ELSEVIER

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Evaluation of the potential of volcanic rock waste from southern Brazil as a natural soil fertilizer



CrossMark

Cleane



^a Laboratory of Environmental Researches and Nanotechnology Development, Centro Universitário La Salle, Mestrado em Avaliação de Impactos Ambientais, Victor Barreto, 2288 Centro, 92010-000, Canoas, RS, Brazil

^b Departamento Nacional de Produção Mineral (DNPM), Washington Luiz, 815, Centro, Porto Alegre, RS, CEP: 90010-460, Brazil

^c Universidade Federal do Rio Grande do Sul (UFRGS), Av. Bento Gonçalves, 9500 Prédio 75, Sala 122, Campus do Vale, Porto Alegre, RS, CEP: 91501-970, Brazil

^d Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C/Luis Solé y Sabarís s/n, 08028 Barcelona, Spain

^e Research group in Environmental Management and Sustainability. Faculty of Environmental Sciences. Universidad de la Costa. Barranquilla, Colombia

ARTICLE INFO

Article history: Received 11 November 2015 Received in revised form 29 October 2016 Accepted 1 November 2016 Available online 3 November 2016

Keywords: Volcanic rock powders Mining waste Safe environmental Natural soil fertilizers

ABSTRACT

This study was developed to evaluate the chemical and mineralogical properties of acid volcanic rock waste from mining activities by measuring the availability of macronutrients and micronutrients in Milli-Q water, and in acidic solutions to evaluate the potential use of this type of waste as natural soil fertilizers. The sample used in this work was obtained from a company of the mining district of Nova Prata, Rio Grande do Sul State, southern Brazil. Petrographic studies using conventional optical microscopy and scanning electron microscope allowed to define the mineral composition of in powder wastes as being comprised mainly by pyroxene, feldspar, and variable contents of amorphous glass in matrix. The primary oxides detected in the samples by X-ray Fluorescence were calcium oxide, silicon dioxide, aluminium oxide, iron oxide, and with concentration minor potassium oxide, and phosphorus oxide. Several important nutrients were transferred into the acidic solutions, indicating the significant potential and feasibility of these wastes to be effectively used as natural fertilizers. This study is of great relevance to the sector of mining and to agriculture in the region because it can create an alternative disposal treatment for tailings, and improve the environmental sustainability of local farms, thereby avoiding excessive chemical fertilizer consumption.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years several researches have been conducted to mitigate the different environmental impacts related to agricultural activities. In particular, the use of chemical fertilizers consisting of nitrogen, phosphorus and potassium, namely NPK, has drawn significant attention due to the adverse environmental impacts caused by the excessive application of these products. The fertilizer in excess is carried by rainwater from the soil surface to other water resources, causing pollution, algae proliferation and the eutrophication of aquatic ecosystems (Hodges and Crozier, 1996; Almeida

* Corresponding author. E-mail address: claudeterms@outlook.com (C.G. Ramos). et al., 2006; Santucci, 2012). The studies of Knapik (2005), Theodoro and Leonardos (2006), Nunes (2012) have intensified the use of rock powder as a soil fertilizer or pH corrective as alternatives to decrease the dependence of Brasil on imported raw materials, and minimize environmental impacts (Fyfe et al., 2006).

The fertilization of soils with volcanic rock powder, also know as a stonemeal technique, can provide a large range of macronutrients such as nitrogen, phosphorus, potassium, calcium, magnesium and sulfur and micronutrients such as iron, manganese, copper, zinc and sodium, to the suitable plant growth. Application of rock powders for soil fertilization is directly related to the composition and amount of minerals phases, and is also dependent of the weathering conditions, including temperature, rainfall amount, organic matter production in soils in order to increase the potential conditions to solubilize inorganic chemical compounds improving soil fertility (Theodoro and Leonardos, 2006; Loureiro et al., 2009). Volcanic rock powder minerals are source of nutrients for plant growth during long periods, and promotes an increasing in cation exchange soil capability due to formation of a series of clay minerals during the process of weathering mineral alteration (Melamed et al., 2005).

Due to the increased construction and building activities was promoted an increase in the exploration of volcanic rock, which are widely applied as ornamental rock. While this development in the mineral sector is relevant, the generation of waste has also increased, causing detrimental environmental problems that must be addressed.

According to Toscan et al. (2007) in Nova Prata Rio Grande do Sul, Brazil, were generated large piles of waste by mining activity of volcanic rock, with approximately 647,000 m³ in 2005, and a monthly production of 7000 m³. Additionally, Kautzmann (2011) showed the growth of the mining sector and estimated production of 17,000 tons of waste for the year 2011.

Several authors (Villiers, 1947; Evans, 1947; Gillman, 1980; Hensel, 1989; Motta and Feiden, 1992; Hinsinger et al., 2001; Theodoro and Leonardos, 2006; van Straaten, 2002; Nunes, 2012) have shown that the addition of crushed rock to agricultural soil dates back to antiquity.

Volcanic rock powder is among the major mineral fertilizers studied, researched and discussed in existing literature (Knapik, 2005; Nunes et al., 2014; Santucci, 2012). The interest in this mineral, in Brazil, is because volcanic rock processing generates a significant amount of rock powder waste, which is composed of important mineral elements that can be used for plant metabolism. These minerals are emitted in dust form from comminution operations or discarded in the solid/solid separation in screening units and thus constitute an adverse environmental impact for the mining sector.

Villiers (1947) after a long series of field experiments recommended the use of powdered basaltic rocks for rejuvenation of depleted soils of humid regions in the Congo, that showed a considerable increase in production of sugar cane with increasing crop production after four cuts. Evans (1947) demonstrated an increase of 33.7% and 56.7% in dry matter production with cultivation of oats in pots, also applying powder basaltic rocks. Gillman (1980) correlated the raise of soil pH with increasing application of crushed basalt in highly weathered soils. Finer ground material and longer incubation times enhanced this effect. Also Julius Hensel (1989) advocated the use of rock powders as an alternative to reduce the use of chemical fertilizers in agriculturable lands to improve soil quality. Motta and Feiden (1992) determined that application of basalt powder was enough to raise the level of available phosphorus, behaving as a corrective fertilizer for soils. Hinsinger et al. (2001) reported the use of crushed silicate rocks or parent rocks rich in primary minerals could be potential nutrient sources for soil fertility. Gillman et al. (2002) also demonstrated correlation among the application of crushed basalt on highly weathered low pH soils, showing reduction in the acidity of soils.

Theodoro and Leonardos (2006) reported an increase in plant production, reaching up to 50% of total with application of "stonemeal" technique. The release of nutrients from the crystal lattice of the minerals is mainly a consequence of the action of organic acids produced by plants and microorganisms in the soil (Moraes, 2014). Regions with natural acidic soils have high potential for the successful application of rock powder as a fertilizer soil supplier.

Experiments using volcanic rock powders $(2.7-3.0 \text{ wt\% } \text{K}_2\text{O})$ and KCl industrial fertilizer (60, 120 e 240 kg ha⁻¹), were applied to millet agriculture (Souza et al., 2010). In that research, the

agronomic efficiency of the volcanic rock powders was close to 40% for each 240 kg ha⁻¹. Considering Brazil to be one of the largest suppliers of agriculture commodities in the world, and its greater potential to expand cultivable soils (Scolari, 2006), detailed studies of volcanic rock powders as soil fertilizers may contribute with the definition of new routes and processes to supply demand of chemical fertilizers.

Through this study it was possible evidence that global mining impacts can be minimized with the total utilization of the exploited resource, the recycling of the generated byproducts and innovative usage of the environmentally impacted areas. In this context, the study of the mining wastes as potential fertilizers is a practice that can be developed to further contribute to sustainability. The use of natural fertilizers is relevant for the development of more sustainable farming and mining activities, thus providing several advantages to a significant portion of our society.

This study evaluated a mineralogical and chemical characterization of volcanic rock powders from mining industry of the Nova Prata region, Rio Grande do Sul State, Brazil, examining the potential of available nutrients to evaluate their use as a soil natural fertilizer.

2. Material, methods and analytical procedures

2.1. Volcanic rock powder samples

In the Nova Prata region, the geological setting consists of phanerozoic volcanic rock sequencies of the Serra Geral Formation, comprising mainly volcanic rocks of basic, intermediate and acid composition. At the bottom of the sequencies dominated by basic-intermediate volcanic rocks, and at the top dominated intermediate-acid composition (Prates et al., 1998). It is relevant emphasize that these rocks are primarily composed of plagioclase and pyroxenes, and are from the same volcanic eruptions and therefore show similar composition in the wide extension of the ore deposits (Nardy et al., 2008).

The studied samples belong to the upper sequencie of the Serra Geral Formation denominated Caxias facies of the Palmas Group (Nardy et al., 2008). Therefore, the studied samples comprise acid volcanic rock powders from rock-cut mining for industry, located in the Nova Prata mining district, southern Brazil (DATUM SAD'69 28°46'27.37″ S/51°38'16.61″ W). Rock-milled powders passing through ASTM Series #170 (90 µm) and #400 (38 µm) sieves were supplied by the Union of the Mining Industry of the Nova Prata district.

2.2. Petrographic and mineralogical analysis

The mineralogical and petrographic studies were developed using thin sections and volcanic rock powders. Petrographic analysis were performed using transmitted light microscope, (Nikon, Eclipse - 50iPOL with five objectives, from $5 \times$ to $100 \times$ across the entire field of view). The mineralogical composition of the samples was evaluated by X-ray powder diffraction (XRD) at the Unidade de Raios X - RIAIDT of the University Santiago de Compostela (Spain). The samples were analyzed with a Philips powder diffractometer fitted with a Philips "PW1710" control unit, vertical Philips "PW1820/00" goniometer and FR590 Enraf Nonius generator. The instrument was equipped with a graphite diffracted-beam monochromator, and Cu-radiation source λ (K α 1) = 1.5406 Å, operating at 40 kV and 30 mA. The XRD pattern has been collected by measuring the scintillation response to Cu Ka radiation versus the 2 Θ value over a 2 Θ 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! ($^{\odot}2003-2011$ CRYSTAL IMPACT, Bonn, Germany). Field emission scanning electron microscope (FE-SEM Zeiss ULTRA) with charge compensation was used for all applications on conductive as well as non-conductive samples. The working distance of the FE-SEM was 5–10 mm, beam voltage 5–20.0 kV, aperture 6, and micron spot size 5 or 5.5.

2.3. Chemical characterization of volcanic rock powders

Major elements concentrations were determined by fusion with LiBO₂ followed by X-ray fluorescence (XRF) analysis on a spectrometer Philips (PW1480).

The rock powder samples were digested in acidic solutions following a digestion method proposed by Querol et al. (1997); this consisted of a HNO₃ hot extract followed by HF:HNO₃:HClO₄. The resulting solutions were analyzed at the Institute of Environmental Assessment and Water Research (Spain) by inductively coupled plasma atomic emission spectrometry (ICP-AES) for major elements, and by inductively coupled plasma mass spectrometry (ICP-MS) for trace elements.

2.4. Availability of macronutrients and micronutrients of volcanic rock powders

Leaching tests with acidic solutions, and Milli-Q water were done under laboratory conditions trying to reproduce the soil environment during the assimilation of nutrients by plant roots. The leaching tests were applied to determine and 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 (Krishna, 2013).

The availability studies of macronutrients and micronutrients were performed in laboratory conditions with six different acidic solutions, and Milli-Q water, the extraction methodologies are shown in Table 1. The particles size of volcanic rock samples used were <90 μ m, and <38 μ m.

Concentrations of major and trace elements presents in the extraction solutions (leachates) were determined by ICP-MS and ICP-AES. The analysis were applied in duplicate.

The pH of each leachate was also measured (with a pH meter DM-2P Digimed) to trace the relationships between this parameter and leaching elements.

3. Results and discussions

3.1. Petrographic and mineralogical analysis

The main mineral phases identified through conventional optical microscopy and SEM in the samples were clinopyroxene (augite) \pm Ca-plagioclase \pm K-feldspar (sanidine/orthoclase) phenocrysts (30–35%), quartz \pm apatite (5%), and other accessory minerals (Ti-magnetite \pm ilmenite). Glomeroporphyritic, spherulitic, and hypocrystalline are the dominant textures identified in thin sections. The hypocrystalline vitrophyric matrix (50–60%) presents devitrified sites with local holo crystalline texture defined by the mineral association feldspar \pm pyroxene (augite) \pm opaque minerals. Many of Ca-plagioclase and sanidine feldspars microphenocrysts contain oxidation paths joint to microfractures indicating secondary mineral phases. Pyroxene microphenocrysts (augite) are generally replaced by Fe-Ti oxides. Small pyroxene grains occur disseminated on the matrix (Fig. 1A–B). The small size

pyroxene grains does not allows definition of the optical properties, and their chemical composition are not been classified. Oxide minerals likely comprise titanomagnetite and ilmenite, which occur as microphenocrysts and aggregates with skeletal shapes, often a product of pyroxene alteration. Apatite comprises an accessory mineral phase. SEM allowed to verify the texture of the mineral phases, and define mineral compositions, helping to characterize the chemical elements (nutrients) (Fig. 2). Semiquantitative X-ray diffraction analysis showed the occurrence of Ca-feldspar (59%), sanidine (15%), quartz (10%), augite (9%), cristobalite (6%), and an undetermined proportion of glassy material in the matrix (Fig. 3). The results concur with the studies of Knapik (2005) who showed an augite concentration of 10%, and 15% of quartz in basalt waste samples used in stonemeal studies. The glassy material is guite susceptible to weathering (Eggleton, 1986; Allen and Hajek, 1989), making it an important source of macro and micronutrients, with effective nutrient release from rock powder under weathering actions. The presence of all these mineral that are susceptible to weathering is a good indication that the wastes have the ability to release macronutrients and micronutrients into the soil.

3.2. Chemical characterization of volcanic rock powders

The results obtained by X-ray Fluorescence demonstrated that the main elements in the rock powder samples are Si (64.8%), Ca (3.56%), and minor Mg (1.27%). Na and K vary from 0.6% to 1.5%. Other inorganic chemicals elements analyzed including P and S represent less than 1.5% of the total composition of the sample. These results agree with those found by Theodoro and Leonardos (2006), who studied the characterization of similar rock powder and their application as natural fertilizers.

Additional elements as Ca could be supplied from pyroxene and feldspars alteration, and K from K-feldspar. Plagioclase and orthoclase are important sources of Ca, and K in soils, and orthoclase may be the largest reservoir of K (Huang, 1989). The results of analysis by ICP-MS, and ICP-AES demonstrates that the volcanic rock samples were characterized by a series of macronutrients and micronutrients described in existing literature (Arnon and Stout, 1939; Song and Huang, 1988), and the low concentrations of potentially toxic elements such as As, Pb, Cd, and Li, among others, do not represent environmental risk (Table 2). These facts has proved that these volcanic rock powder will be effectives for applicability in agriculture.

3.3. Availability of macronutrients and micronutrients of volcanic rock powder

The results of studies on the availability of macronutrients and micronutrients showed a suitable potential for the application of volcanic rock waste as a natural fertilizer. These rocks wastes released several nutrients from the solid structure to the aqueous solutions as shown in Table 3. It is relevant to emphasize that the smaller the pH value, the greater the availability of nutrients becomes. In additional, the leaching elements concentrations are higher in samples with particle sizes smaller than 38 μ m, and in extractor solution with 1% oxalic acid – extractor 6 (Table 3). These results are in agreement with studies of Blum et al. (1989), who compared the dissolution of basalt at different grains sizes (<200 μ m and <2000 μ m) in 1% citric acid solution and found that nutrient release was greatest for the <2000 μ m fraction.

This study showed considerable concentrations of Fe, Ca, Al, P, Si, Mg, Na, and K in all acidic solutions, therefore in Milli-Q water the availability for all nutrients was insignificant. The results showed that, specially the phosphorus, was available in high

Table 1	
Methods used in the availability experiments of macronutrients and micronutrients of volcanic rock waste.	

Extractor Extraction solutions		Conc. (mol L ⁻¹)	Sample Qty (g)	Qty solution (ml)	AgitationPeriod of agitation(rpm)(min)		Method				
1 Milli-Q water			1	10	60	1440	EN 12457-2, European Committee for Standardization, 2002				
2	Citric Acid	0.02	5	500	40	30	MAPA– Brasil (2007)				
3	Citric Acid	0.02	5	100	40	1440	Adapted from MAPA- Brasil (2007)				
4	Citric Acid	0.01	5	50	300	1440	(Silva, 2009)				
5	Oxalic Acid	0.05	5	50	300	1440	Adapted from Silva (2009)				
6	Oxalic Acid	0.01	5	100	300	1440	Silva (2009)				
7	Rhizosphere Organic	1.00	25	100	40	360	Pires et al. (2004)				
	acids	0.72									
	43% acetic acid;	0.49									
	31% citric acid;	0.12									
	21% lactic acid,										
	5% oxalic acid										



Fig. 1. 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 10 ×/graphic scale 0.2 mm) characterizing the occurrence of crystallites of plagioclase in association with mafic minerals and incipient micrographic texture.



Fig. 2. Dominant textures identified by SEM in the volcanic rock waste; (1): In detail, glomeroporphyritic, spherulitic, and hypocrystalline as textures.

concentrations, above 90% of rock total composition (Table 2) in extractor 6 (Table 3). In general, the availability of P found in this study supports the application of volcanic rock powder as a natural soil fertilizer.

The available Potassium concentrations were also high $(132-537 \text{ mg kg}^{-1})$ for all extractor solutions. Therefore, the availability of potassium obtained in this study indicates that this nutrient may be of great potential in aiding several processes of plant growth through fertilization with volcanic rock waste.

Magnesium (245–1655 mg kg⁻¹), Na (123–655 mg kg⁻¹), P

(227–661 mg kg⁻¹) and Mn (157–668 mg kg⁻¹) levels showed a similar extractable proportion in all extractor solutions, even less abundant, as expressed in Table 3.

The extractor solutions 2–5 and 7 have showed similar concentrations of all nutrients. Therefore, in extractor solution 6 the Si availability was around five-times greater than in the other extraction solutions (Table 3). According to Gillman et al. (2002) the application of volcanic rock powders is able to raise Si in soils above the critical levels, but field trials are necessary to accurate assess of the criteria.



Fig. 3. Diffractogram of X-rays of the volcanic rock waste.

 Table 2

 Chemical composition of macronutrients and micronutrients of volcanic rock waste.

Nutrients	mg kg ⁻¹	Element	${ m mg}~{ m kg}^{-1}$	Element	${ m mg~kg^{-1}}$	Element	mg kg $^{-1}$
Al	43769	V	84	Мо	1	Но	2
Ca	16536	Cr	7	Pb	19	Er	4
Fe	28398	Со	14	Sn	5	Dy	7
К	16054	Ni	3	Nb	44	Yb	4
Mg	5047	Cu	66	Cs	7	Th	13
Na	14029	Zn	116	Ba	647	Hf	6
Р	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
В	31	Sr	170	Eu	2		
Sc	19	Y	45	Gd	8		

It is relevant to note that elements of high toxicity such As, Cd, and Pb, among others, have low availability (Table 3) by being present in the sample at low concentrations (Table 2). This reinforces the implementation of such material in food production, after all, even in extremely acid pH there was no high fraction leaching of these elements.

High aluminum concentration (4350 mg kg⁻¹) was found in extractor solution 6, particle size <38 μ m, but corresponding to a low potential release, of 10% approximately of total rock composition. The interpretation for this behavior could be the presence of high content of aluminosilicate glassy matrix (with low resistance to weathering processes). Aluminum released during dissolution in soils above pH 5 is generally precipitated as secondary aluminosilicates (Lindsay, 1979). Thus aluminum toxicity from dissolution of silicate rock powders is not expected (Harley and Gilkes, 2000).

Calcium is slightly soluble in water (Harley and Gilkes, 2000). Its solubility increases in acidic solutions showing variable concentrations in the leachates, although extractor 6 presents higher concentrations than the others extractors.

The leachate obtained from extractor 6 provides 10.95 mg kg⁻¹ (547.67 mg L⁻¹) of Fe, representing a potential release of 38.5% (Table 3). Fe is immobile at pH higher than 4.5, and its release increases with decreasing pH (Silva et al., 2011). According Sposito (1989), the level of this nutrient in the soil should range from 25,000 to 40,000 mg L⁻¹. This demonstrates that, although the sample has a high concentration of iron in its composition, the availability for the soil will be low.

The results in Table 3 show availability for micronutrients such as B, and Cu that appear in low concentrations as beneficial for plant nutrition. In addition, some of the nutrients studied may be available as a function of time, allowing for a gradual weathering of the rock powder maintaining nutrition in the soil.

4. Conclusions

According to the results obtained in this study, it is concluded that the volcanic rock can be used as a source of macronutrients and micronutrients to the soil, as it has in its composition several silicate minerals such as pyroxene, plagioclase and easily alterable ferromagnesian by weathering. The crystalline texture of volcanic rock is glassy. This fact turns this type of rock suitable for stonemeal due to the easy glass destabilization in exogenous conditions. The oxidation of feldspar and pyroxene, in addition to clay minerals that fill fractures and veinlets, and also occur in the matrix, it may indicate a hydrothermal process, bringing the destabilizing potential (replacement and/or processing) of these mineral phases, with consequent increase in the potential release of cations such as Ca, Fe, K, Mg, Na, P and Si, among others that may contribute to soil fertilization. Nutrient release experiments in acidic solutions conducted in the laboratory showed that the oxalic acid solution 1% (extractor 6) had the best extraction efficiency. Iron, Ca, Al, P, Si, Mg, Na, and K were the main nutrients available in the acidic solutions. The agronomic advantages of using volcanic rocks waste as a fertilizer may be the insolubility of nutrients in water, resulting in

Table 3	
pH and levels of macronutrients and micronutrients available in extractor solutions (m	ng kg $^{-1}$).

İ i j	-														
pH 7.55 2.80 7.80 <th<< td=""><td>Extractor</td><td>1</td><td></td><td>2</td><td></td><td>3</td><td></td><td>4</td><td></td><td>5</td><td></td><td>6</td><td></td><td>7</td><td></td></th<<>	Extractor	1		2		3		4		5		6		7	
Particle 9490 9400 <	pН	7.55		2.89		2.89		3.04		2.99		1.91		2.55	
Nutrients Nutrients <t< td=""><td>Particle size</td><td><90 µm</td><td><38 µm</td><td><90 µm</td><td><38 µm</td><td><90 µm</td><td><38 μm</td><td><90 µm</td><td><38 µm</td><td><90 µm</td><td><38 µm</td><td><90 µm</td><td><38 µm</td><td><90 µm</td><td><38 µm</td></t<>	Particle size	<90 µm	<38 µm	<90 µm	<38 µm	<90 µm	<38 μm	<90 µm	<38 µm						
Al<1<11<141<161<1646<1659<162<169<179<1130<1757<160<1370<126Fe<1	Nutrients														
Ca119441082461481779112411352575280613731426K-12113428461049621275168219118480105313301340K-1-1256381185217169186132137609655132131Ma11276311148255221230237230257260254256559661235256Si11433464424407424256338491207265422425Man00118188247209264157163539668229229Man00000000000000Be00 <td>Al</td> <td><1</td> <td><1</td> <td>541</td> <td>762</td> <td>546</td> <td>659</td> <td>632</td> <td>766</td> <td>698</td> <td>737</td> <td>3805</td> <td>4350</td> <td>759</td> <td>820</td>	Al	<1	<1	541	762	546	659	632	766	698	737	3805	4350	759	820
Fe<1<181713484610481621275168132139476537153130170Mg<1	Ca	1	1	394	1109	2018	2246	1482	1779	1124	1135	2575	2806	1373	1426
K<1<1<256385<185<17<169<186<132<139<16<57<153<170Mg<1<1<270341<243<300<277330207307<120<123<137<120<155<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<121<	Fe	<1	<1	897	1342	846	1048	962	1275	1682	1911	8498	10953	1336	1440
Mg Na<1<124724724824827032027732029730714271655312341Na11276331348255221243123137609651235256Si1143346442440742452633849120572625442475Si0019819824729026415716353966025229Li00000000001100Be0000000000111011101100 <td< td=""><td>К</td><td><1</td><td><1</td><td>256</td><td>385</td><td>185</td><td>217</td><td>169</td><td>186</td><td>132</td><td>139</td><td>476</td><td>537</td><td>153</td><td>170</td></td<>	К	<1	<1	256	385	185	217	169	186	132	139	476	537	153	170
Na P11276 (71)331 (74)484 (74)255 (75)221 (74)260 (75)137 (75)660 (75)765 (75)176 (75) <t< td=""><td>Mg</td><td><1</td><td><1</td><td>247</td><td>341</td><td>245</td><td>300</td><td>277</td><td>330</td><td>297</td><td>307</td><td>1427</td><td>1655</td><td>332</td><td>341</td></t<>	Mg	<1	<1	247	341	245	300	277	330	297	307	1427	1655	332	341
P<1<11834834234224225725425625425655961235235432475Si114334344244074245203844912055668225229Li0000000000000265378668220229Li0000000000001100 </td <td>Na</td> <td>1</td> <td>1</td> <td>276</td> <td>331</td> <td>148</td> <td>255</td> <td>221</td> <td>243</td> <td>123</td> <td>137</td> <td>609</td> <td>655</td> <td>176</td> <td>192</td>	Na	1	1	276	331	148	255	221	243	123	137	609	655	176	192
Si1143346440440742452633849120572625422475Mn00159198198247209264157163539660225229Li000000000010102300Be0001111121111001110011	Р	<1	<1	318	348	312	342	227	260	254	256	559	661	235	256
Mn00159198198247209264157163539668225229Li00 <td>Si</td> <td>1</td> <td>1</td> <td>433</td> <td>464</td> <td>424</td> <td>407</td> <td>424</td> <td>526</td> <td>338</td> <td>491</td> <td>2057</td> <td>2625</td> <td>442</td> <td>475</td>	Si	1	1	433	464	424	407	424	526	338	491	2057	2625	442	475
Li 0 0 0 0 0 0 0 0 1 1 1 0 0 Be 0 0 0 0 0 0 0 0 0 1 <td>Mn</td> <td>0</td> <td>0</td> <td>159</td> <td>198</td> <td>198</td> <td>247</td> <td>209</td> <td>264</td> <td>157</td> <td>163</td> <td>539</td> <td>668</td> <td>225</td> <td>229</td>	Mn	0	0	159	198	198	247	209	264	157	163	539	668	225	229
Be 0 0 0 0 0 0 1	Li	0	0	0	0	0	0	0	0	0	0	2	3	0	0
B 0 0 1	Ве	0	0	0	0	0	0	0	0	0	0	1	1	0	0
Sc 0 0 1 1 1 1 1 0 0 1 2 1 1 V 0 0 2 3 1 2 2 2 2 3 12 15 2 2 Cr 0 0 1 2 2 2 2 2 2 7 7 2 2 Co 0 0 1 0 1 1 0 1 2 <t< td=""><td>В</td><td>0</td><td>0</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td>2</td><td>1</td><td>1</td><td>2</td><td>3</td><td>1</td><td>1</td></t<>	В	0	0	1	1	1	1	1	2	1	1	2	3	1	1
V 0 0 2 3 1 2 2 2 2 3 12 15 2 2 Cr 0 0 3 4 2 2 2 2 1 1 5 4 2 2 Ni 0 0 1 1 0 1 1 1 1 0 1 2 2 1 1 Cu 0 0 0 1 0 1 1 0 1 2 2 1 1 Cu 0 0 0 0 1 1 1 1 0 1 2 2 1 1 Cu 0	Sc	0	0	0	1	1	1	1	1	0	0	1	2	1	1
Cr 0 0 3 4 2 2 2 2 1 1 5 4 2 2 Co 0 0 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 1 <td>V</td> <td>0</td> <td>0</td> <td>2</td> <td>3</td> <td>1</td> <td>2</td> <td>2</td> <td>2</td> <td>2</td> <td>3</td> <td>12</td> <td>15</td> <td>2</td> <td>2</td>	V	0	0	2	3	1	2	2	2	2	3	12	15	2	2
Co 0 0 1 2 2 2 2 2 2 7 7 2 2 Ni 0 0 0 1 0 1 1 0 1 2 2 1 1 Cu 0<	Cr	0	0	3	4	2	2	2	2	1	1	5	4	2	2
Ni 0 0 1 1 1 1 0 1 2 2 1 1 Cu 0 0 8 12 7 8 7 8 7 8 34 34 9 8 Zn 0 <th< td=""><td>Со</td><td>0</td><td>0</td><td>1</td><td>2</td><td>2</td><td>2</td><td>2</td><td>2</td><td>2</td><td>2</td><td>7</td><td>7</td><td>2</td><td>2</td></th<>	Со	0	0	1	2	2	2	2	2	2	2	7	7	2	2
	Ni	0	0	0	1	0	1	1	1	0	1	2	2	1	1
Zn 0	Cu	0	0	8	12	7	8	7	8	7	8	34	34	9	8
Ga 0	Zn	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ge 0	Ga	0	0	0	0	0	0	0	0	0	0	0	0	0	0
As 0 1	Ge	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Rb 0	As	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sr 0 0 1 1 1 1 1 0 0 1 1 1 1 Y 0 0 1 1 1 1 1 0 0 0 0 1 1 1 Zr 0 0 1 1 1 1 1 1 1 2 3 1 1 Nb 0	Rb	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Y 0 0 1 1 1 1 1 0 0 0 0 1 1 1 Zr 0 0 1 1 1 1 1 1 1 1 2 3 1 1 Nb 0 0 0 0 0 0 0 0 0 1 1 0 0 0 Mo 0 1 1 1 1 1 1 <th1< td=""><td>Sr</td><td>0</td><td>0</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td>0</td><td>0</td><td>1</td><td>1</td><td>1</td><td>1</td></th1<>	Sr	0	0	1	1	1	1	1	1	0	0	1	1	1	1
Zr 0 0 1	Y	0	0	1	1	1	1	1	1	0	0	0	0	1	1
Nb 0 0 0 0 0 0 0 1 1 0 0 Mo 0 <td>Zr</td> <td>0</td> <td>0</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>2</td> <td>3</td> <td>1</td> <td>1</td>	Zr	0	0	1	1	1	1	1	1	1	1	2	3	1	1
Mo 0	Nb	0	0	0	0	0	0	0	0	0	0	1	1	0	0
Sn 0	Mo	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ba 0 0 3 3 2 3 3 3 2 2 8 8 3 3 La 0 0 0 0 0 1 0 1 0 0 0 0 1 1 Ce 0 0 2 2 2 2 2 0 0 0 0 1 1 Ce 0 0 2 2 2 2 1 2 0 0 0 0 2 2 2 Nd 0 0 1 1 1 1 1 1 0 0 0 0 1 1 Hf 0	Sn	0	0	0	0	0	0	0	0	0	0	0	0	0	0
La 0 0 0 0 1 0 1 0 0 0 0 1 1 Ce 0 0 2 2 2 2 1 2 0 0 0 0 2 2 Nd 0 0 1 1 1 1 1 0 0 0 0 2 2 Nd 0 0 0 1 1 1 1 1 0 0 0 0 1 1 Hf 0	Ba	0	0	3	3	2	3	3	3	2	2	8	8	3	3
Ce 0 0 2 2 2 1 2 0 0 0 0 2 2 Nd 0 0 1 1 1 1 1 0 0 0 0 1 1 Hf 0<	La	0	0	0	0	0	1	0	1	0	0	0	0	1	1
Nd 0 0 1 1 1 1 1 0 0 0 0 1 1 Hf 0	Ce	0	0	2	2	2	2	1	2	0	0	0	0	2	2
Hf 0	Nd	0	0	1	1	1	1	1	1	0	0	0	0	1	1
Ta 0	Hf	0	0	0	0	0	0	0	0	0	0	0	0	0	0
W 0	Ta	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Pb 0 0 1 0	W	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Th 0	Pb	0	0	0	1	0	1	0	0	0	0	0	0	0	0
U 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Th	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	U	0	0	0	0	0	0	0	0	0	0	0	0	0	0

reduced losses by leaching and fixation, and the solubility of nutrient solution of weak acids such as exists in the soil solution, resulting in slow and efficient release of important nutrients for plant development. The volcanic rock, beyond their potential for use as natural fertilizer the soil, can reduce the environmental impacts of conventional agriculture and give appropriate destination to the waste produced in mining areas.

Acknowledgments

The authors are thankful to the research group of the Laboratory of Environmental and Development Studies Nanotechnology (LEADN) for sample preparation techniques, and James Hower for editing. We also wish to thank CNPq (Grant No. 550203/2011-7) and FAPERGS/BMT (Grant No. 014/2012) for the financial support by the scholarship, and to the Syndicate of the Mining Industry of the Nova Prata Quarries for the samples.

References

- Allen, B.L., Hajek, B.F., 1989. Mineral occurrence in soil environments. In: Dixon, J.B., Weed, S.B. (Eds.), Soils in Mineral Environments, second ed. Soil Science Society of America, Madison, Wisc, pp. 199–278.
- Almeida, E., Silva, F.J.P., Ralisch, R., 2006. Powdered Rock to Revitalise Soils, vol. 22. Leisa Mag., pp. 12–13
- Arnon, D.I., Stout, P.R., 1939. The essentiality of certain elements in minute quantity

for plant with special reference to copper. Plant Physiol. 14, 371–375. Available in. http://www.plantphysiol.org/content/14/2/371.full.pdf+html.

- Blum, W.E.H., Herbinger, B., Mentler, A., Ottner, F., Pollack, M., Unger, E., Wenzel, W.W., 1989. The use of rock powders in agriculture. I. Chemical and mineralogical composition and suitability of rock powders for fertilization. Z Pflanzenernaehr Bodenk 152, 421–425.
- Eggleton, R.A., 1986. The relation between crystal structure and silicate weathering rates. In: Colman, S.M., Dethier, D.P. (Eds.), Rates of ChemicalWeathering of Rocks and Minerals. Academic Press, Orlando, FL, pp. 21–40.
- European Committee for Standardization, 2002. Characterization of Waste Leaching – Compliance Test for Leaching of Granular Waste Materials and Sludges – Part 2: One Stage Batch Test at a Liquid to Solid Ratio of 10 L/kg for Materials with Particle Size below 4 Mm. EN 12457–2:2002.
- Evans, H., 1947. Annual report. In: Investigations on the Fertilizer Value Os Crushed Basaltic Rock. in: Mauritius Sugar Cane Research Station, vol. 18, p. 227.
- Fyfe, W.S., Leonardos, O.H., Theodoro, S.H., 2006. Sustainable farming with native rocks: the transition without revolution. Ann. Braz. Acad. Sci. 78, 715–720.
- 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.
- Gillman, G.P., Burkett, D.C., Coventry, R.J., 2002. Amending highly weathered soils with finely ground basalt rock. Appl. Geochem. 17, 987–1001.
- Harley, A.D., Gilkes, R.J., 2000. Factors influencing the release of plant nutrient elements from silicate rock powders: a geochemical overview. Nutrient Cycl. Agroecosyst. 56, 11–36.
- Hensel, J., 1989. Bread from Stones: a New and Rational System of Land Fertilization and Physical Regeneration. Available in: http://soilandhealth.org/wp-content/ uploads/01aglibrary/010173.hensel.pdf. Access in 06 june 2015.
- Hinsinger, P., Barros, O.N.F., Benedetti, M.F., Noack, Y., Callot, G., 2001. Plant induced weathering of a basaltic rock: experimental evidence. Geochim. Cosmochim. Acta 65, 137–152.
- Hodges, S.C., Crozier, C., 1996. Soil Fertility Basics. North Carolina State University. Huang, P.M., 1989. Feldspars, olivines, pyroxenes, and amphiboles. In: Dixon, J.B.,

Weed, S.B. (Eds.), Soils in Mineral Environments, second ed. Soil Science Society of America, Madison, Wisconsin, pp. 635–674.

- Kautzmann, R.M., 2011. Levantanlento das áreas de passivo ambiental da mineração de basalto no Distrito Mineiro de Nova Prata, RS: Relatório de Atividades 2010.
- Knapik, J.G., 2005. Utilização do pó de basalto como alternativa à adubação convencional na produção de mudas de Mimosa Scabrella BENTH e Prunus sellowii KOEHNE, Pós-Graduação em Engenharia Florestal. Universidade Federal do Paraná, Paraná, p. 163. http://hdl.handle.net/1884/2213.
- Krishna, K.R., 2013. Agroecosystems: Soils, Climate, Crops, Nutrient Dynamics and Productivity. CRC Press, p. 552.
- Lindsay, W.L., 1979. Chemical Equilibria in Soils. John Wiley & Sons, New York. Loureiro, F.E.L., Melamed, R., Figueiredo Neto, J., 2009. Fertilizantes, agroindústria e sustentabilidade. CETEM/MCT, Rio de Janeiro.
- Ministério da agricultura, pecuária e abastecimento (MAPA) Brasil, 2007. Instrução Normativa SDA Nº 28, de 27 de Julho de. Diário Oficial da União de 31/07/2007c, Secão 1. p. 11.
- Melamed, R., Gaspar, J.C., Mierkeley, N., 2005. Pó-de-rocha como fertilizante alternative para sistemas de produção sustentáveis em solos tropicais, Rio de Janeiro, p. 72.
- Moraes, V., 2014. Pó de rocha será nova fonte de potássio para agricultura. http:// www.floraefauna.com/artigostecnicos/artigo16.htm.
- Motta, A.C.V., Feiden, A., 1992. Avaliação do P em LE submetido a diferentes doses de basalto. Agrárias, Curitiba, vol. 12, pp. 47–54.
- Nardy, A.J.R., Machado, F.B., Oliveira, M.A.F., 2008. As rochas vulcânicas mesozóicas ácidas da Bacia do Paraná: litoestratigrafia e Considerações geoquímico-estratigráficas. RBG 38, 178–195.
- Nunes, J.M.G., 2012. Caracterização de resíduos e produtos da britagem de rochas basálticas e avaliação da aplicação na rochagem, Mestrado em Avaliação de Inpactos Ambientais em Mineração Unilasalle, Canoas, p. 95.
- Nunes, J.M.G., et al., 2014. Evaluation of the natural fertilizing potential of basalt dust wastes the mining district of Nova Prata (Brazil). J. Clean. Prod. http:// dx.doi.org/10.1016/j.jclepro.2014.04.032.
- Pires, A.M.M., Mattiazzo, M.E., Berton, R.S., 2004. Ácidos orgânicos como extratores de metais pesados fitodisponíveis em solos tratados com lodo de esgoto. Pesq. Agropec. Bras. [online] 39 (7) (Brasília).

Prates, F.B.S., Veloso, H.S., Sampaio, R.A., Zuba Jr., G.R., Lopes, P.S.N., Santos, E.L.,

Maciel, L.A.C., Filho, J.A.Z., 1998. Distrito Mineiro de Nova Prata, Distritos Mineiros do Estado do Rio Grande do Sul. 1º Distrito – DNPM, Porto Alegre, pp. 13–14.

- Querol, X., Whateley, M.K.G., Fernandez-Turiel, J.L., Tuncali, E., 1997. Geological controls on the mineralogy and geochemistry of the Beypazari lignite, central Anatolia, Turkey. Int. J. Coal Geol. 33, 255–271.
- Santucci, P.J., 2012. Rochagem: alternativa sustentável aos fertilizantes convencionais, vol. 89. Revista bimestral do Conselho Regional de Engenharia e Agronomia do Rio Grande do Sul, pp. 16–19. http://www.crea-rs.org.br/site/ arquivo/revistas/ed89.pdf.
- Scolari, D.D.G., 2006. Produção Agrícola Mundial: O Potential Do Brasil. Revista FMC, Brasília, DF.
- Silva, A.S.S., 2009. Caracterização de flogopitito da Bahia como fertilizante alternativo de potássio. Dissertação de Mestrado, IQ/UFRJ, p. 72.
- Silva, L.F.O., Izquierdo, M., QueroL, X., Finkelman, R.B., Oliveira, M.L.S., Wollenschlager, M., Towler, M., Pérez-López, R., Macias, F., 2011. Leaching of potential hazardous elements of coal cleaning rejects. Environ. Monit. 175, 109–126.
- Song, S.K., Huang, P.M., 1988. Dynamics of potassium release from potassium bearing minerals as influenced by oxalic and citric acids. Soil Sci. Soc. Am. J. 52, 383–390.
- Souza, F.N.S., et al., 2010. Rejeito mineral como fonte de fertilizante. In: Congresso Brasileiro de Rochagem, 1., Planaltina. Anais. Planaltina: EMBRAPA Cerrados, 2010. 1 CD-ROM.
- Sposito, G., 1989. The Chemistry of Soils. Oxford University Press, New York, p. 345. Theodoro, S.H., Leonardos, O.H., 2006. The use of rocks to improve family agriculture in Brazil. An. Acad. Bras. Ciênc 78 (4). Rio de Janeiro Dec. 2006.
- Toscan, L., Kautzmann, R.M., Sabedot, S., 2007. O rejeito da mineração de basalto no nordeste do Estado do Rio Grande do Sul: diagnóstico do problema. R. Esc. Minas, Ouro Preto 60, 657–662.
- van Straaten, P., 2002. Rocks for Crops: Agrominerals of Sub-Saharan Africa. Fidelity National Information Solutions; Canada, Nairobi, Kenya.
- Villiers, O.D'Hotman, 1947. Sur des resultants d'etudes relatives a la rejuvenation de nos sols épuiés dês region humides par incorporation de poussiére basaltique. Revve Agric. I'lle Maurice 26.