



Understanding the mobility of potential nutrients in rock mining by-products: An opportunity for more sustainable agriculture and mining

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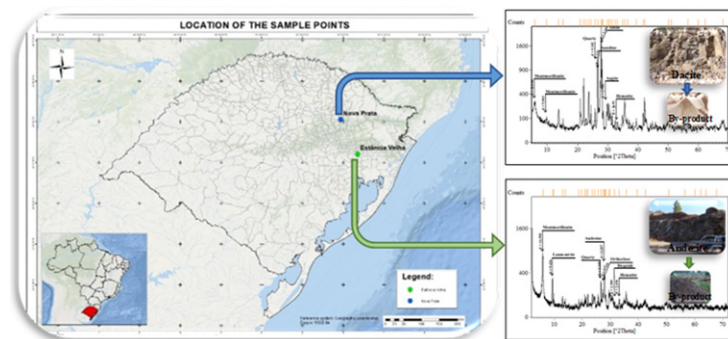
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HIGHLIGHTS

- The dissolution experiments of by-products were performed with different extraction solutions.
- Volcanic rock by-product as a source of multi-nutrients.
- Three mathematical models were used to describe and estimate the behavior of multi-nutrients release from by-products.

GRAPHICAL ABSTRACT



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ABSTRACT

The increase in demand for highly soluble fertilizers brings a global sustainability concern. Alternative sources for traditional fertilization are therefore needed. Rock powder use has been proposed as an alternative approach to soil remineralization. However, research on the agricultural potential of minerals and rocks as alternative sources of nutrients is limited to changes in soil chemical attributes or effects on crop yield. In this work, we report an experimental study addressing the dissolution of two silicate rock-derived powders (andesite and dacite) that were produced during mining activities in Southern Brazil. The rock powders were exposed to Milli-Q water at pH (7.4–8.8) range, in solutions of 0.1 mol L^{-1} citric acid at pH range 2.1–3.3, and Milli-Q water acidified with 0.5 mol l^{-1} acetic acid (pH 5–5.8), in a continuous mechanical rotatory shaker at room temperature. Dissolution kinetics were determined as a function of reaction times at 24 to 5760 h, and solution pH. Based on this kinetics, dissolution rates were determined for the individual powders and compared to expected values for aluminosilicates. Based on this comparison, it was shown that the application of andesite and dacite rock-derived powder to replace high soluble fertilizers is feasible due to high dissolution rates of their minerals. The average andesite dissolution rates in Milli-Q water, in citric acid solution, and in Milli-Q water acidified with acetic acid were 2.1×10^{-5} , 1.92×10^{-1} and $6.3 \times 10^{-4} \text{ mmol cm}^{-2} \text{ s}^{-1}$, respectively for Ca, being 183%, 22.6%, and 69.2% higher than for the dacite rock. This makes andesite rock a potential substitute for carbonate-based liming. In contrast, the average dacite dissolution rates in Milli-Q water, in citric acid solution, and in Milli-Q water acidified with acetic

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acid were 1.05×10^{-5} , 7.22×10^{-5} , and 3.72×10^{-5} mmol cm⁻² s⁻¹, respectively for K, being 72.0%, 61.4%, and 73.6% higher than the andesite rock. This highlights its potential use as a K source for agriculture to replace highly soluble K-fertilizers.

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1. Introduction

For a society increasingly aware of the degree of systemic disturbances caused by the increasing demand for several consumer products and by intensification in the exploitation of natural resources, particularly as in agriculture, alternative sources to traditional fertilization, are therefore needed (Korchagin et al., 2019).

The use of rock powders as an alternative of soil fertilizer is a very old practice to increase soil nutrient content and crop productivity, particularly for tropical soils (Silva, 2016; Manning and Theodoro, 2018). This practice can be applied in many countries by exploiting local geological sources (Manning and Theodoro, 2018).

Investigations into the agricultural potential of minerals and rocks as alternative sources of mainly K have been oriented by the fertility notion prevailing in agrarian sciences, restricting itself to the evaluation of changes in the soil chemical attributes or in the productivity of crops, without considering the factors associated with release kinetics and to the effects of weathering on the alteration of by-product minerals. Among the nutrients that may be supplied by volcanic rock powders, K has been the most widely studied to determine whether it can become immediately available in soils at rates significant for crops.

According to Manning (2018), determine the dynamics of mineral nutrient release from rocks and understanding the processes of weathering and alteration of minerals, is critical to neutralize soil acidity in mined areas, for the remediation of contaminated areas, or as a nutrient source for agricultural crops, by the rock-derived powders application.

Mineral dissolution rates can be influenced by the presence of organic ligands, as such ligands may bind metal cations in solution, or may form complexes on the mineral surface that enhance dissolution rates. The dissolution effects are strongly dependent on ligand, mineral species, and on pH (van Noort et al., 2018).

Several studies on K release kinetics were carried out with rock dust in dilute salt solutions, low molecular weight organic acids (citric and oxalic) and cation exchange resins (Silva et al., 2013; Meira et al., 2014). These acids were also used as extractors in the K and Mg release kinetics by Silva (2016), and in the evaluation of the solubility of minerals of volcanic rock by Ramos et al. (2015). There is concern about the real effectiveness of these materials with the low solubility of rock minerals being the major limiting factor. Knowledge of dissolution kinetics is required to properly determine the nutrient supply capacity of rocks to soils; optimize its efficiency as a fertilizer to reduce the use of soluble fertilizers and develop guidelines for the safe and proper disposal of by-products, and reduce environmental pollution (Nishanth and Biswas, 2008).

In Southern Brazil, tonnes of rock powder are produced in different quarries (Korchagin et al., 2019). Little research has been done on the kinetics of Al, Ca, Fe, K, Mg, Na and Si release from silicate rock-derived powders intended for agricultural use.

To study the applicability of andesite and dacite rock-derived by-products, leaching tests have been carried out. These by-products have been dissolved over a period of 24 to 5760 h, in Milli-Q water at pH (7.4–8.8) range, in solutions of 0.1 mol L⁻¹ citric acid at pH (2.1–3.3) range, and Milli-Q water acidified with 0.5 mol L⁻¹ acetic acid at pH (5–5.8) range, under stirred continuous on a mechanical rotatory shaker, at room temperature. These conditions were chosen to approximate natural weathering conditions, including the potential to form concentration gradients in the liquid phase, and limiting particle collisions that may abrade leached or precipitated layers. According to

Hochella and Banfield (1995), such leached or precipitated layers may form on the particles during weathering in agricultural fields. During the experiment, the solutions pH was measured to observe the effects of different solution in the elements release and mineral dissolution rates. After the experiment, the concentrations of Al, Ca, Fe, K, Mg, Na and Si were used to calculate element release rates through the fluid flow rate, the specific surface area and mass of the solid used in the experiment (Gudbrandsson et al., 2011). The Information of this study are fundamental for ensuring safe and efficient use of silicate rock-derived by-products as soil fertilizer.

2. Material and methods

2.1. By-product samples

Twenty kilograms of each by-product powder with particle sizes below 5.0 mm for chemical characterization and kinetic release experiment were used in this investigation. Vesicular andesite and dacite rocks, respectively, were from Estância Velha, and Nova Prata, both of Rio Grande do Sul state, Southern Brazil (Fig. 1).

The study region is recognized for the large volume generated (52,400 m³ annually) of mining tailings (Toscan et al., 2007). According to Nardy et al. (2008) in the Serra Geral Group the dominant volcanic rocks are basalt, basaltic andesite and andesite, followed by riodacite and little rhyolite, composed of 30 to 50% of plagioclase, 20 to 35% of augite and pigeonite and 5 to 15% of opaque minerals.

2.2. By-products particle size distribution

The granulometry of the by-products has great influence in nutrients release, because the smaller the grain size, the larger the surface area exposed to exogenous conditions (Ramos et al., 2017). The particle size distribution of the particles was determined by using laser diffraction equipment (CILASTM1064).

The specific surface areas of andesite and dacite were determined by an N2 adsorption Brunauer–Emmett–Teller method (BET, Shimadzu, Micromeritics FlowSorb II 2300).

2.3. By-products mineralogy

The mineralogical phases of the by-products were determined by X-ray diffraction (XRD) in a Philips X-ray diffractometer, according to Ramos et al. (2019).

2.4. By-products chemical composition

The determination of the chemical composition of major elements (in % of oxides weight) of the by-product samples was performed by X-ray fluorescence (XRF). Quantitative analysis was performed using the lithium tetraborate fused powder sample technique, with calibration curve from rock patterns. X-ray fluorescence technique was employed to determine the chemical composition of the by-products. This analysis was performed in compliance with Ramos et al. (2019).

2.5. Mineral dissolution and procedures

Dissolution experiments were carried out in a continuous shaken mechanical system for 5760 h in a plastic vial, hermetically sealed, at

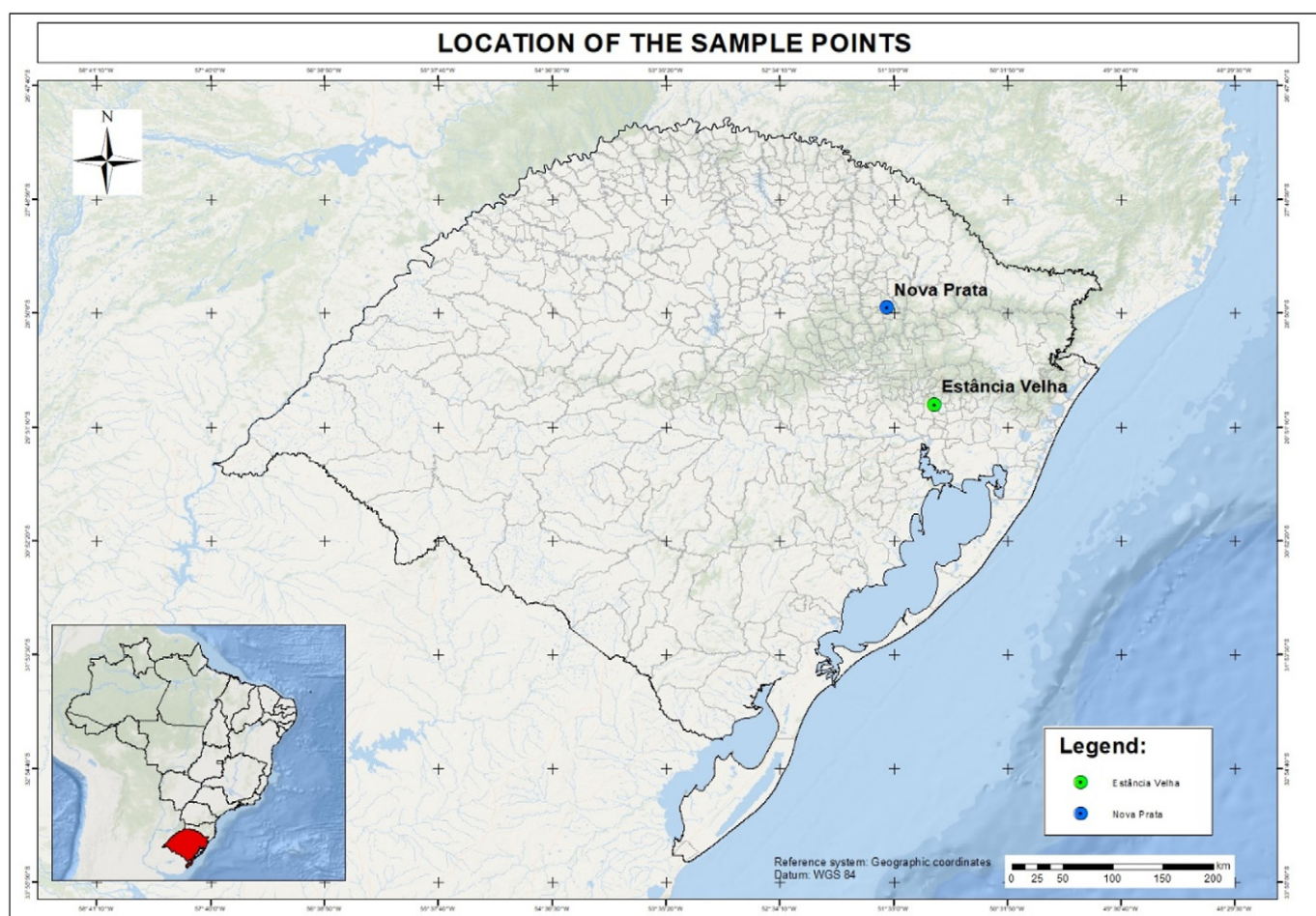


Fig. 1. Studied area.

room temperature (25 ± 1 °C). Table 1 shows the dissolution experimental conditions.

In experiment with mildly acidified water by acetic acid (AA), the solutions pH was adjusted at 5 ± 0.2 by addition of 10 mL of 0.5 mol L^{-1} acetic acid solution, every seven days. An amount of 20 mL of each solution was collected at 24, 48, 72, 96, 168, 336, 504, 720, 1440, 2160, 2880, 3600, 4320, 5040, and 5760 h and filtered. Before aliquots collect, the pH of the extraction solutions was measured in DM-2P Digimed pH-meter, to verify the relationships between this parameter with the mineral dissolution rates. After each collect was made the replacement of the solutions and the by-products remaining in the filters for vials. These experiments were performed in laboratory conditions with three replicates. The concentrations of multi-elements released in each solution were quantified by ICP-AES.

The Al, Ca, Fe, K, Mg, Na, and Si concentrations, were used to calculate element release rates ($r_{i,j}$) using the dissolution equation (Gudbrandsson et al., 2011):

$$r_{i,j} = C_iFR / (A_jm) \quad (1)$$

where c_i represents the concentration of the element in the outlet fluid, FR designates the fluid flow rate, A_j and m refer to the specific surface area and mass of the solid, respectively.

3. Results and discussion

3.1. By-product particle size characterization

The particle size distribution of the by-products, obtained by a sieving, is shown in Fig. 2. The size distribution analysis showed that 100% of the particles of andesite had a minimum size of $500 \mu\text{m}$ and 50% had a minimum size of $31 \mu\text{m}$. Dacite had 100% of the particle sizes below $500 \mu\text{m}$ and 50% below $99 \mu\text{m}$. This lower size distribution of andesite may increase nutrients release. Priyono and Gilkes (2008) investigated the multi-nutrients dissolution kinetics of silicate rock with particle sizes below 0.25 mm and 0.15 mm in organic acid solution. The authors showed that the dissolution rate of cations increased with smaller particle size.

Table 1

Methods and procedures to extract and determine multi-nutrients release from solid to liquid phase.

Extractor solutions	pH	Concentrations (mol L^{-1})	Amount of by-products (g)	Amount of solution (L)	Shaking (rpm)	Methods
Milli-Q water (W)	7.05	–	250	2.5	30	BSEN (2002) ^a
Citric acid (CA)	1.87	0.1	250	2.5	150	Teixeira et al. (2015)
W + acetic acid (AA)	5.00	0.5 acetic acid	100	2.0	30	Etim and Onianwa (2013)

^a British Standard European Norm.

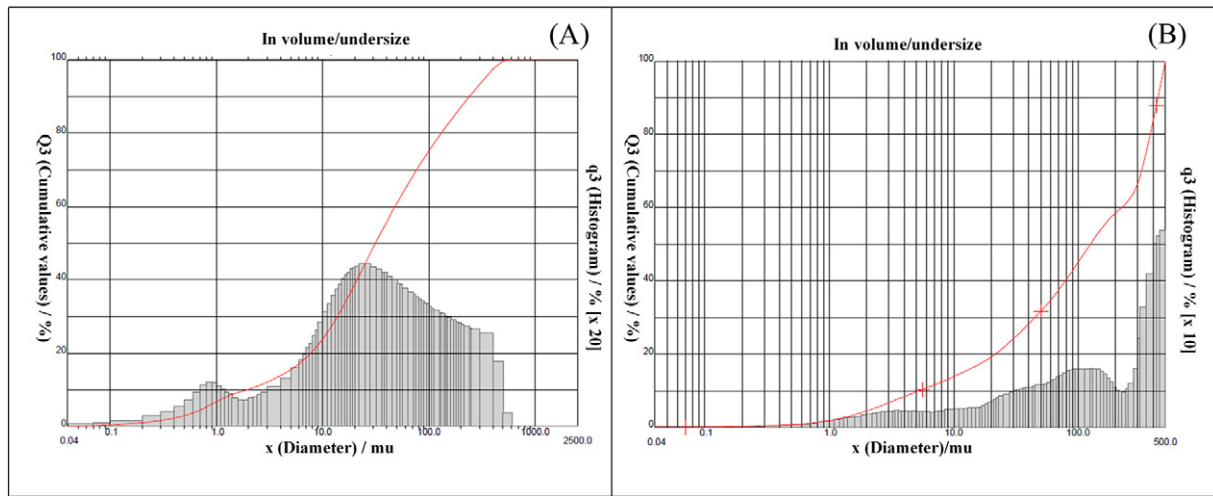


Fig. 2. Granulometric distribution curves obtained by laser diffraction. (A): Andesite rock powder; (B) Dacite rock powder.

The specific surface area, as determined by BET method, was $10.05 \text{ m}^{-2} \text{ g}^{-1}$ for andesite and $4.90 \text{ m}^{-2} \text{ g}^{-1}$ for dacite. These results agree with those obtained by Nielsen and Fisk (2008) that measured the specific surface area of 13 samples of silicate rock taken from the sea using the BET method and showed a range of $0.3\text{--}52 \text{ m}^{-2} \text{ g}^{-1}$.

3.2. Mineralogy

Table 2 shows the main mineral phases of the by-product samples, and the semi-quantitative approximation based on the intensity of the X-ray diffraction peaks (Fig. 3).

The andesite rock mineralogical studies showed the high content of laumontite, a zeolite group mineral (Fig. 3A), which is related to vesicles filling, which gives the rock an alkaline characteristic and high cation exchange capacity (Mastinu et al., 2019). This feature is fundamental to provide the exchange of nutrients between mineral particles and soil/ water/roots (Nunes et al., 2014). This shows great potential for by-products application as soil fertilizer (Ramos et al., 2017). The presence of montmorillonite, with smaller proportion in dacite rock, and hematite shows the marked condition of weathering of the rocks (Fig. 3A-B). Andesine occurs in andesite and albite in dacite, that are

feldspar class minerals (Fig. 3A-B). Andesine has a high proportion of calcium and sodium, and albite has a high sodium content in their structure. These minerals resistance to weathering is low (Alleoni and Melo, 2009), with high potential for the release of calcium and sodium to medium. X-ray diffraction analysis show the occurrence of orthoclase in the andesite and sanidine in the dacite (Fig. 3 A-B), that are minerals of K-feldspar group. Potassium is released when these minerals are slowly weathered (Rawat et al., 2016). The pyroxenes such as diopside in andesite, and augite in dacite can release Mg, Fe, and Ca, and form new minerals. These results concur with Deer et al. (2013), that most common rock-forming minerals were plagioclases, pyroxenes, and feldspar. The susceptibility to weathering that the mineral phases present in the studied samples, are a good indication of the ability of multi-nutrients release to the soil.

3.3. By-products chemical composition

Table 3 shows the concentration of the major and minor elements of by-products expressed by respective oxides. These results agree with those obtained by Ramos et al. (2019), which characterized a similar rock to those of this study and its application as soil remineralizer in black oat and maize crops.

The chemical composition of the by-products, expressed as major and minor elements, allowed to classify the rocks as andesite (Szymański and Szkaradek, 2018) and dacite (Streckeisen, 1976). According to the Total Alkali Silica (TAS) classification of andesite, it includes an average amount of silica (57% to 63%), more than basalt and less than dacite (Gill, 2010). Compared to each other, and as expected, andesite contains higher Al_2O_3 , Fe_2O_3 , CaO, MgO, TiO_2 , Na_2O and MnO contents. In dacite the SiO_2 and K_2O contents are higher than in andesite (Table 3). Based on macronutrient K content, the dacite would be the most indicated as potassium fertilizer. Potassium is very necessary nutrient for enhance the productivity of many crops (Carvalho et al., 2018). The andesite has higher levels of Mg and Ca, which are also important macronutrients to agriculture. These elements could be supplied from pyroxene alteration (Buchs and Howie, 2016). The role of calcium is to regulate nutrient transport, and to support many enzyme functions (Gilliham et al., 2011). Magnesium is important to the photosynthetic process (Guo et al., 2016). The P_2O_5 content of by-products are similar (Table 3), representing more than three times the P_2O_5 content of the Earth's crust average. According to Donatello et al. (2010) the P_2O_5 crustal average concentration is 1.18 g kg^{-1} (0.1%). Phosphorus is essential to all life, including plants (Vance et al., 2003). Silicon is essential to crop growth, although it is not regarded as an essential nutrient. According to Epstein (1999) Si-deficient plants have generally

Table 2
Semi-quantitative approximation (%) of the main mineral phases present in the andesite and dacite samples.

Mineral species	Chemical formulas	Mineral groups	Abundance (%)
Andesite			
Andesine	$(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$	Plagioclases	27.1
Laumontite	$\text{Ca}_4\text{Al}_8\text{Si}_{16}\text{O}_{48} \cdot 14\text{H}_2\text{O}$	Zeolite	12.9
Hematite	Fe_2O_3	Hematite	2.70
Orthoclase	KAlSi_3O_8	K-Feldspars	13.3
Quartz	SiO_2	Silica	5.40
Montmorillonite	$(\text{Na,Ca})(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{n}(\text{H}_2\text{O})$	Smectites	14.1
Augite	$(\text{Ca,Na})(\text{Mg,Fe,Al,Ti})(\text{Si,Al})_2\text{O}_6$	Pyroxenes	24.6
Total			100.1
Dacite			
Albite	$\text{NaAlSi}_3\text{O}_8$	Plagioclases	35.3
Hematite	Fe_2O_3	Hematite	1.00
Cristobalite	SiO_2	Silica	5.80
Quartz	SiO_2	Silica	12.4
Montmorillonite	$(\text{Na,Ca})(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{n}(\text{H}_2\text{O})$	Smectites	2.20
Sanidine	$(\text{K,Na})(\text{Si,Al})_4\text{O}_8$	K-Feldspars	28.6
Augite	$(\text{Ca,Na})(\text{Mg,Fe,Al,Ti})(\text{Si,Al})_2\text{O}_6$	Pyroxenes	14.7
Total			100.0

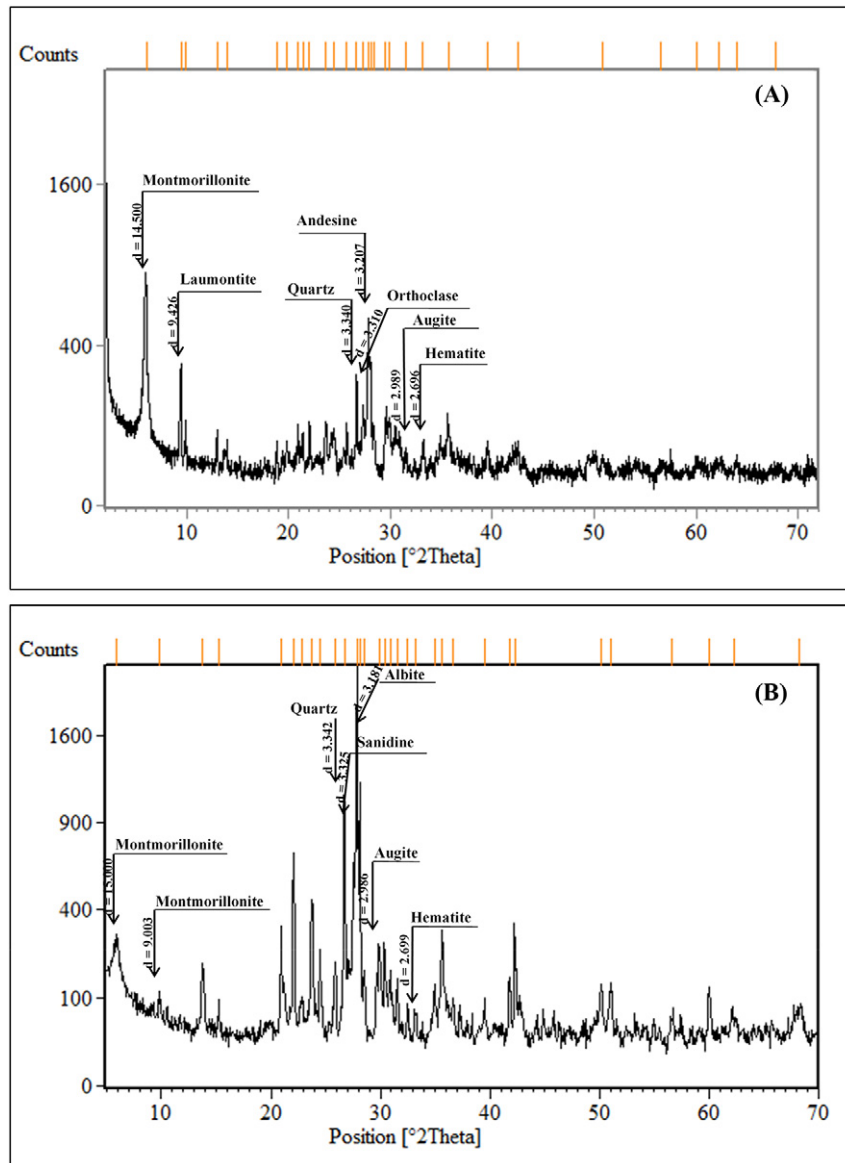


Fig. 3. (A) X-ray diffractogram of andesite; (B) X-ray diffractogram of dacite.

structurally weaker and more prone to growth, development and reproduction irregularity. Silicon is the only nutrient that is not harmful when over-absorbed. In addition, it helps to control pests and increase the

Table 3

Concentration of the major elements of by-products samples (%) expressed by respective oxides.

Oxides	Andesite (%)	Dacite (%)
SiO ₂	57.1	67.1
TiO ₂	1.17	0.92
Al ₂ O ₃	14.1	12.6
Fe ₂ O ₃	9.50	6.41
MnO	0.17	0.11
MgO	3.57	2.18
CaO	5.38	3.14
Na ₂ O	3.22	2.92
K ₂ O	2.49	3.79
P ₂ O ₅	0.26	0.28
LOI ^a	2.70	0.53
Total	99.7	99.9

^a Loss on ignition.

productivity and quality of agricultural products (Keeping, 2017; Beerling et al., 2018).

An important concern when applying silicate rock-derived powders to agricultural soils is the potential toxic elements release, as these rocks can contain such elements in relatively high concentrations. Ramos et al. (2017, 2019), studied the nutrients release of silicate rock-derived powder and concluded that the rock has low concentrations of potential toxic elements, which do not represent an environmental risk.

3.4. Multi-elements release and their rates

The concentration of multi-elements released from andesite and dacite in extractant solutions, and the solutions pH values, as a function of reaction time are showed in supplementary material. Fig. 4 shows the accumulated multi-nutrient concentrations released by the by-products at 24–5760 h.

The all multi-elements release from both by-products in Milli-Q water was very low (Fig. 4); the accumulated release of Al (8.03 mmol kg⁻¹) and K (11.2 mmol kg⁻¹) from andesite at 5740 h was smaller than from dacite (12.2 mmol kg⁻¹ of Al and 19 mmol kg⁻¹ of K). Calcium, Na and Si cumulative released was similar from both

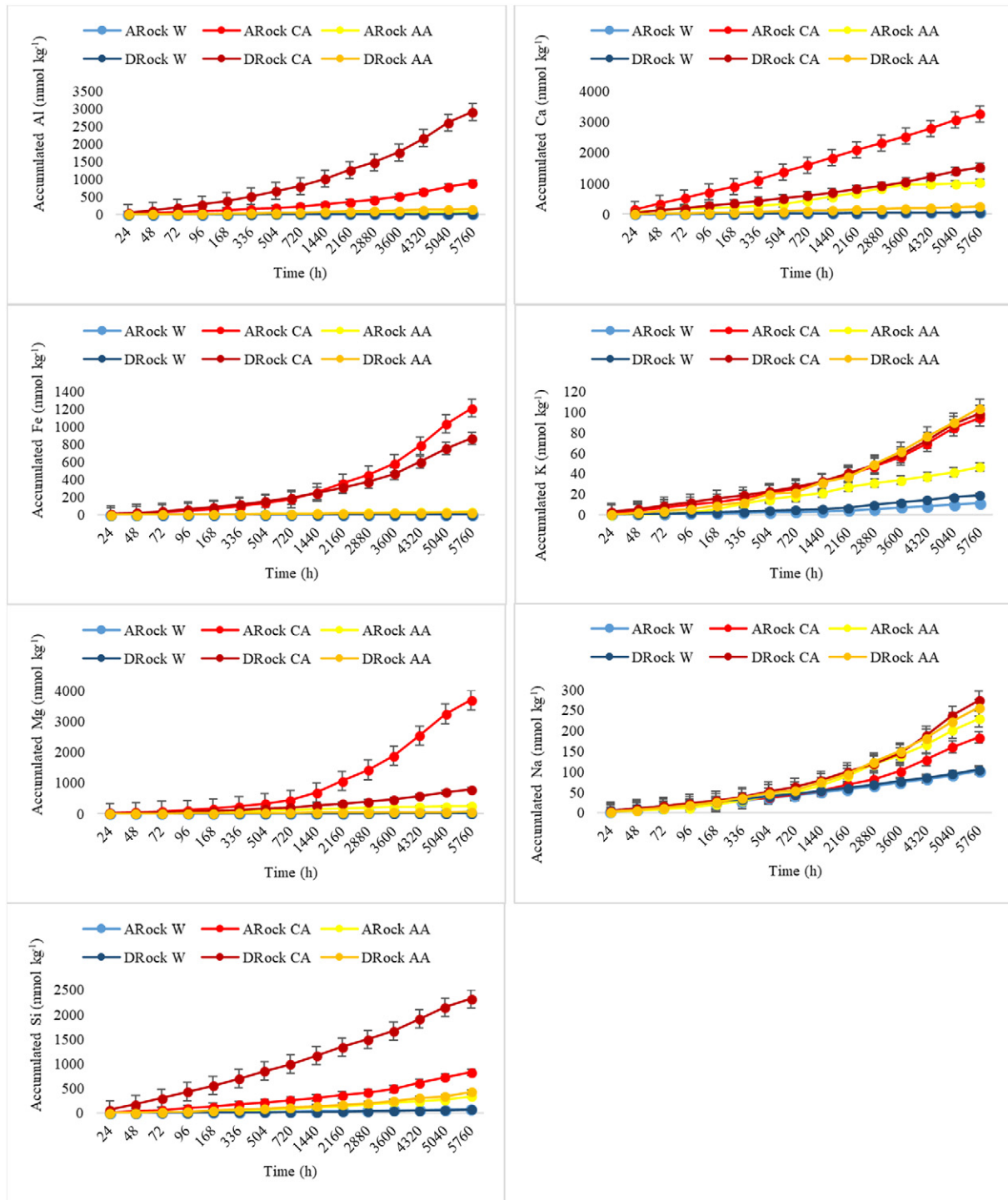


Fig. 4. Accumulated amounts of Al, Mg, Si and Fe (mmol kg^{-1}) released from biotite under different extractants solution, plotted against experimental time (h) at room temperature. Vertical bars (I) represent the standard error from three replications.

by-products, around 60, 103 and 70 mmol kg^{-1} , respectively. The Mg and Fe (32.4 and $1.31 \text{ mmol kg}^{-1}$) accumulated release from andesite was significantly higher than from dacite (9.2 and $0.62 \text{ mmol kg}^{-1}$). This low release in water, suggests the precipitation of (Al, Ca, Fe, K, Mg, Na and Si)-bearing mineral (s) (Sugimori et al., 2009), that make up the andesite and dacite rocks. The low release of multi-elements from andesite and dacite rock powder in water, also can be explained by its high pH value, and its low ability to remove interlamellar cations from rock minerals (Silva et al., 2013).

The most distinguished differences were observed in the accumulated release of Ca, Mg and Fe from andesite rock, and of Al, K, Na and Si from dacite rock, in citric acid solution (Fig. 4); andesite rock released $3263 \text{ mmol kg}^{-1}$ of Ca, $3687 \text{ mmol kg}^{-1}$ of Mg and $1209 \text{ mmol kg}^{-1}$ of Fe, while the dacite released 1523 , 783 and 870 mmol kg^{-1} , respectively.

In andesite and dacite rock mineral dissolution in water acidified with acetic acid (Fig. 4), the behavior of accumulate multi-elements release was like in Milli-Q water. There were a lot of differences in

released amounts between Milli-Q water acidified with acetic acid, >100% above than Milli-Q water, and >100% below than citric acid solution. The dissolution rates (r) from andesite and dacite are shown as a function of time in Fig. 5, and as a function pH in Fig. 6, where the differences in the amounts of releases between extraction solutions are emphasized. All multi-elements release rates of both by-products decreased with increasing pH, and increased with decreasing pH (Fig. 6), displaying a synclinal shaped pH dependence.

Silicon release rates are important in silicate dissolution because Si is a network former and represent silicate dissolution rates. The release rate of Si from andesite at pH < 3.25 was faster by about 6% above than

dacite (Figs. 5-6). The faster Si release was also evident for dacite dissolution at pH < 5.1, about 9% higher andesite. The release rates of Si from andesite and dacite rock, at pH < 3.25 can be characterized by much faster rates by about two orders of magnitude than those at pH < 5.1, and by similar rates for dissolution of both andesite and dacite (Fig. 5A-B). These faster Si release rates can be attributed to the Si adsorption onto Fe³⁺ oxides/hydroxides surfaces (Siever and Woodford, 1979); precipitation of Si-bearing secondary minerals; inhibition of silicate dissolution by the formation of secondary precipitates or altered layers on mineral surfaces (Morris and Fletcher, 1987); and direct dissolved oxygen (DO) interaction with silicate surfaces (Ouyang et al.,

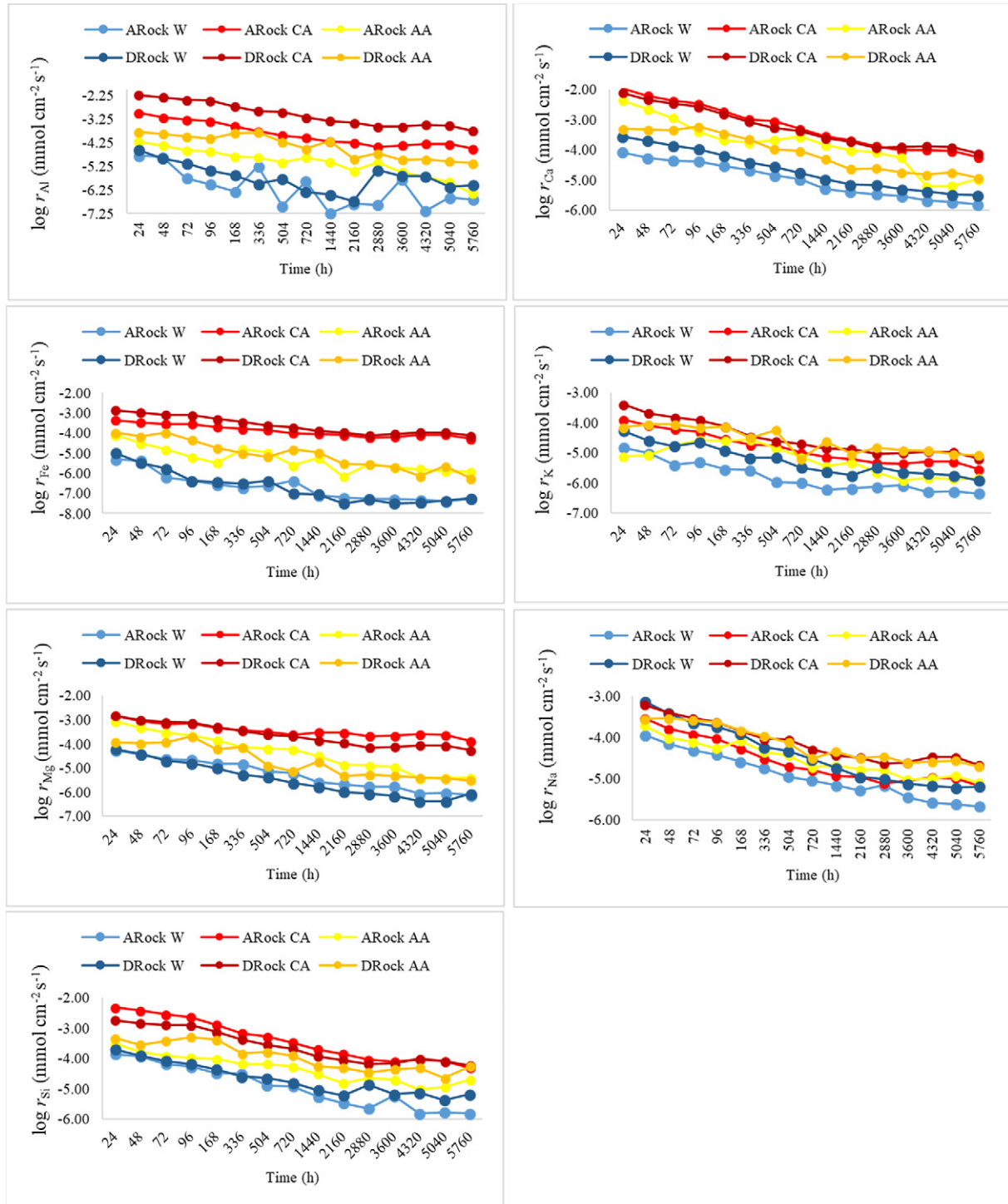


Fig. 5. Multi- elements release rates from andesite and dacite as a function time.

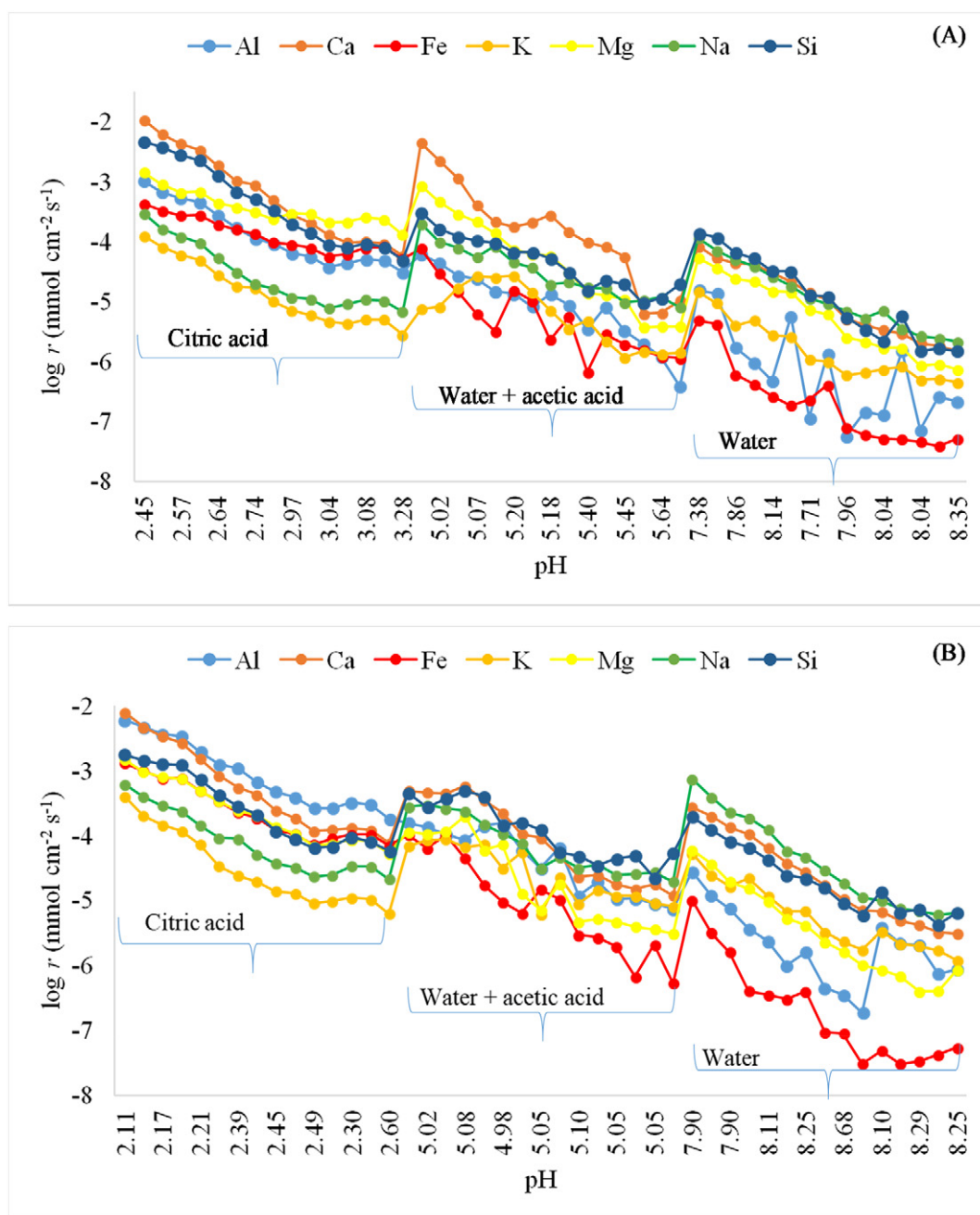


Fig. 6. Multi-elements release rates from (A) andesite and (B) dacite versus solutions pH.

2003). Experiments at $\text{pH} > 9$ (in Milli-Q water) (Fig. 6) have the lowest release rates and exhibit the greatest dispersion, possibly due to the effects of precipitation. These results confirm the observation of Sugimori et al. (2009), cited earlier in this study. Thus, Milli-Q water does not affect the dissolution rates of either andesite or dacite at $\text{pH} 7.6\text{--}8.8$.

The average rate constants for release of Na and Al from andesite ($\log r = -7.6$ and $-6.9 \text{ mol cm}^{-2} \text{ s}^{-1}$) and dacite ($\log r = -7.1$ and $-6.8 \text{ mol cm}^{-2} \text{ s}^{-1}$) are about three order of magnitude fast than those reported by Declercq et al. (2013) for rhyolite dissolution at $\text{pH} 2$ and 25°C . The rates constants reported for plagioclase are higher to those reported by Holdren and Speyer (1987) for dissolution of andesine at a pH of 3, which ranger from $\log r = -15.1$ to $-14.6 \text{ mol cm}^{-2} \text{ s}^{-1}$. The variation of dissolution rates from dacite with pH was similar to that obtained by Hellmann (1994) for albite dissolution ($-4.1 \text{ mol cm}^{-2} \text{ s}^{-1}$ at $\text{pH} 5$), and for K-Feldspar

($-6.2 \text{ mol cm}^{-2} \text{ s}^{-1}$ at $\text{pH} 5\text{--}8.6$) from andesite and dacite (Fig. 6). It's important to highlight, that the andesite and dacite dissolution rates in all extraction solutions were higher than the K-Feldspar dissolution rates ($1.67 \times 10\text{--}12 \text{ mol cm}^{-2} \text{ s}^{-1}$ at $\text{pH} 5$) reported by Bevan and Savage (1989). Andesite and dacite dissolution rates were like pyroxenes dissolution rates obtained by Sverdrup (1990) at $\text{pH} < 6$ ($-7.3 \text{ mol cm}^{-2} \text{ s}^{-1}$) (Fig. 6).

White and Brantley (2003) reported experimental weathering rates that decreased constantly with time over at least six years. The authors showed that ongoing weathering will lead to a slowing down of mineral dissolution. It is notable that weathering rates based on natural systems are of 1 to 3 orders of magnitude less than those estimated in laboratory experiments (Sverdrup, 1990). In contrast to this interpretation, in experiment conducted by Leonardos and Theodoro (1999) at the Água Limpa farm in Brasília, Brazil were used three forms of fertilization over 13 years in latosols (volcanic rock powder, NPK combined with

volcanic rock powder, and NPK). According to the authors, the growth of the eucalyptus plants grown in the NPK-fertilized plot was rapid until the fourth year. After this period, tree growth decreased significantly as compared to the growth of plants treated only with rock dust, which grew linearly, although more slowly at the beginning.

The weathering rates estimated in laboratory experiments of the present work, although they are upper to 1–3 orders of magnitude than those on natural systems are of great relevance for providing subsidies for better rock choice and adaptation of fertilization recommendations.

4. Conclusions

This work analyzed the kinetics rates of the releasing of multi-nutrients from two volcanic rock mining by-products to providing subsidies for better adaptation of fertilization recommendations. The agricultural use of by-products in tropical soils suggests replacing soluble fertilizers because there are primarily composed of aluminosilicates, whose nutritional properties significantly influence soil fertilization. The important elements, such as Ca, K, Mg, P, and Si, for agricultural production are also present in both by-products. However, several factors restrict the rock dust use as alternative source of nutrients for soil and are the main challenges of the technique. We can highlight the complex composition of the rocks; location of the deposits of these rocks in relation to the site of application; the presumed low-cost methods of milling; and the behavior of these rocks in the interaction with the environment where they will be applied.

The results of kinetics of multi-nutrients release of this study indicated that the by-products have potential to be used as a multi-nutrients fertilizer and liming. These results reinforce the importance of deepen researches related to rocks, which should be tested for use in varying conditions of soils, crops and agricultural systems in different regions of the world. This is justified by the fact that these rocks are abundant with wide distribution and variable in the earth.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.136240>.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Alleoni, L.R.F., Melo, V.F., 2009. *Química e Mineralogia do Solo*. SBCE, Viçosa.

Beerling, D.J., Leake, J.R., Long, S.P., Scholes, J.D., Ton, J., Nelson, P.N., Kelland, M., 2018. Farming with crops and rocks to address global climate, food and soil security. *Nature plants* 4, 138. <https://doi.org/10.1038/s41477-018-0108-y>.

Bevan, J., Savage, D., 1989. The effect of organic acids on the dissolution of K-feldspar under conditions relevant to burial diagenesis. *Mineral. Mag.* 53, 415–425. <https://doi.org/10.1180/minmag.1989.053.372.02>.

BSEN, 2002. Characterization of Waste – Leaching – Compliance Test for Leaching of Granular Waste Materials and Sludges – Part 2: Onestage Batch Test at a Liquid to Solid Ratio of 10 L/Kg for Materials With Particle Size Below 4 mm. EN 12457–2. p. 2002.

Buchs, D.M., Howie, R.A., 2016. Pyroxenes, Reference Module in Earth Systems and Environmental Sciences, Elsevier. <https://www.sciencedirect.com/science/article/pii/B9780124095489096974?via%3Dihub> (accessed 9 April 2019). doi:<https://doi.org/10.1016/B978-0-12-409548-9.09697-4>.

Carvalho, M.D., Nascente, A.S., Ferreira, G.B., Mutadiua, C.A., Denardin, J.E., 2018. Phosphorus and potassium fertilization increase common bean grain yield in Mozambique. *Revista Brasileira de Engenharia Agrícola e Ambiental* 22, 308–314. <https://doi.org/10.1590/1807-1929/agriambi.v22n5p308-314>.

Declercq, J., Diedrich, T., Perrot, M., Gislason, S.R., Oelkers, E.H., 2013. Experimental determination of rhyolitic glass dissolution rates at 40–200 °C and 2 < pH < 10.1. *Geochim. Cosmochim. Acta* 100, 251–263. <https://doi.org/10.1016/j.gca.2012.10.006>.

Deer, W.A., Howie, R.A., Zussman, J., 2013. *An Introduction to the Rock-Forming Minerals*. third ed. The Mineralogical Society, London.

Donatello, S., Tong, D., Cheeseman, C.R., 2010. Production of technical grade phosphorus acid from incinerator sewage sludge ash (ISSA). *Waste Manag.* 30, 1634–1642. <https://doi.org/10.1016/j.wasman.2010.07.011>.

Epstein E., 1999. Silicon, Annual Review of Plant Physiology and Plant Molecular Biology, vol. 50, pg. 641–664. doi:<https://doi.org/10.1093/aob/mcm247>.

Etim, E.U., Onianwa, P.C., 2013. "Leachate quality characteristics: a case study of two industrial solid waste dumpsites," *J. Environ. Prot.* 4, 984–988.2013. doi:<https://doi.org/10.4236/jep.2013.49113>.

Gill, R., 2010. *Igneous Rocks and Processes: A Practical Guide*. first ed. John Wiley & Sons, Oxford.

Gillham, M., Dayod, M., Hocking, B.J., Xu, B., Conn, S.J., Kaiser, B.N., Leigh, R.A., Tyermann, S.D., 2011. Calcium delivery and storage in plant leaves: exploring the link with water flow. *J. Exp. Bot.* 62, 2233–2250. <https://doi.org/10.1093/jxb/err111>.

Gudbrandsson, S., Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., 2011. An experimental study of crystalline basalt dissolution from 2 < pH < 11 and temperatures from 5 to 75 °C. *Geochim. Cosmochim. Acta* 75, 5496–5509.

Guo, W., Nazim, H., Liang, Z., Yang, D., 2016. Magnesium deficiency in plants: an urgent problem. *The Crop Journal* 4, 83–91. <https://doi.org/10.1016/j.cj.2015.11.003>.

Hellmann, R., 1994. The albite-water system: part I. the kinetics of dissolution as a function of pH at 100, 200 and 300°C. *Geochim. Cosmochim. Acta* 58, 595–611. [https://doi.org/10.1016/0016-7037\(94\)90491-X](https://doi.org/10.1016/0016-7037(94)90491-X).

Hochella, M.F., Banfield, J.F., 1995. Chemical weathering of silicates in nature; a microscopic perspective with theoretical considerations. *Rev. Mineral. Geochem.* 31, 353–406.

Holdren, G.R., Speyer, P.M., 1987. Reaction rate-surface area relationships during the early stages of weathering, n. data on eight additional feldspars. *Geochim. Cosmochim. Acta* 51, 2311–2318. [https://doi.org/10.1016/0016-7037\(87\)90284-5](https://doi.org/10.1016/0016-7037(87)90284-5).

Keeping, M.G., 2017. Uptake of silicon by sugarcane from applied sources may not reflect plant-available soil silicon and total silicon content of sources. *Front. Plant Sci.* 8, 760. <https://doi.org/10.3389/fpls.2017.00760>.

Korchagin, J., Caner, L., Bortoluzzi, E.C., 2019. Variability of amethyst mining waste: a mineralogical and geochemical approach to evaluate the potential use in agriculture. *J. Clean. Prod.* 210, 749–758. <https://doi.org/10.1016/j.jclepro.2018.11.039>.

Leonardos, O.H., Theodoro, S.C.H., 1999. Fertilizer tropical soils for sustainable development. Proceedings. International workshop on Science for Sustainable development in Latin America and Caribe. Rio de Janeiro. Acad. Bras. Cienc. 1, 143–153.

Manning, D.A., 2018. Innovation in resourcing geological materials as crop nutrients. *Nat. Resour. Res.* 27, 217–227. <https://doi.org/10.1007/s11053-017-9347-2>.

Manning, D.A., Theodoro, S.H., 2018. Enabling food security through use of local rocks and minerals. The Extractive Industries and Society. Elsevier. <https://doi.org/10.1016/j.exis.2018.11.002>.

Mastinu, A., Kumar, A., Maccarinelli, G., Bonini, S.A., Premoli, M., Aria, F., Gianoncelli, A., Memo, M., 2019. Zeolite clinoptilolite: therapeutic virtues of an ancient mineral. *Molecules* 24, 1517. <https://doi.org/10.3390/molecules24081517>.

Meira, L.D.A.S., Machado, A.O.D.V., Leite, J.Y.P., 2014. Potassium release kinetics in vermiculite tailings. https://www.researchgate.net/publication/325722019_Potassium_release_kinetics_in_vermiculite_tailings/, Accessed date: 24 April 2019.

Morris, R.C., Fletcher, A.B., 1987. Increased solubility of quartz following ferrous-ferric iron reactions. *Nature* 330, 558–561.

Nardy, A.J.R., Machado, F.B., de Oliveira, M.A.F., 2008. As rochas vulcânicas mesozóicas ácidas da Bacia do Paraná: litoestratigrafia e considerações geoquímico-estratigráficas. *Revista Brasileira de Geociências* 38, 178–195.

Nielsen, M.E., Fisk, M.R., 2008. Data report: Specific surface area and physical properties of subsurface basalt samples from the east flank of Juan de Fuca ridge. Proceedings of the Integrated Ocean Drilling Program. Oregon State University. <https://doi.org/10.2204/iodp.proc.301.205.2008>.

Nishanth, D., Biswas, D.R., 2008. Kinetics of phosphorus and potassium release from rock phosphate and waste mica enriched compost and their effect on yield and nutrient uptake by wheat (*Triticum aestivum*). *Bioresour. Technol.* 99, 3342–3353. <https://doi.org/10.1016/j.biortech.2007.08.025>.

Nunes, J.M.G., Kautzmann, R.M., Oliveira, C., 2014. Evaluation of the natural fertilizing potential of basalt dust wastes from the mining district of Nova Prata (Brazil). *J. Clean. Prod.* 84, 649–656. <https://doi.org/10.1016/j.jclepro.2014.04.032>.

Ouyang, J.H., Zhao, X.S., Li, T., Zhang, D.C., 2003. Direct measurement of the etching rates on Si (1 1 1) and Si dioxide surfaces in 40% ammonium fluoride aqueous solution via atomic force microscopy. *J. Appl. Phys.* 93, 4315–4320. <https://doi.org/10.1063/1.1559001>.

Priyono, J., Gilkes, R.J., 2008. Dissolution kinetics of milled-silicate rock fertilizers in organic acid. *J. Tanah Trop.* 13, 1–10. <https://doi.org/10.5400/jts.2008.v13i1.1-10>.

Ramos, C.G., Querol, X., Oliveira, M.L.S., Pires, K., Kautzmann, R.M., Oliveira, L.F.S., 2015. A preliminary evaluation of volcanic rock powder for application in agriculture as soil a remineralizer. *Sci. Total Environ.* 512–513, 371–380. <https://doi.org/10.1016/j.scitotenv.2014.12.070>.

Ramos, C.G., Querol, X., Dalmora, A.C., Pires, K.C.J., Schneider, I.A.H., Oliveira, L.F.S., Kautzmann, R.M., 2017. Evaluation of the potential of volcanic rock waste from southern Brazil as a natural soil fertilizer. *J. Clean. Prod.* 142, 2700–2706. <https://doi.org/10.1016/j.jclepro.2016.11.006>.

- Ramos, C.G., Medeiros, D.S. de, Gomez, L., Oliveira, L.F.S., Schneider, I.A.H., Kautzmann, R.M., 2019. Evaluation of soil re-mineralizer from by-product of volcanic rock mining: experimental proof using black oats and maize crops. *Nat. Resour. Res.* 28, 1–18. <https://doi.org/10.1007/s11053-019-09529-x>.
- Rawat, J., Sanwal, P., Saxena, J., 2016. Potassium and its role in sustainable agriculture. Potassium Solubilizing Microorganisms for Sustainable Agriculture. Springer, New Delhi. https://doi.org/10.1007/978-81-322-2776-2_17.
- Siever, R., Woodford, N., 1979. Dissolution kinetics and the weathering of mafic minerals. *Geochim. Cosmochim. Acta* 43, 717–724. [https://doi.org/10.1016/0016-7037\(79\)90255-2](https://doi.org/10.1016/0016-7037(79)90255-2).
- Silva, A.D.A., Sampaio, J.A., Luz, A.B.D., França, S.C., Ronconi, C.M., 2013. Modeling controlled potassium release from phlogopite in solution: exploring the viability of using crushed phlogopite rock as an alternative potassium source in Brazilian soil. *J. Braz. Chem. Soc.* 24, 1366–1372, 2013. doi:<https://doi.org/10.5935/0103-5053.20130173>.
- Silva, R.C., 2016. Intemperismo de minerais de um remineralizador. Tese (Doutorado). Escola Superior de Agricultura Luiz de Queiroz, Piracicaba, SP 183 p. <http://www.teses.usp.br/teses/disponiveis/11/111140/tde-01082016-171821/pt-br.php/>, Accessed date: 20 April 2019.
- Streckeisen, A., 1976. To each plutonic rock its proper name. *Earth Sci. Rev.* 12, 1–33. [https://doi.org/10.1016/0012-8252\(76\)90052-0](https://doi.org/10.1016/0012-8252(76)90052-0).
- Sugimori, H., Yokoyama, T., Murakami, T., 2009. Kinetics of biotite dissolution and Fe behavior under low O₂ conditions and their implications for Precambrian weathering. *Geochim. Cosmochim. Acta* 73 (13), 3767–3781. <https://doi.org/10.1016/j.gca.2009.03.034>.
- Sverdrup, H., 1990. *The Kinetics of Chemical Weathering*. Lund University Press, Lund, Sweden (and Chartwell-Bratt Ltd, London, ISBN 0-86238-247-5, 245pp).
- Szymański, W., Szkaradek, M., 2018. Andesite weathering and soil formation in a moderately humid climate: a case study from the Western Carpathians (Southern Poland). *Carpathian Journal of Earth and Environmental Sciences* 13, 93–105. <https://doi.org/10.26471/cjees/2018/013/010>.
- Teixeira, A.M.S., Garrido, F.M.G., Medeiros, M.E., Sampaio, J.A., 2015. Effect of thermal treatments on the potassium and sodium availability in phonolite rock powder. *Int. J. Miner. Process.* 145, 57–65. <https://doi.org/10.1016/j.minpro.2015.07.002>.
- 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. 60. *Revista Escola de Minas*, pp. 657–662. <https://doi.org/10.1590/S0370-44672007000400011>.
- van Noort, R., Mørkved, P., Dundas, S., 2018. Acid neutralization by mining waste dissolution under conditions relevant for agricultural applications. *Geosciences* 8, 380–405. <https://doi.org/10.3390/geosciences8100380>.
- Vance, C.P., Uhde-Stone, C., Allan, D.L., 2003. Phosphorus acquisition and use: critical adaptations by plants for securing a non-renewable resource. *New Phytol.* 157, 423–447. <https://doi.org/10.1046/j.1469-8137.2003.00695.x>.
- White, A.F., Brantley, S.L., 2003. The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? *Chem. Geol.* 202, 479–506.