1	4	1	5	<1	2	1	7
V	0	0	2	3	1	2	2	2	3	3	13	16
Cr	0	0	3	50	2	25	2	30	1	17	4	67
Co	0	0	2	11	2	13	2	15	2	12	7	49
Ni	0	0	<1	24	<1	22	<1	26	<1	20	2	76
Cu	0	0	8	12	7	11	8	12	7	11	34	52
Zn	0	0	14	12	9	8	9	8	8	7	27	23
Ga	0	0	<1	2	<1	2	<1	2	<1	2	2	8
Ge	0	0	0	0	0	0	0	3	<0.1	2	<1	5
As	0	0	1	42	1	29	<1	23	<1	22	2	68
Rb	0	0	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Sr	0	0	7	4	6	3	6	3	2	1	9	5
Y	0	0	6	13	6	14	6	13	<1	<1	<1	<1
Zr	0	0	8	3	5	3	9	4	7	3	25	10
Nb	0	0	1	2	<1	2	<1	2	2	5	13	29
Mo	0	0	<1	60	<1	15	<1	20	<1	9	<1	45
Sn	0	0	<1	5	<1	4	<1	3	<1	8	1	20
Ba	0	0	29	5	28	4	28	4	22	3	76	12
La	0	0	4	10	5	12	4	10	<1	<1	<1	<1
Ce	0	0	16	19	17	21	16	20	<1	<1	<1	<1
Nd	0	0	8	23	8	24	7	21	<1	<1	<1	<1
Hf	0	0	<1	9	<1	8	<1	9	<1	8	2	28
Ta	0	0	<1	11	<1	6	<1	8	1	43	3	83
W	0	0	<1	36	<1	33	<1	37	<1	41	<1	54
Pb	0	0	4	24	3	15	2	8	<1	1	<1	3
Th	0	0	<1	6	2	12	2	16	<1	1	<1	1
U	0	0	<1	6	<1	5	<1	6	<1	2	<1	16

elements present in the sample of rock powder. Because, while the sample at pH = 7.55 has low nutrient release, in acid solution (that are present in the rhizosphere), the mobility of nutrients present in the sample increases considerably (Table 4).

Typically the fertilizers are applied directly into the soil near the plant roots (the rhizosphere). Specifically in this region, there is natural production of citric and oxalic acids (Ernani et al., 2007). Therefore, the present study shows that this practice also applies using powder of rock, causing it to reduce the cost of agriculture and agrochemical consumption.

Chemical elements considered essential for the plants and, therefore, primary macronutrients are N, P, and K; secondary macronutrients—Ca, Mg, and S; and micronutrients—Al, B, Co, Cu, Cl, Fe, Ni, Mn, Mo, and Zn (Arnon and Stout, 1939). Concentrations of nutrients present in leachate of rock powder are presented in Table 4. Therefore, it can easily demonstrate that the lower the pH value (Fig. 4), the greater the mobility of the elements present in the rock powder and, with it, greater bioavailability. Specially, these elements associated to the amorphous phase can be more easily solubilized given that this amorphous component can be more weathered by acidic solutions than the crystalline minerals.

It is important to note that elements of high toxicity such As, Cd, and U, among others, have low bioavailability by being present in the sample at low concentrations. This reinforces the implementation of such

material in food production, after all, even in extremely acid pH there was no high fraction leachable.

Aluminum, Fe, Ca, Si, Mg, Na, Mn, and K are the most mobile elements in the leaching tests (Fig. 4), because they were detected in higher concentrations in the chemical composition of the sample (Table 3).

The acidic extractor solutions of the numbers 2 until 5 obtained similar concentrations, both for major elements as trace elements (Table 4). Table 4 shows that the concentrations of major elements and trace elements were the most abundant in the leachate of extractor 6 (extremely acid extractor). These elements can be easily explained given that the sample contains considerable proportions of aluminosilicate glass matrix (of low resistance to weathering) which when, proved during the leaching test, were attacked by oxalic acid releasing their nutrients. Additionally, the high acidity conditions of extraction solution favor the amendment of the rock species that may contain macro- and micronutrients, thus contributing to the increase of the concentration resulting in the dissolution of the leaching test. Additionally, it became clear that the mobility of all elements was dependent on pH.

Despite the sample contains high concentrations of Al in its composition (Table 3), the leachable fraction of this element was 4077 mg/kg (6 extractor), which corresponds to a potential release of 9.3%. This element undergoes weathering in acidic soil, releasing the aluminum to the environment, which can precipitate in the form of aluminum

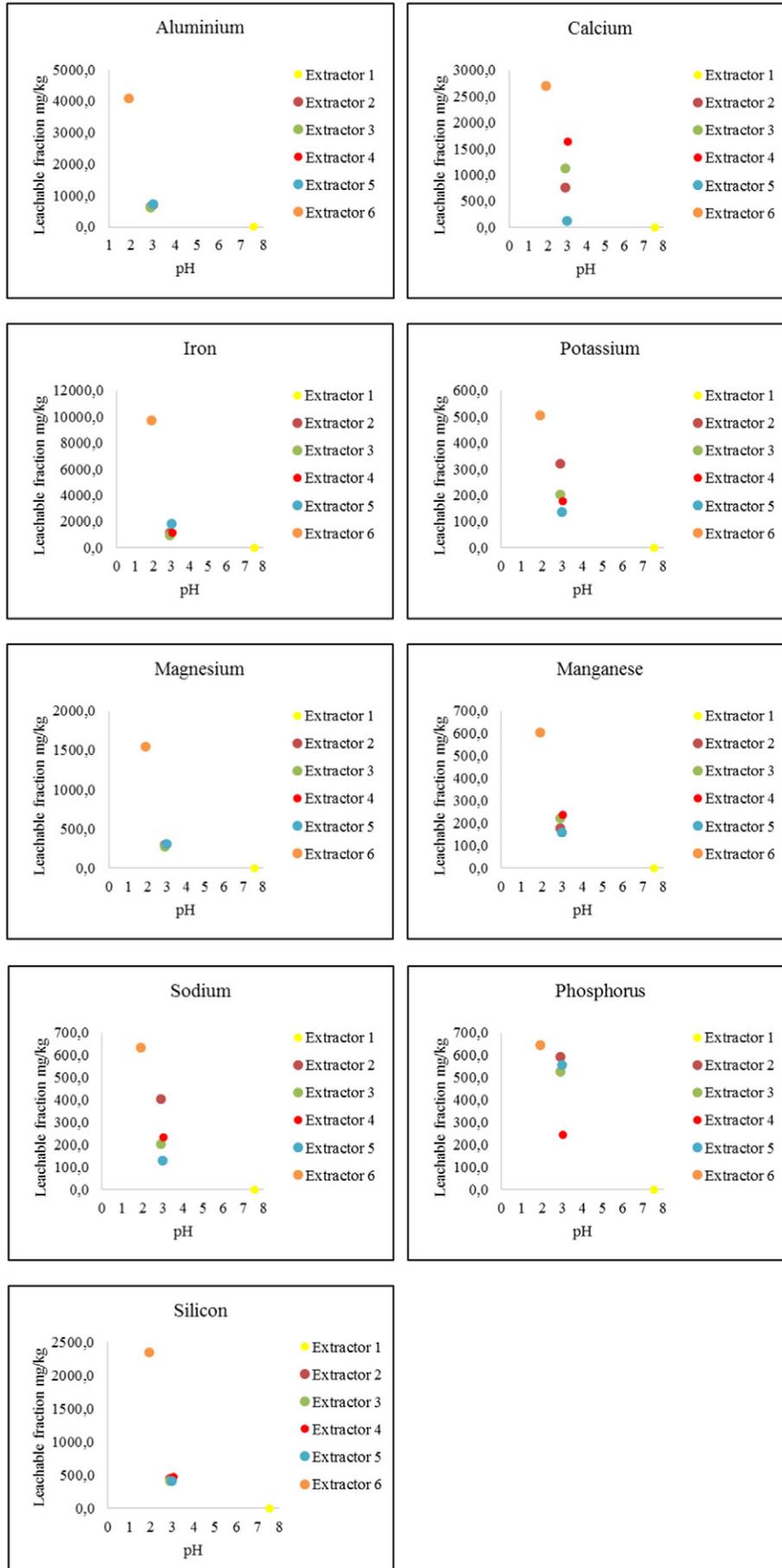


Fig. 4. pH values and extractable proportions for different elements.

hydroxide (Alleoni and Melo, 2009) that is practically insoluble in water. This can be confirmed with the data presented in Table 4, which presents a concentration of 0.2 mg/kg of water-soluble aluminum. However, the application of rock powder on the soil would not be impaired by the release of toxic elements for plants.

Calcium is slightly soluble in water, but its solubility in acidic solutions increased, presenting variable concentrations (751.5 mg/kg, 1132.4 mg/kg, 1630.7 mg/kg, and 129.3 mg/kg) in the leachate of the extractor solutions (2–5), respectively. However the extractor 6 presents a higher concentration (2690.6 mg/kg) than the other extractors. The pH influences mobility of this element, because calcium concentrations increased in the leachate with higher acidity.

The data in Table 4 shows that the sample provided a 9725 concentration mg/kg (486.27 mg/L) of Fe in leachate from 6 extractor, representing a potential release of 34.2%. Iron is highly immobile at pH greater than 4.5 and its release increases with decreasing pH (Silva et al., 2011). However, according to Sposito (1989), the ideal level of this nutrient in the soil must be in the range of 25,000 to 40,000 mg·L⁻¹. This demonstrates that although the sample has a high concentration of this micronutrient in its composition, the availability for the soil will be low.

Potassium levels (135.5–506.2 mg/kg), Mg (272.5–1541.3 mg/kg), Na (129.9–631.8 mg/kg), P (243.3–644.4 mg/kg) and Mn (160.2–603.2 mg/kg) leachate (Fig. 4) leached an extractable proportion similar to other elements, even if they are less abundant, but of similar geochemical mobility, as expressed the quantification in Tables 3 and 4.

Phosphorous presented a high mobility in all leaching tests, mainly in the 6 extractor leachate, where practically the entire amount of P was released (93.3%) (Fig. 4). In leachate of extractors (2–5), the concentration of Si was similar (448.8 mg/kg, 415.6 mg/kg, 475.2 mg/kg, and 414.5 mg/kg). In the leachate of the 6 extractor, their mobility was approximately five times greater (2341 mg/kg) than in other leachates, which indicates that, if necessary, the rock powder can be tested together with other wastes in order to increase the mobility of this macronutrient in case cultivation requires the element to be bioavailable.

4. Conclusions

According to the results obtained in this study, it is concluded that the volcanic rock powder can be used as a source of macro- and micro-nutrients to the soil, because it presents in its composition a relevant proportion of easily weathered glassy amorphous matrix as well as many silicate minerals such as plagioclase, pyroxene, and iron–magnesium minerals easily amendable. Leaching tests in an acidic medium demonstrated an influence on the release speed of these minerals, making the process faster and, consequently, the release of the elements/nutrients to the soil. The best extraction efficiencies were observed when the solution of oxalic acid 1% (6 extractor) was used as an extractor. However, the tests of nutrient release in acid solutions showed that only a fraction of the minerals are soluble. The characteristics of devitrification observed in the sample studied make interesting rock for jobs in stonemeal, by the ease of destabilization of glass in exogenous conditions. The weathering of this glassy matrix with the weathering of feldspars and pyroxenes, in addition to the clay which fill fractures and venules and that also occur in the array may be indicating a process of hydrothermal alteration, raising the potential for destabilization (replacement and/or transformation) of these mineral phases, with consequent increase of the cations release potential that can contribute to soil remineralization in the region. With that, great there are advantages of agronomic use of volcanic rocks as fertilizer, as, for example:

- Insolubility of nutrients in water, resulting in smaller losses by leaching and fixation;
- Solubility of the nutrients in solution of weak acid, as existing in soil solutions, resulting in slow and efficient release of same for the cultures.

However, it can be concluded that the dust of volcanic rock has a promising potential as alternative fertilizer application of slow release in cultures that require nutrients in the long run, as for example, perennial crops.

Additionally, future studies will be carried out by mixing with volcanic rock powder and other materials such as sludge from the dairy and sweet industries, aiming at modifications in the structure of the rock powder and largest release of nutrients in smaller time interval.

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