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Geochemical of Volcanic Rock Powder Sample from Serra Geral Formation: An Important Remineralizer

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Abstract

Geochemical and mineralogical 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 to define its potential application as soil amendment in agriculture. About 52,400 m³ of mining waste are 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 was made up by CaO, K₂O, SiO₂, Al₂O₃, Fe₂O₃, and P₂O₅. The analysis by X-ray diffraction (XRD) showed the major occurrence of quartz, Ca-plagioclase, 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 data demonstrates that volcanic rock powder is a potential natural fertilizer for agriculture in the Mining District of the Nova Prata, Rio Grande do Sul, Brazil.

Keywords: *mining waste, volcanic rock, particle characterization, leaching of nutrient, nutrient availability*

1. Introduction

Brazil has an important role in the world mineral industry. Regarding to fertilizers, Brazil is the fourth largest consumer of fertilizers in the world but is responsible for only 2% of world fertilizers production (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 of the leading in agricultural producers in the world, with a growing demand in recent years, the use of fertilizers has been 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 Tapira region 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 K₂O 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).

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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 products have grown in recent years and the use of rock powder in agriculture (stonemeal) has presented advantages, mainly because 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 minerals characteristics and its interaction with the environment in which it will be applied, in order to improve the conditions of soil fertility (Theodoro, 2000).

Given that Brazil is one of the largest suppliers of agriculture commodities in the world, the study of volcanic rock powder as a potential remineralizer of soil, certainly contributes with the management of new routes to the supply of potential fertilizer elements to Brazil agriculture. Thus, the main aim of this study are: 1) characterize a residue of a volcanic rock sampled from a mining plant located in the Nova Prata region, Brazil; 2) evaluate the potential of rock powder provides macro and micro-nutrients to contribute to soil fertility through leaching tests performed in laboratory simulations; 3) support future studies of rock powder as a natural fertilizer to supply the chemical fertilizers production and reducing agriculture costs, considering that Brazil is one of the few countries in the world with potential to expand its agricultural production, whether by increased productivity, or the expansion of cultivable areas (Scolari, 2006).

The present study may contribute, not only to meet the growing intern of its population, but also for a greater agriculturable products supply in the world global economic context. Additionally, the Brazilian Government is giving stimulus the projects for alternative routes for production of fertilizers. The study looking for use the waste quarry generated. Toscan et al. (2007) estimated around 524.00 m³/a of waste is generated in the city of Nova Prata, where only a part fraction of this is use for the production of gravel and the rest remains in the quarry without a proper disposition.

2. Methods

Samples used in this study came from the Nova Prata mining district, Rio Grande do Sul state, region with a geological setting dominated by the Phanerozoic volcanic rock sequence of the Serra Geral Formation comprising mainly of basic, intermediate, and acid volcanic rocks. At the basal to the intermediate level, the volcanic rock sequence is dominated by basic to intermediate rock compositions (Prates et al., 1998), and at the top of the sequence dominate intermediate to acid volcanic rocks. The studied sample of volcanic rock belongs to the Caxias facies, part of the upper level of the volcanic sequence, and corresponds to a volcanic lava flows with intermediate to acid composition. Nardy et al. (2008) have classified this same rock sequence as belonging to the Palmas Group of the Serra Geral Formation.

In this study five random samples (with 4kg) of volcanic rock powder were collected from a crushing plant storage area of the Nova Prata municipality (28°46'27,37" S and 51°38'16,61' W) with a polypropylene shovel, and were subsequently transferred to clean polypropylene bags. The samples were then blended, resulting in a primary sample of 20kg that was then submitted homogenization and quartering procedures, according to standard methods for mineral particles (Oliveira and Aquino, 2007), resulting in two parts of 10kg each. One portion (10kg) was reprocessed by quartering, resulting in ten samples of approximately 1kg each that were stored in plastic bags and randomly selected to use in this work.

To achieve the results are used the followed analytical and experimental procedure.

2.2 Petrography and Mineralogy

Petrographic analyzes 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.

The mineral composition of the sample 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 $\lambda(\text{K}\alpha_1) = 1.5406\text{\AA}$, operating at 40 kV and 30mA. The XRD pattern has been collected by measuring the scintillation response to Cu K α radiation versus the 2θ value over a 2θ range of 2-65, with a step size of 0.02° and counting time of 3s 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 images mode and then quantified using ES Vision software that uses the thin-foil method to convert X-ray counts of each element into atomic or weight percentages.

2.3 Chemical characterization and mobility of the elements

The Si concentration was determined by fusion with LiBO₂ followed by analysis of X-ray fluorescence spectrometer on a Philips model PW1480. The rock dust sample was acid digested following a two-step 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 leachate. 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 phenomena leaching (Arroio, 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 analyzes were performed in duplicate. The development of this research was based on six leaching methods (Table 1).

Table 1. Composition of the solutions extractors, processes and methodologies used in the leaching of nutrients.

Extractor	Extracting solution	Conc. (mol.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 (C ₆ H ₈ O ₇)	0.02	5	500	40	30	MAPA – Brasil (2007)
3	AC (C ₆ H ₈ O ₇)	0.02	5	100	40	1440	Adapted of MAPA – Brasil (2007)
4	AC (C ₆ H ₈ O ₇)	0.01	5	50	300	1440	Silva (2009)
5	AO (C ₂ H ₂ O ₄ .2 H ₂ O)	0.05	5	50	300	1440	Adapted of Silva (2009)
6	AO (C ₂ H ₂ O ₄ .2 H ₂ O)	0.01	5	100	300	1440	Silva (2009)

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

3. Results and discussions

3.1 Petrography and mineralogy

The mineralogical and petrographical studies applied on two representative rock samples from the mining site showed an essential mineralogy defining a hypocrySTALLINE texture made by spherulitic aggregates of clinopyroxene \pm Ca-plagioclase \pm K-feldspar (sanidine) phenocrysts (30-35 %), accessory mineralogy composed by opaque minerals (Ti-magnetite \pm ilmenite) \pm quartz \pm apatite (5%) and traces of on a hypocrySTALLINE vitrophyric matrix (50-60%) presenting desvetrified sites with hollocrySTALLINE sites with microlites of feldspar \pm pyroxene \pm opaques. The dominate texture is hollocrySTALLINE represented by glomoporphyritic and spherulitic facies of microphenocryst plagioclase aggregates. Many of the plagioclase microphenocrysts of Ca-plagioclase and sanidine present oxidation paths along of microfractures. There is probably two pyroxene generations, one occurring as microphenocrysts of clinopyroxene (augite) generally replaced by opaque minerals, and small pyroxene grains disseminated on the matrix. However, the small size of pyroxene grains does not permit determination of the optical properties. Opaque minerals likely comprise titanomagnetite and ilmenite, which occur as microphenocryst and aggregates with skeletal shapes, often replacing the pyroxene. Apatite occur with relative abundance constituting the main accessory mineral phase.

The results of mineralogical analysis performed by X-ray diffraction are presented in Table 2.

Table 2. Semiquantitative mineralogical characterization by X-ray Diffraction.

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

According to the results, the crystalline mineral assemblage is made of Ca-plagioclase 54%, augite10%, and an undetermined proportion of glassy that can be easily weathering supplying a number of macro and micro nutrients to the soil.

3.2 Chemical characterization and mobility of the elements

The volcanic acid rock from the studied area is composed mainly by SiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, Na₂O, K₂O, and CaO (Ramos et al., 2014; Nunes et al., 2014). The chemical analyses performed by X-ray Fluorescence demonstrates that the main elements in the rock powder sample are besides SiO₂, which accounts for 64.8% of the whole rock, Ca 3.56% and minor Mg 1.27% (Table 3). Both sodium and potassium appeared in the sample with levels close to 0.6-1.5%.

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

Element	mg/kg	Element	mg/kg	Element	mg/kg	Element	mg/kg
Al	43769	V	84	Mo	1	Ho	2
Ca	16536	Cr	7	Pb	19	Er	4
Fe	28398	Co	14	Sn	5	Dy	7
K	16054	Ni	3	Nb	44	Yb	4
Mg	5047	Cu	66	Cs	7	Th	13
Na	14029	Zn	116	Ba	647	Hf	6
P	691	Ga	21	La	42	Ta	3
S	449	Ge	1	Ce	81	W	1
Mn	863	As	3	Pr	12	Tl	1
Li	17	Tb	1	Nd	35	Zr	243
Be	3	Rb	116	Sm	8	U	4
B	31	Sr	170	Eu	2		
Sc	19	Y	45	Gd	8		

According to the mineralogical and petrographical studies performed by optical microscopy and X-ray diffraction, the results obtained helps to correlate the geological material and the mineral phases responsible for the chemical elements supplie. Major Si and Ca, and minor Mg and K are probably from the amorphus glassy matrix that comprises more than 30% of the sample. Additional elements supplied come from neso and tectosilicates pyroxenes, feldspars and quartz (poorly cristalized as cristobalite). Ca is the main element of Ca-plagioclase and pyroxene (augite), and K is a constituent of K-feldspar (sanidine) and mica (biotite)

The presence of opaque minerals, probably titanomagnetite and ilmenite should be evaluated considering the pH conditions of the soil in the region, once the excess of iron can led to growth problems in plants as the necrosis of the leaves (Malavolta, 2006).

Other inorganic chemicals 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 under weathering conditions mainly by hydrolysis are easily available to the soil (Alleoni and Melo, 2009), thus providing macro and micronutrients essencial for plant growth. Analysis by ICP-MS, and ICP-AES demonstrates that the low concentrations of potentially toxic elements such as As, Pb, and Li, among others, do not represent environmental risk (Table 3).

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

3.3 Leaching tests

The concentrations of the fractions of the elements leached during standardized test of the European Union (EN 12457-2, 2000) and other methodologies along with pH are expressed in Tables 4. The latter was a factor of great importance in geochemical mobility of the elements present in the sample of rock powder. Because, while the sample at pH = 7.55 have low nutrient release, in acids solution (that are present in the rhizosphere), the mobility of nutrients present in the sample increases considerably (Table 4).

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

pH	7,55		2,89		2,89		3,04		2,99		1,91	
Nutrients	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

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, the greater 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, because they were detected in higher concentrations in the chemical composition of the sample (Table 3).

The acidics extractors solutions of the number 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 aluminosilicates 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 favors 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 contain high concentrations of Al in its composition (Table 3), the leachable fraction of this element was 4,077 mg/kg (6 extractor), which corresponds to a potential release of 9.3%. This element undergoes weathering in acidic soil, releasing the aluminium to the environment, which can precipitate in the form of aluminum 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 aluminium. 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, 1,132.4 mg/kg, 1,630.7 mg/kg, and 129.3 mg/kg) in the leachate of the extractors solutions (2-5), respectively. However the extractor 6 presents a higher concentration (2,690.6 mg/kg) than the other extractors. The pH influence on 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 9,725 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 (272.5-1,541.3 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 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 high mobility in all leaching tests, mainly if considering the 6 extractor leachate, wich shows that practically the entire amount of P (93.3%) was released (. In the 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 (2,341 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, the volcanic rock powder from the studied area 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 and pyroxenethat in environmental conditions can be altered. 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 sweets industries, aiming at modifications in the structure of the rock powder and largest release of nutrients in smaller time interval.

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