Extractant efficiency in the solubilization of alternative sources of potassium

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ABSTRACT. Knowledge of a rock's composition allows for inferences regarding several properties, ranging from its physical characteristics to its solubility. This study aimed to evaluate the use of different extractants to solubilize the K present in rocks as a potential source of nutrients and the effects of extractant contact time and temperature on rock solubilization. Samples of two rocks and a mineral concentrated from a granitic rock were treated with ammonium dihydrogen phosphate ($NH_4(H_2PO_4)$), calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$), sodium hydroxide (NaOH) and water (control). Sample-extractant treatments were performed using a water bath shaker at temperatures of 25 and 50°C for periods of 3, 7, 10, 20, and 30 days. The amounts of K extracted from rocks using the extractants were in the following order: $NH_4H_2PO_4 > Ca(HPO_4)_2 > NaOH > water$. The sequence of K release (ppm) based on the rocks studied was as follows: nepheline syenite > green banded argillite > concentrated biotite. Increasing the extractant contact time and temperature enhanced the solubilized K content.

Keywords: minerals, soluble K, fertilizers, powdered rock.

Eficiência de extratores na solubilização de fontes alternativas de potássio

RESUMO. O conhecimento da mineralogia de rochas permite conclusões sobre propriedades que vão desde suas características físicas até a facilidade de solubilização. O objetivo do presente estudo foi avaliar o uso de diferentes extratores na solubilização do potássio (K) presente em rochas potenciais fontes de nutrientes e os efeitos do tempo de contato dos extratores e temperatura na solubilização das rochas. Amostras de rochas e mineral concentrado de rocha granítica foram tratadas com di-hidrogenofosfato de amônio ($NH_4(H_2PO_4)$), di-hidrogenofosfato de cálcio ($Ca(H_2PO_4)_2$), hidróxido de sódio (NaOH) e água (controle). Os tratamentos rochas-extratores foram submetidos ao banho de agitação em água a temperaturas de 25 e 50°C durante períodos de 3, 7, 10, 20, e 30 dias. As quantidades de K extraídos de rochas usando os extratores foram na seguinte ordem: $NH_4H_2PO_4 > Ca(H_2PO_4)_2 > NaOH > água$. A sequência de solubilização de potássio (ppm) baseado nas rochas estudadas foi a seguinte: nefelina sienito > argilito verde bandado > concentrado de biotita. O tempo de contato dos extratores e temperatura aumentaram o conteúdo de K solubilizado.

Palavras-chave: minerais, K solúvel, fertilizantes, pó de rocha.

Introduction

Stonemeal (*rocks for crops*) (Luz, Lapido-Loureiro, Sampaio, Castilhos, & Bezerra, 2010; Straaten, 2007) is defined as crushed rocks or materials containing naturally occurring soil fertilizers used as a soil amendment. The application of stonemeal to soils may represent an alternative to minimizing dependence on imported fertilizers in Brazil, which, in the specific case of potassium (K), is the world's fourth largest importer (Associação Nacional para a Difusão De Adubos e Corretivos Agrícolas (ANDA, 2012).

The use of unconventional and globally available geological K sources that can be weathered to provide sufficient K for agronomic benefits might be considered in agricultural systems in which K is the limiting nutrient and oxisols predominate (Manning, 2010), a common situation in Brazil. Whereas phosphatic rocks are feedstock for both conventional and unconventional phosphate fertilizers, potassium silicates, such as feldspars, biotite, phlogopite, and muscovite, and rocks with feldspathoids, such as leucite, nepheline and clay-rich sediments, especially illite, are the basis for alternative potassium fertilization (Straaten, 2010).

Mineralogical knowledge of rocks as potential sources of plant nutrients is essential to predicting their weathering behavior according to the Goldich dissolution series (Goldich, 1938), which, in turn, aids in the development of methods to promote mineral dissolution or solubilization with a consequent nutrient release. Among the factors that should be considered regarding mineral dissolution are the extractant solution's effect on the rate of dissolution, solution pH, ionic strength, concentrations of individual elements, temperature, and reactive mineral surface (Lasaga, Soler, Ganor, Burch, & Nagy 1994).

Recent studies have related mineral dissolution to variations in extractant, temperature, solution ionic strength and pH for the minerals kaolinite (Cama, Metz, & Ganor, 2002), fluorapatite (Guidry & Mackenzie, 2003), muscovite (Kuwahara, 2008; Oelkers, Schott, Gauthier, & Herrero-Roncal, 2008; Zhou & Huang, 2006), montmorillonite (Rozálen, Brady, & Huertas, 2009), smectite (Amram & Gaynor, 2005; Rozálen et al., 2008); potassium sources such as illite, biotite and microcline (Zhou & Huang, 2007); and even biotite and phlogopite bacterial dissolution (Balland, Pozwa, Leywal, & Mustin, 2010).

The use of rocks as alternative sources of potassium in the form of stonemeal, combined with phosphate reagents or even phosphate rocks, whose properties can promote the solubilization of potassium and the release of phosphorus and other nutrients, such as nitrogen, in satisfactory quantities, represents an alternative to the use of commercial fertilizers for use in organic agriculture and to minimize environmental damage caused by mining wastes.

In the present study, we aimed to characterize the mineralogy and evaluate the effects of using different extractants, contact times, and temperatures on the solubility of K present in rocks considered to be potential alternative sources of this nutrient.

Material and methods

The studied rocks were concentrated biotite ("biotite") (Mogi das Cruzes, São Paulo State), nepheline syenite ("syenite") (Poços de Caldas plateau, Minas Gerais State), and green banded argillite ("argillite") (Cedro de Abaeté region, Minas Gerais State). The concentrated biotite consisted of the material resulting from the magnetic separation of fine granite to obtain the mineral biotite.

The rocks were first subjected to grinding in a rotating ball mill for 20 minutes, and the material was separated using a sieve of 0.354 mm (Brasil, 2007), repeating the procedure until all samples reached this granulometry.

Major oxides were analyzed by Acme Analytical Laboratories Ltd. (Vancouver) using methods FullSuite 4A (major oxides) and 4B (trace elements) on a inductively coupled plasma emission spectrometer (ICP-ES). Ignition losses were determined by the weight difference of the sample before and after heating to 1000°C (Table 1).

For the X-ray diffraction (XRD) analysis of rocks obtained by the powder method, XRD patterns were obtained on a Shimadzu XRD-6000 diffractometer operating at 40 kV with a current of 20 mA and CuK radiation with a graphite monochromator. The amplitude sweep was 3 to 70 (2θ), and the recording speed was 1.5° 2θ min^{-1}.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed at Geoscience Laboratories (Sudbury) using a Zeiss Evo SEM scanning electron microscope, model EVO 50.

The experiments were conducted in the laboratories of the School of Environmental Sciences at the University of Guelph. The rocks were initially crushed in jaw crushers, followed by a disk mill. Rock size separations were performed using a WS Tyler Ro-Tap Sieve Shaker, Model RX-29, to homogenize the particle size to less than 125 microns (0.125 mm).

For the solubilization experiment, protocols described in the literature (Zhou & Huang, 2006; 2007) were followed with adaptations related to rock/extractant relationships, molar concentrations, rock-extractant contact times, and temperature. The procedure consisted of mixing 1 g of each rock with 10 mL of the following solutions: 1 mol L^{-1} ammonium dihydrogen phosphate ($NH_4(H_2PO_4)$), 0.07 mol L^{-1} monocalcium phosphate ($Ca(H_2PO_4)_2$), 0.1 mol L^{-1} sodium hydroxide (NaOH), and distilled water (control) in 15 mL centrifuge tubes.

Table 1. Total chemical compositions of rocks (% weight).

Rock	SiO₂	Al₂O₃	Fe₂O₃	MgO	CaO	Na₂O	K₂O	TiO₂	P₂O₅	MnO	Cr₂O₃	L.I.[1]
						%						
Biotite	52.53	15.00	14.99	3.33	1.98	1.72	6.41	1.89	0.41	0.22	0.003	1.1
Syenite	53.95	20.95	3.59	0.27	1.52	7.10	8.57	0.56	0.06	0.23	0.002	2.7
Argillite	51.70	14.48	6.02	3.68	4.83	0.08	9.87	0.70	0.09	0.08	0.014	8.2

[1]L.I.: loss of ignition.

Pure chemical salts were used to prepare the solutions, and the term "extractant" will be adopted to refer to solubilizing potassium and other elements in the rocks and minerals studied.

Treated samples were subjected to agitation at 120 rpm in an Eppendorf water shaker bath, model Innova 3100, at a water temperature of 25°C for periods of 3, 7, 10, 20, and 30 days of rock-extractant contact. Each treatment was performed three times. For the extractant $Ca(H_2PO_4)_2$, a molarity that corresponded to the maximum salt solubility (1.8 g in 100 mL) was used. The second experiment consisted of the same conditions as the first, with the water shaker temperature at 50°C.

At the end of each contact time period, treated samples in centrifuge tubes were removed from the shaker. Separation of the extractant-rock samples was performed by centrifugation at 3,000 rpm for 20 minutes in a Thermo Scientific centrifuge model Heraeus Megafuge 16. Solubilized potassium (K sol) in extractants was determined by spectrometric flame atomic absorption (FAAS) on a Varian spectrometer, model SpectrAA 50, equipped with an air-acetylene flame atomizer and HLA-4S cathode lamp.

The soluble K (K sol) was calculated based on the amount of K released by the sample (mg kg^{-1}), dividing this value by the total K amount present in the rock, as determined by the geochemical analysis (Table 1). The quantification of Al, Si, Fe, Ca, Mg, Mn, Zn, Sr, Ba, Cu, As, Cd, Pb, and Cr contents for treated samples under both temperatures at thirty days was performed by optical emission spectrometry with an induced plasma source (ICP-OES, Varian Vista Pro Model). Na was determined by FAAS. Ca was determined only for the extractant $NH_4(H_2PO_4)$ and water.

The experiment was performed using a randomized block design. Soluble K values for extractants, temperatures, and reaction times for each rock were submitted to analysis of variance, and when relevant, means grouping by the Tukey probability test was performed. Regression models correlating the amount of solubilized potassium (dependent variable) versus contact time for each extractant at both temperatures were generated at SISVAR (Ferreira, 2011).

Results and discussion

Rock characterization – X-ray diffraction (XRD) and scanning electron microscopy (SEM)

The mineralogical characterization of the rocks biotite, syenite and argillite, with identification of their respective minerals, is described below (Figure 1).
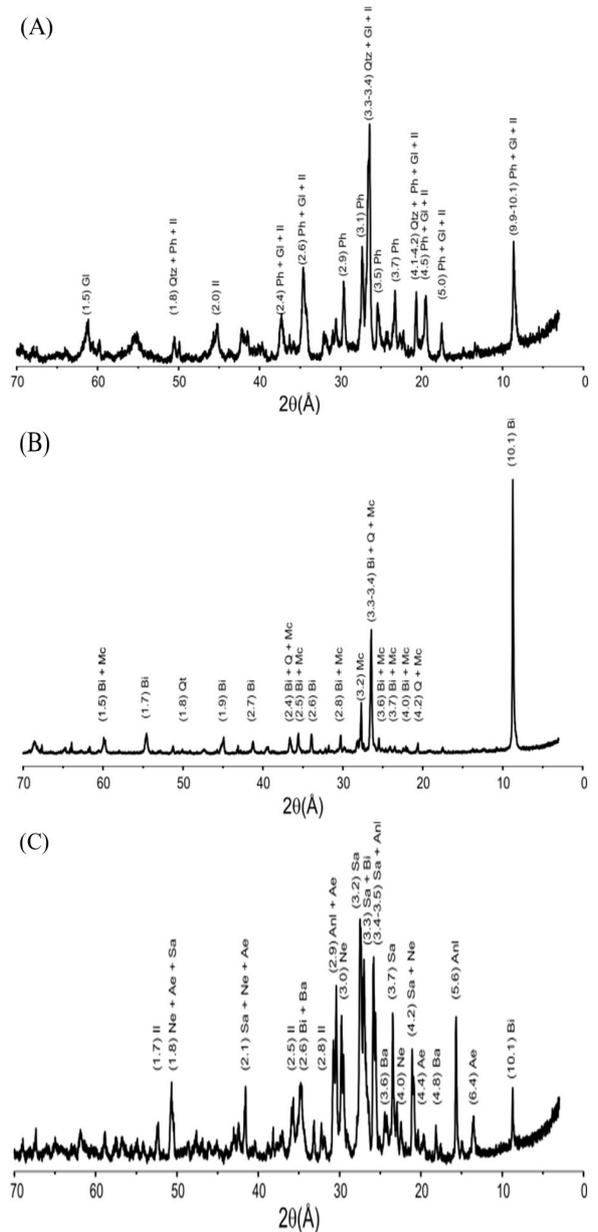

Figure 1. X-ray diffractograms from rocks. A) Argillite, where phengite (Ph): 9.95(1), 2.57(0.85), 4.47(0.78); illite (Il): 3.34(1), 10.0(0.9), 5.01(0.5); glauconite (Gl): 10.1(1), 2.59(1), 4.53(0.8); and quartz (Qtz): 3.34(1), 4.26(0.22), 1.81 (0.14). B) Biotite, where biotite (Bi), peaks/intensity: 10.07(1), 2.63(0.31), 3.36(0.27); quartz (Qtz): 3.34(1), 4.26(0.22), 1.81 (0.14); microcline (Mc): 3.76(1), 3.247(0.84), 3.241(0.75). C) Syenite, where nepheline (Ne): 3.06(1), 4.25(0.75), 4.015(0.7); sanidine (Sa) 3.35(1), 3.79(0.9), 3.24(0.8); biotite (Bi): 10.1(1), 3.37(1), 2.66(0.8), analcime (An): 3.43(1), 2.925(0.8), 5.61(0.8); aegirine (Ae): 2.9(1), 6.369(0.9), 4.416(0.8); balliranoite (Ba) 4.797(1), 3.281(0.73), 2.662(0.58); ilmenite (Il): 2.754(1), 2.544(0.7), 1.7261(0.55).

In the studied rocks, some minerals identified by XRD were visualized by SEM, and the chemical composition was also confirmed by dispersive X-ray spectrometry (EDX) of the mineral phases present (Figure 2).

For biotite, the minerals quartz, sodic and potassic feldspars albite and microcline and mica biotite were observed, with the last two considered as potential sources of K.

Syenite contained the minerals nepheline, sanidine and titanite. DRX also indicated the minerals biotite, analcime, aegirine and balliranoite (Figure 1). As K sources, the feldspathoids nepheline and balliranoite and biotite mica could be considered, with high weathering rates of the latter according to the Goldich dissolution series (Goldich, 1938).

In argillite rock, the minerals glauconite, phengite and illite, observed by DRX, constitute the main potential K sources (Figure 1C). Phengite, a dioctahedral mica similar to muscovite, and glauconite and illite belong to the phyllosilicate group. Glauconite and titanite were also observed by SEM according to EDX (Figure 2).
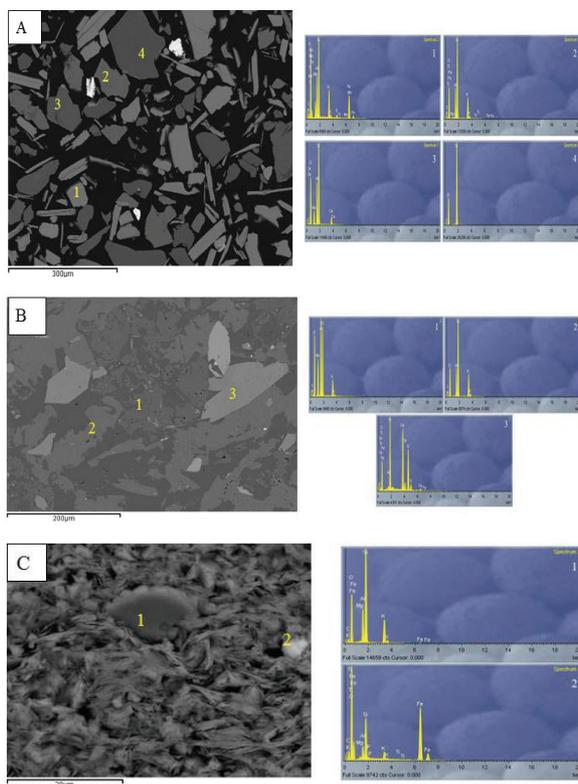

Figure 2. Scanning electron microscopy (SEM) images and chemical compositions of mineral phases present in rocks and minerals. A) Biotite: 1 - biotite, 2 - microcline, 3 - albite, 4 - quartz; B) Syenite: 1 - nepheline, 2 - sanidine, 3- titanite; C) Argillite: 1 - glauconite, 2 - titanite.

Extractants and K solubilization

The percentages of soluble K (K sol) of biotite, syenite, and argillite were significantly different under the effects of the extractors 1 mol L^{-1}

$NH_4(H_2PO_4)$, 0.07 mol L^{-1} Ca $(H_2PO_4)_2$, 0.1 mol L^{-1} sodium hydroxide (NaOH) and water at temperatures of 25C and 50°C (Figure 3). For the same extractor, there were also differences in the K sol between rocks.

The highest values of K sol for syenite and argillite were observed with the use of the extractant $NH_4(H_2PO_4)$ at 25 and 50°C. The similarity between the ionic radii of potassium and ammonium and the high concentration of ammonium in solution (ionic strength) might have contributed to the displacement and solubilization of the K present on the outer surfaces and exchange points of the external surfaces of mineral components of the rocks. For biotite, the extractant $Ca(H_2PO_4)_2$ promoted the release of more soluble K (Figure 3).

A hypothesis to explain the lower soluble K verified for biotite (< 1 mg kg^{-1}) may be related to the phenomenon of Fe^{3+} oxidation, promoting the release of some cations at octahedral sites, leaving them empty. This activity causes the reorientation of H^+ and OH^- ions away from K, occasioning a high retention of K and increasing mineral stability (Melo, Castilhos, & Pinto, 2009).

For water, the highest K sol was observed for argillite, which is due to the mineralogical composition of this rock, with the phyllosilicates glauconite, phengite and illite (XRD). In phyllosilicates, the protonation of aluminol (Al-OH) and silanol groups (Si-OH) with ruptures of metal-oxygen bonds followed by the dissolution of basic cations from interlayers and octahedral sheets predominates in hydrolysis reactions (Kampf, Curi, & Marques, 2009), releasing high amounts of K.

The average pH levels of the extractant solutions were 4.05 ($NH_4(H_2PO_4)$), 3.5 ($Ca(H_2PO_4)_2$), 12.8 (NaOH), and 6.0 (water). In the initial stage of mineral dissolution, the rates of surface complexation reactions increase with the increased concentration of protons (acidic conditions) and some ligands as well as under alkaline conditions (OH^- groups) (Sokolova, 2013), with the minimum dissolution at pH values near the zero point of charge (pH $_{pzc}$) from minerals (e.g., some oxides and aluminosilicates) (Oelkers et al., 2008; Rozalén et al., 2008; White, 2008).

Higher K sol was observed under acidic solution pH, with the extractants $NH_4(H_2PO_4)$ and $Ca(H_2PO_4)_2$. Even with a pH difference of only 0.55, the high K sol observed for the more acidic extractant could be related to its ionic strength.

In mineral dissolution, a higher molar concentration (ionic strength) of reagents (extractants) can promote higher reaction velocities (law of mass action) and, therefore, higher element

solubilization. The ionic strength of the extractants $NH_4(H_2PO_4)$: 1 mol L^{-1}, $Ca(H_2PO_4)_2$: 0.07 mol L^{-1}, and NaOH: 0.01 mol L^{-1} implies higher solubilization rates for the $NH_4(H_2PO_4)$ extractant, as was observed for K sol and other elements quantified (Table 2).
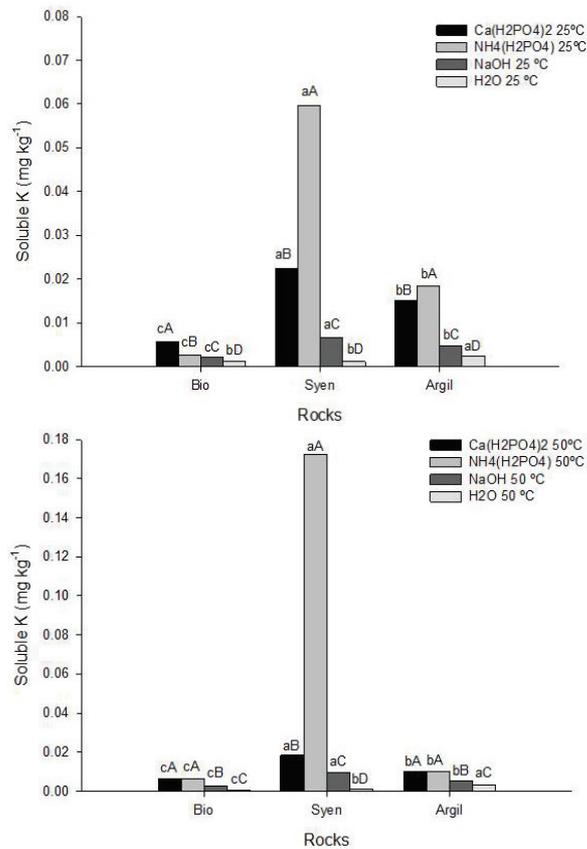

Figure 3. Soluble potassium (mg kg^{-1}) from rocks for different extractants at 25 and 50°C.

Means followed by the same lowercase letter for each extractant (rocks) and uppercase letter on each rock (extractants) do not differ by the Tukey test at 5% probability.

With respect to phosphorus extractants, $H_2PO_4^-$ ions are the predominant form of phosphorous in soil at pH values near neutrality (5.5-6.5), whereas the HPO_4^{2-} form present in the extractant $Ca(H_2PO_4)_2$ prevails at higher pH values and is less soluble due to the presence of Ca^{2+} (Lindsay, 2001; Mello & Perez, 2009).

In addition to the similar ionic radii of the ions NH_4^+ and K^+, the binding effect of phosphate ions (Zhou & Huang, 2006; 2007) and the predominant ion form $H_2PO_4^-$ for $NH_4(H_2PO_4)$ may also explain the higher soluble K^+ levels for this extractant.

The contact time did not influence the amounts of soluble K for the treatments $Ca(H_2PO_4)_2$ syenite (50°C), NaOH syenite (25°C) and NaOH argillite (25 and 50°C), and even reduced the amounts for the treatments $Ca(H_2PO_4)_2$ syenite (25°C), $Ca(H_2PO_4)_2$ argillite (50°C), NaOH biotite (25 and 50°C) and NaOH syenite (50°C), water biotite (25°C), water syenite (25°C) and water argillite (50°C) (Table 2).

Rock sample preparation (crushing and milling) may affect the reactive site density and distribution (Baere, François, & Mayer, 2015), and the presence of ultrafine particles on the mineral surface may promote an initial intense element release, decreasing mineral dissolution over time (Sokolova, 2013).

Increasing temperature results in an increase in soluble K for most rock-extractor combinations (Table 2). Elevated temperatures suggest a high energy (agitation) of ions and molecules dissolved in the solutions, enhancing the number of collisions at the mineral surface and occasioning the release of elements (including K).

Table 2. Effects of contact time (per extractant) at each temperature on the percentage of soluble potassium (mg kg^{-1}) for biotite, syenite, and argillite.

Rock	Time (d)	$NH_4(H_2PO_4)$		$Ca(H_2PO_4)_2$		NaOH		Water	
		25°C	50°C	25°C	50°C	25°C	50°C	25°C	50°C
Biotite	3	0.0023bA	0.0018dA	0.0057aA	0.0057bA	0.0021aA	0.0020aA	0.0010aA	0.0010bA
	7	0.0023bB	0.0028cA	0.0056aB	0.0065abA	0.0023aA	0.0020aA	0.0012aA	0.0008abB
	10	0.0026bA	0.0031cA	0.0058aB	0.0065abA	0.0022aA	0.0021aA	0.0011aA	0.0007aB
	20	0.0028bB	0.0053bA	0.0060aA	0.0064abA	0.0022aA	0.0021aA	0.0015aA	0.0007abA
	30	0.0035aB	0.0071aA	0.0059aB	0.0072aA	0.0021aA	0.0022aA	0.0010aA	0.0008abB
Syenite	3	0.0420cB	0.1163bA	0.0221aA	0.0200aA	0.0070aB	0.0093aA	0.0011aA	0.0009aB
	7	0.0555bB	0.1421aA	0.0216aA	0.0209aA	0.0070aB	0.0097aA	0.0011aA	0.0011aA
	10	0.0547bB	0.1293abA	0.0238aA	0.0182bcB	0.0068aB	0.0098aA	0.0010aA	0.0009aA
	20	0.0711aB	0.1336abA	0.0226aA	0.0161cB	0.0067aB	0.0094aA	0.0012aA	0.0011aA
	30	0.0749aB	0.1232abA	0.0229aA	0.0172cB	0.0054bB	0.0103aA	0.0011aA	0.0012aA
Argillite	3	0.0136cB	0.0167eA	0.0115abA	0.0104aB	0.0060aA	0.0057aA	0.0021bB	0.0028aA
	7	0.0180bA	0.0154dB	0.0111bA	0.0106aB	0.0052abA	0.0052abA	0.0024abB	0.0031aA
	10	0.0186bcA	0.0166cB	0.0111bA	0.0097aB	0.0045bcB	0.0051bA	0.0024aB	0.0032aA
	20	0.0197aB	0.0209bA	0.0115abA	0.0099aB	0.0042cdB	0.0048bA	0.0025aB	0.0031aA
	30	0.0191abB	0.0234aA	0.0124aA	0.0113aB	0.0035dB	0.0048bA	0.0025aA	0.0031aA

For each rock and extractant, means followed by the same lowercase letter (column) and uppercase letter (line) do not differ by the Tukey test at 5% probability.

The lack of differences in soluble K for biotite for the extractor NaOH with both temperatures and reaction times may be related to the pH of NaOH, as acidic conditions promote higher potassium release (Bray et al., 2015).

In a dissolution kinetics study of illite under the influence of phosphates (0.5 M $Ca(H_2PO_4)_2$ at pH 2.5, 1 M $NH_4(H_2PO_4)$ at pH 4.0, and 1 M $(NH_4)_2HPO_4$ at pH 8.0) at temperatures of 25 and 45°C, the effect of H^+ on K^+ release was weaker for pH values greater than 4.0, with an increase in K^+ release for the $NH_4(H_2PO_4)$ solution due to the combined effect of phosphate ions and H^+. With increasing temperature, the differences in the K^+ release rates between the $NH_4(H_2PO_4)$ and $(NH_4)_2HPO_4$ solutions decreased, with no differences observed at a temperature of 45°C, with phosphate ions being the most important factor for K^+ release at high temperatures (Zhou & Huang, 2007).

The effect of phosphate ions with increasing temperature resulted in a greater solubility of syenite with the extractant $NH_4(H_2PO_4)$ in the present study, whereas for other rocks and extractants, no effects of ions and temperature on K sol were observed, and there was even a reduction in K sol with increasing temperature in some treatments.

A potassium solubilization experiment was conducted by Silva, Medeiros, Sampaio, and Garrido (2012) using sequential extractions (10 extractions each for contact times of 1, 8, 24, 48, 72, 144, 288, 312, 336, and 624 hours) with 0.1 mol L^{-1} citric acid, 0.1 mol L^{-1} oxalic acid, and Mehlich-1 solution (HCl 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1}) on Verdete Cedro do Abaeté rock. After the 1857-hour experiment, extraction rates of 2.4, 10.7, and 3%, respectively, were achieved for the total potassium present in the samples.

In the present study, argillite rock, similar to Verdete, presented a maximum K sol value of 0.0234 mg kg^{-1} for the extractant $NH_4(H_2PO_4)$. The reduced evaluation time (30 days) and lack of sequential extractions on samples after each contact time may explain the reduced values compared to the work cited above.

The relationship between contact time and K sol (mg kg^{-1}) was linear for biotite and the extractant $NH_4(H_2PO_4)$, with coefficients of determination (R^2) of 0.9541 and 0.9874 for temperatures of 25 and 50°C, respectively, with more soluble K at 25°C (Figure 3A).

For the extractants $Ca(H_2PO_4)_2$ and water, respectively, at 50°C, linear and quadratic correlations best described the amount of K sol with reaction time (Figure 3B). In addition to the

negative effect of increased pH on dissolution rates, the grain size, superficial mineral area and chemical mineral composition may also influence the release of K and other nutrients, such as Fe, Mg and Al, from biotite (Bray et al., 2015).

Quadratic equations best described the relationship between K sol and contact time for the extractant $NH_4(H_2PO_4)$ at both temperatures (25 and 50°C) for syenite. More K sol was observed at 25°C (Figure 4A). The extractants NaOH (25°C) and $Ca(H_2PO_4)_2$ (50°C) showed linear and quadratic relationships between the variables, with R^2 values of 0.8162 and 0.7682, respectively (Figure 4B).
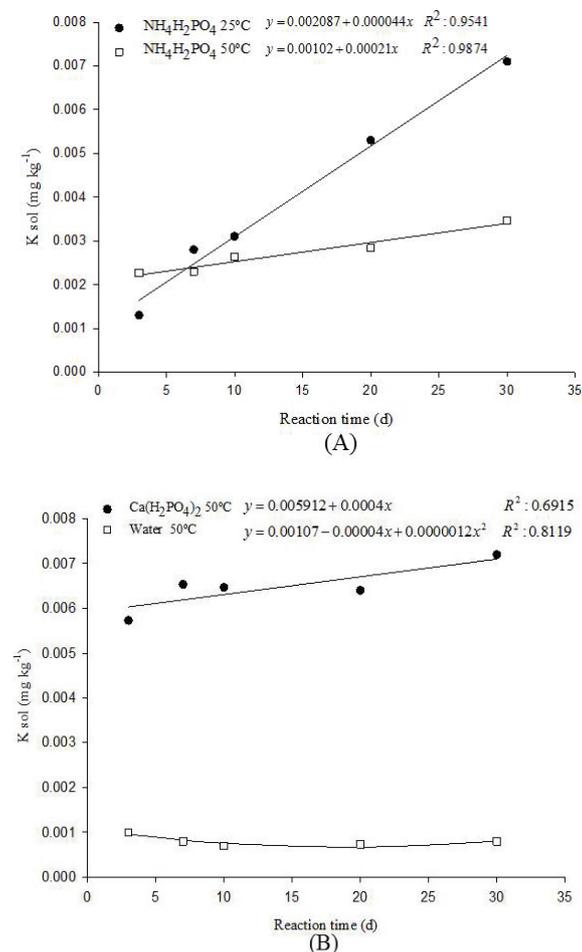

Figure 4. Percentage of soluble potassium (K sol) as a function of reaction time (d) for biotite with different extractants: (A) – $NH_4(H_2PO_4)$ and (B) – $Ca(H_2PO_4)_2$ and water.

A linear K release over the period of 1 year was observed for the feldspathoid nepheline at pH 5, with reduced K release at pH 7. The K release from nepheline (38 meq g^{-1}) was an order of magnitude higher than for K feldspars (lower than 5 meq g^{-1}). Rocks containing nepheline are more effective K sources than rocks with K feldspar alone (Manning,

2010). The presence of nepheline in syenite rock (Figure 1) and the effects of extractant pH effects on this mineral might also have influenced the amounts of K released from this rock (Figure 5).
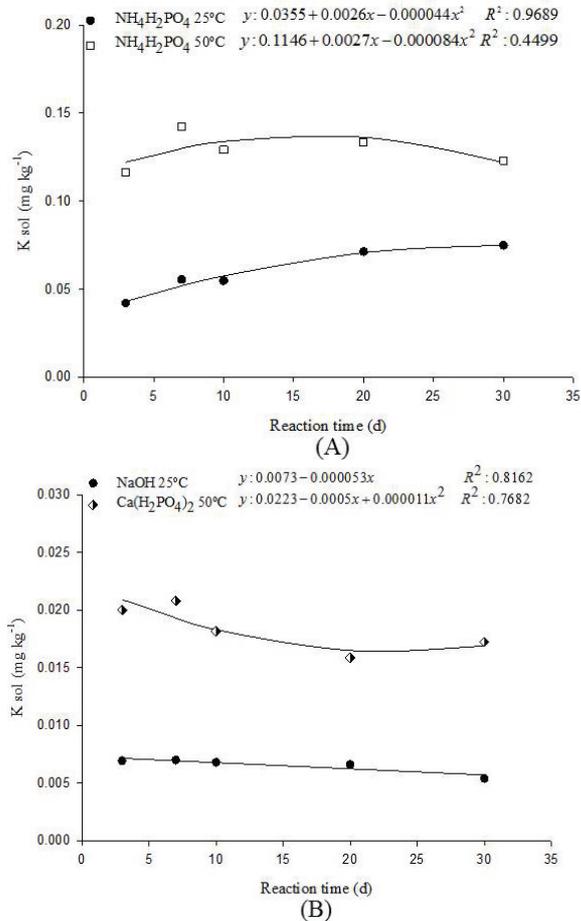

Figure 5. Percentage of soluble potassium (K sol) as a function of reaction time (d) for syenite with different extractants: (A) – $NH_4(H_2PO_4)$ and (B) – NaOH and $Ca(H_2PO_4)_2$.

The relationship between K sol and contact time for the extractants $NH_4(H_2PO_4)$ and NaOH, at both temperatures studied, for argillite rock were best described by quadratic equations, with R^2 values of 0.9975 and 0.9986 for $NH_4(H_2PO_4)$ and 0.9854 and 0.9697 for NaOH at 25 and 50°C, respectively (Figures 6A and B). For the extractants $Ca(H_2PO_4)_2$ and water, linear and quadratic equations best described the relationships between K sol and contact time (Figure 6C).

For the extractant NaOH, an initial high release of K, decreasing with contact time, suggests K solubilization from external surfaces or exchange points from the clay minerals composing argillite or even the presence of ultrafine particles on the mineral surface.

The effects of acidic pH and phosphate extractants on K solubilization were verified for illite (Zhou & Huang, 2007), a mineral composing argillite rock (Figure 1C), which may explain the higher solubilization for the extractants $NH_4(H_2PO_4)$ and $Ca(H_2PO_4)_2$.
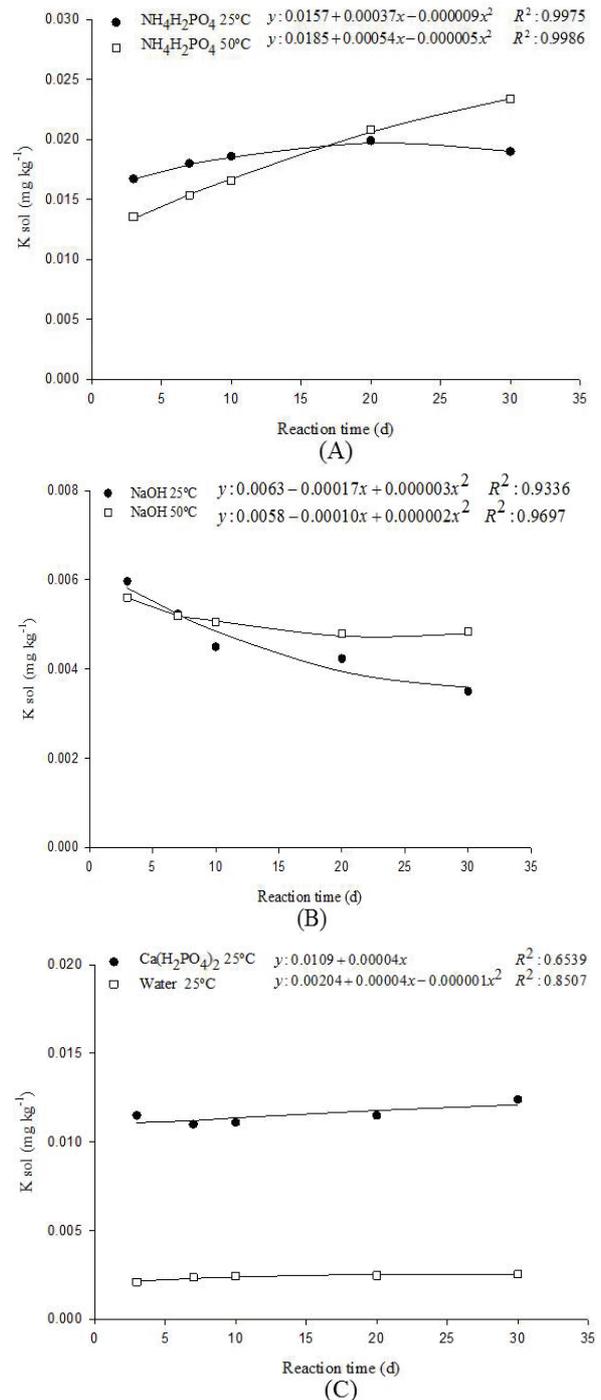

Figure 6. Percentage of soluble potassium (K sol) as a function of reaction time (d) for argillite with different extractants: (A) – $NH_4(H_2PO_4)$, (B) – NaOH, and (C) – $Ca(H_2PO_4)_2$ and water.

The amounts of the main mineral elements included in the studied rocks, quantified at 3 (initial) and 30 d (final) of contact time for the extractants $NH_4(H_2PO_4)$, $Ca(H_2PO_4)_2$, and water at 25 and 50°C, are presented in Table 3.

The extractor $NH_4(H_2PO_4)$ produced higher solubilization of the elements present in the mineral components of the rocks under study. For syenite, high amounts of calcium (Ca), magnesium (Mg) and sodium (Na) were released for the extractant $NH_4(H_2PO_4)$ along with a high release of Mg and Na for extractant $Ca(H_2PO_4)_2$.

The feldspathoids nepheline and balliranoite, zeolite analcime and feldspar sanidine, which include Na in their chemical composition, may be the minerals that release Na, making it available in solution. Minerals proposed to promote the release of Ca and Mg include balliranoite (feldspathoid), aegirine (pyroxene) and biotite (mica). Based on the mineralogical composition of syenite, a sequence of mineral weathering was proposed based on the Goldich dissolution series: feldspathoids> pyroxenes>micas>zeolites>feldspars.

In the analysis of biotite, for the extractants $NH_4(H_2PO_4)$ and $Ca(H_2PO_4)_2$, considerable amounts of Fe and Mg were present in solution, indicating the weathering of this iron-magnesium phyllosilicate. For the $NH_4(H_2PO_4)$ extractant, the high amounts of Ca might be related to alteration of the mineral albite, which, compared to other minerals present in the modified biotite rock, such as quartz and microcline, presents lower resistance to weathering according to the Goldich dissolution series.

For argillite, the high Na and Mg levels after treatment with $NH_4(H_2PO_4)$ and $Ca(H_2PO_4)_2$ (Table 3) suggest the high weathering of glauconite phyllosilicate based on its mineral chemical formula: $(K,Na)(Al,Fe,Mg)_2(Si,Al)_4O_{10}(OH)_2$.

Other elements that might also be solubilized by the extractants used in this study, such as As, Cd, Pb, Cr, Hg, Ba, and Cu, showed readings below the device detection limit and were not considered in this work. The levels of these elements were below the maximum limits allowed for K mineral fertilizer, according to Normative Instruction No. 27 (Brasil, 2006).

In practical terms, the agronomic application of this rocks to soybean culture as fertilizers, with recommended doses of 38 kg of K_2O per ton of grain produced (Junior, Castro, Oliveira, & Jordão, 2013) based on the maximum values of soluble K (mg kg^{-1}) of rocks studied, would require 4,920,000 tons of biotite, 529,321.6 tons of syenite or 1,714,801.4 tons of argillite to supply soybean demand, whereas for KCl fertilizer, less than 0.5 ton is used (0.063 ton).

Considering the high masses of rocks to be applied and the economic costs of both material transport and the processes used to obtain the rocks (e.g., concentrated biotite), the proposal is to adopt these rocks as complementary fertilizers rather than substitute them for conventional fertilizers.

Table 3. Elemental analysis of solutions of $NH_4(H_2PO_4)$, $Ca(HPO_4)_2$, and water at 30 days (contact time) on biotite (bio), syenite (syen), and argillite (argil), at 25 and 50°C.

Extractant	Rock	Al	Si	Fe	Ca	Mg	Na	Mn	Zn	Sr
$NH_4(H_2PO_4)$/ 25°C	Bio	0.0026	0.0443	0.0050	0.5027	0.1656	0.0081	0.4655	0.0085	0.0162
	Syen	0.0111	0.0544	0.0033	0.9199	0.0148	2.2154	0.0241	0.0232	0.2642
	Argil	0.0015	0.0436	0.0075	<LD	0.1651	0.1163	1.0150	<LD	0.0162
$NH_4(H_2PO_4)$/ 50°C	Bio	0.0048	0.0651	0.0014	0.5604	0.4126	0.0156	0.4360	0.0048	0.0233
	Syen	0.0245	0.0527	0.0009	0.8263	0.3852	3.4189	0.3365	0.0571	0.0556
	Argil	0.0010	0.0600	<LD	0.0713	0.4423	0.1853	0.9339	<LD	0.0129
$Ca(H_2PO_4)_2$/ 25°C	Bio	0.0010	0.0301	0.0002	N.D.	0.1246	0.1489	0.3461	<LD	<LD
	Syen	0.0279	0.2982	<LD	N.D.	0.2568	0.7976	0.0172	<LD	<LD
	Argil	0.0014	0.0391	0.0003	N.D.	0.1399	0.3942	0.8211	<LD	<LD
$Ca(H_2PO_4)_2$/ 50°C	Bio	0.0005	0.0692	0.0002	<LD	0.2724	0.0640	0.4526	<LD	<LD
	Syen	0.0074	0.1679	<LD	<LD	0.5580	0.4757	0.0695	<LD	0.1403
	Argil	0.0007	0.0664	0.0004	<LD	0.1746	0.3774	1.2228	0.0941	<LD
Water/ 25°C	Bio	<LD	0.0011	<LD	0.1097	0.0032	0.0147	<LD	<LD	<LD
	Syen	0.0006	0.0012	0.0004	0.0558	0.0284	0.0869	<LD	<LD	0.0339
	Argil	<LD	0.0058	<LD	0.0035	0.0043	0.3268	<LD	<LD	<LD
Water/ 50°C	Bio	<LD	0.0028	<LD	0.1196	0.0051	0.1011	<LD	<LD	<LD
	Syen	0.0001	0.0021	<LD	0.0721	0.0432	0.1716	<LD	<LD	0.0453
	Argil	0.0197	0.0273	<LD	0.0000	0.0311	0.3420	0.0534	<LD	<LD

n.d.: element not detected; <L.D.: element below detection limit (< 0.001 mg L^{-1})

Knowledge of the mineralogy of rocks and the main mineral contributors to the release of elements (nutrients) can suggest potential alternative sources for use in soil fertilization and plant nutrition. Future experiments under field conditions with combinations of different rocks, extractors and plants for long-term evaluation periods are suggested.

Conclusion

The contact time, temperature, and extractants enhanced K solubilization from the rocks studied.

The extractants that promoted greater solubility according to the content of soluble potassium (K sol) in biotite, syenite, and argillite were, in the following order, $NH_4(H_2PO_4) > Ca(HPO_4)_2 > NaOH > water$.

The sequence of K release (ppm) based on the rocks studied was as follows: nepheline syenite > green banded argillite > concentrated biotite.

Acknowledgements

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