

## EFFECT OF MECHANICAL ACTIVATION ON THE POTASSIUM AVAILABILITY OF PHONOLITE ROCK

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### ABSTRACT

**Background:** Researches are carried out to assess rocks containing potassium as an alternative source of fertilizers. These studies are important in reducing the external dependence of Brazil on this commodity. Phonolite is a rock of volcanic origin that has in its mineralogical composition the predominance of feldspar and has been potential to use as an alternative potassium source. The studied rock has 6% total-K but is unavailable to plants in natural rock. **Aim:** This project evaluated the effect of mechanical activation, wet and dry, on K availability for extractors different and its K leaching curves of phonolite from Poços de Caldas, MG, Brazil. **Methods:** Phonolite rock was subjected to mechanical activation for 30 and 60 min by wet and dry processes. Particle size distribution, XRD, and FTIR analyses characterized phonolite activated. These results were compared to the behavior of the rock with no activation. K availability (total; water-soluble; exchangeable, non-exchangeable, and structural) was determined in samples activated and no activation. K leaching curves were obtained by successive extractions with 0.01 mol L<sup>-1</sup> citric acid and Mehlich-1 solutions to 1812 h and analyzed by FAAS. **Results:** The samples mechanical activation promoted a reduction in the intensity of the diffraction peaks. In the sample dry mechanical activation for 60 min, K released increased by 15% in relation to the no activation sample. K leaching curves were observed with similar behavior for the extractors and higher K availability after 235 h of total contact time. **Discussion:** Mechanical activation promoted a decrease in structural K and an increase in non-exchangeable K, released into the soil solution in the medium term. Since the mineralogical composition was not changed, the process action is more efficient in creating the structural defects suggested. K leaching curves corroborate these results, with a continuous and slow K released for a longer contact time. **Conclusions:** It was concluded that the phonolite activated by dry mechanical activation for 60 min increased K-released content compared with the wet process and ratified the possibility of the activated phonolite rock as a slow-release fertilizer.

**Keywords:** *phonolite, alternative fertilizer, mechanical activation, potassium exchangeable, leaching curve.*

### 1. INTRODUCTION

The direct use of rocks in agriculture is a natural fertilization technique called stonemeal (rocks for crops) or remineralization. This technique consists of gradually releasing nutrients from the stone powder into the ground through chemical weathering (Straaten, 2007).

The advantages of the stonemeal are the geological diversity of rocks with potential for application in Brazilian agriculture which contributes to lower transport costs and helps streamline family agriculture and agro-ecological production (Plata *et al.*, 2021; Ramos *et al.*, 2014; Straaten, 2006; Theodoro and Leonardos, 2006). In addition, the use of rocks for crops is considered a global strategy for sustainable land

use and lower production cost than synthetic fertilizers, as these new commodities consist of crushed or ground minerals that release nutrients slowly (Jena, 2021; Kleiv and Thornhill, 2007; Plata *et al.*, 2021; Ramos *et al.*, 2014; Straaten, 2006).

Several articles report application experiences with rocks in nature or associated with other rocks as alternative sources for agriculture, as well as concomitant use with organic or biological materials that may favor the availability of potassium nutrients (Bhatti *et al.*, 2011; Jena, 2021; Manning, 2010; Sanz Sconivo and Rowell, 1988; Silva *et al.*, 2013; Straaten, 2007). The use of rock dust as an alternative source for agriculture can also be applied in organic and conventional farming systems (Bhatti *et al.*, 2011; Guelfi-Silva *et al.*, 2013; Manning, 2010; Silva *et al.*, 2013), provided that the physical and chemical characteristics of such materials are known (Teixeira *et al.*, 2011; Teixeira *et al.*, 2012). However, for a mineral to be considered an alternative source for application in agriculture, it is not enough that it has a high content of nutrients; it is necessary that these nutrients are available for the plants. Thus, mineralogy is one of the most important factors in the selection of rocks that can release nutrients (Bhatti *et al.*, 2011; Guelfi-Silva *et al.*, 2013; Jena, 2021; Manning, 2010; Nascimento and Loureiro, 2004; Silva *et al.*, 2013; Teixeira *et al.*, 2011; Teixeira *et al.*, 2012). For example, feldspars potassium, mica, vermiculite, and smectite are minerals primarily related to the presence and K availability in the soil; however, rocks containing nepheline mineral are more effective in the release K than rocks that have only potash feldspar (Kleiv and Thornhill, 2007; Manning, 2010; Nascimento and Loureiro, 2004; Sanz Sconivo and Rowell, 1988; Straaten, 2007).

Phonolite is a rock of volcanic origin that has the predominance of potassium feldspar, plagioclase feldspar, and feldspathoids in its mineralogical composition. The high presence of alkaline oxides makes phonolite a melting rock widely used by the ceramic industries (Andrade *et al.*, 2005). Additionally, the application of this rock has been evaluated as an alternative potassium source, especially in acidic soils, once the release of the nutrient in potassium-rich silicates involves a surface reaction that increases with decreasing pH (Kleiv and Thornhill, 2007; Manning, 2007; Straaten, 2007; Teixeira *et al.*, 2011).

Mechanical activation is considered a

branch of the mechanochemical science that features a wide variety of potential applications (d'Azevedo *et al.*, 2006; Baláz and Dutková, 2009; Baláz *et al.*, 2008; Erdemoğlu and Baláz, 2012; Kleiv and Thornhill, 2007; Pourghahramania and Akhgar, 2015; Sabah *et al.*, 2013; Sandvik *et al.*, 2011; Silva, 2009; Silva *et al.*, 2012; Temuujin *et al.*, 2003; Vdovic *et al.*, 2010). The literature contains several examples demonstrating that mechanical activation can accelerate the reaction rate and the leaching of the activated minerals, allowing reactions to occur in shorter times and at lower temperatures (d'Azevedo *et al.*, 2006; Baláz and Dutková, 2009; Baláz *et al.*, 2008; Kleiv and Thornhill, 2007; Pourghahramania and Akhgar, 2015; Temuujin *et al.*, 2003). For example, studies of mechanically activated rock by high-intensity milling for the production of ultrafine fertilizer powder have shown that mechanical activation can be used to increase the release of potassium from materials containing potassium feldspar (Kleiv and Thornhill, 2007). The increased reactivity of the products obtained by grinding was attributed to the increase of the specific surface area and structural disorder. Furthermore, adding a small amount of water in the grinding makes it possible to obtain products with higher specific surface area, greater structural disorder, and greater reactivity (Kleiv and Thornhill, 2007).

To determine the efficiency of potassium release in mineral sources, several extractors are used to facilitate the mineral weathering and simulate the acidic environment produced by the plant in the rhizosphere region (near the root). Ion exchange resins usually perform these studies, dilute salt solutions, and low molecular weight organic acids such as citric and oxalic acids, which facilitate mineral wear by forming metal-organic acid complexes (Castilhos and Meurer, 2001; Silva, 2009). Considering its availability to plants, soil, and rocks, potassium can be classified into four categories: water-soluble, exchangeable, non-exchangeable, and structural. These categories follow a decreasing order of potassium availability (Villa *et al.*, 2004). The water-soluble K corresponds to the amount of  $K^+$  extracted by a specific volume of water and represents the content of this ion adsorbed by the colloidal particles of the soil. Exchangeable K, by definition, is one that is free to exchange with cations of saline solution added to the soils and corresponds to the ionic form that is electrostatically bound to minerals that make up the solid part of the soil or rock. The non-exchangeable K is the  $K^+$  of reserve or

replacement of soils, for example,  $K^+$  retained in the interlayer of some expandable 2:1 clay mineral. Finally, the structural K is the  $K^+$  strongly bound to the crystalline structure of the minerals (Castilhos and Meurer, 2001; Nascimento and Loureiro, 2004; Silva, 2009; Straaten, 2007; Villa *et al.*, 2004).

In this context, this study aimed to verify the effect of mechanical activation on  $K^+$  availability of phonolite rock from the Poços de Caldas Plateau, MG, Brazil. The different forms of potassium (total; water-soluble; exchangeable, non-exchangeable, and structural) were determined for the unmilled rock and for samples subjected to mechanical activation for 30 and 60 minutes, both by wet and dry processes. We also obtained K leaching curves for samples with mechanical activation.

## 2. MATERIALS AND METHODS

### 2.1. Pre-preparation of the rock

The phonolite rock in a study is from Poços de Caldas Plateau, Minas Gerais, Brazil, and has 6% of  $K^+$  total and is mainly composed of alkali feldspar and feldspathoids, i.e., microcline and orthoclase, sanidine and nepheline (Andrade *et al.*, 2005; Teixeira *et al.*, 2011; Teixeira *et al.*, 2012). In addition, in preliminary studies on K availability, the results obtained with the phonolite rock corroborate with the results found in the literature for different silicate rocks rich in potassium (Araújo and Sampaio, 2010; Silva *et al.*, 2012; Teixeira *et al.*, 2012; Teixeira *et al.*, 2015).

The phonolite samples preparation was performed by the following steps: comminution, screening, homogenization, and quartering. First, the comminution was performed by the jaw and roller crusher to allow fragmentation of the sample up to particle size below 4.7 mm, with little production of thin materials. Next, the sample homogenization and quartering were carried out by employing a conical pile followed by a longitudinal pile to obtain a uniform distribution of the rock constituents (Sampaio *et al.*, 2007). Thus, after the preparation steps, the samples have the appropriate mass and particle size for the tests, i.e., samples of 1 to 20 kg with a particle size of less than 4.7 mm (Teixeira *et al.*, 2011; Teixeira *et al.*, 2012).

### 2.2. Mechanical Activation Tests

The mechanical activation assays were performed in a stainless-steel cylindrical mill with dimensions of 150 x 297 mm (diameter x length) and a body grinder of 10 bars with dimensions of 500 x 293 mm (diameter x length). The rock samples were submitted to mechanical activation, wet and dry, for 30 to 60 minutes, with a mill rotation speed of 70 rpm. In dry mechanical activation, 1 kg of rock sample was used, while in the wet mechanical activation tests, a paste containing about 1 kg of rock and 1 L of water was used. The mass of the bars used in milling was 9 kg, so the ratio of the mass of the sample to the mass of the bars was 1:9.

After mechanical activation, the samples were homogenized and quartering by means of a Jones-type splitter for obtaining aliquots with appropriate mass for conducting the characterization, K availability tests, and K leaching curves.

### 2.3. Samples Characterization

The homogenized unmilled phonolite and the activated samples were characterized in terms of particle size distribution and phase analysis. The unmilled phonolite was submitted to chemical and mineralogical characterization by techniques of X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM-EDS). XRD and FTIR characterized the active samples.

The wet particle size distribution of the prepared samples was performed with a 250 g sample and in a vibratory sifter with sieves according to Tyler series from 3.3 to 0.038 mm. The fractions obtained from the particle size distribution assays were dried in an oven at a temperature of 70 °C and weighed the sample fractions to obtain the passing percentage.

XRF analysis was performed in a PANalytical, Axios model with a rhodium tube (4kw) and a wavelength dispersion detector (WDS). The sample was fused with lithium tetraborate, and the results were expressed as oxides and standard to 100%. Humidity and fire assay were realized by gravimetric analyses at 100 and 1000 °C, respectively.

XRD analysis were performed in a Bruker-D4 Endeavor equipment, with 0.02°

goniometer step in  $2\theta$  and 1.0 second of count time and radiation Co-K $\alpha$  ( $\lambda = 1.789 \text{ \AA}$ ; 35 kV/40 mA), with angular range ( $2\theta$ ) between 4 to  $80^\circ$ . X-ray diffraction for samples is shown as a function of Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) to facilitate comparison with the data normally found in the literature. In addition, interpretations of XRD patterns were made by comparison with the standards of the Web ICSD database.

FTIR analysis was performed in a Magna 760 Nicolet equipment, and wave numbers range from 4000 at 400  $\text{cm}^{-1}$  to 4  $\text{cm}^{-1}$  of resolution. The spectrums were obtained using anhydrous KBr discs. Assignments of observed bands in infrared spectra were performed by trial-and-error and based on literature data.

SEM-EDS analysis were performed in a FEI Quanta 400, Bruker Quantax, in high vacuum mode was used to identify the morphology and essential components of the rock sample. Particles were placed on proper support and covered with gold (Au), using the voltaic arc method and vacuum injection, producing a gold layer of 20 nm. Samples images were obtained using a secondary electron (SE) and backscattered electron detector (BSED).

## 2.4. Potassium Availability

Total K, water-soluble K, exchangeable K, non-exchangeable K, and structural K were determined by procedures described in the literature (Castilhos and Meurer, 2001; Mancuso *et al.*, 2014; Melo *et al.*, 2005; Song and Huang, 1988; Villa *et al.*, 2004). For total K determination, the samples were submitted to digestion with HCl, HNO<sub>3</sub>, and HF acids, followed by the solubilization of salts formed with diluted HNO<sub>3</sub> (Castilhos and Meurer, 2001; Mancuso *et al.*, 2014; Melo *et al.*, 2005; Song and Huang, 1988). The exchangeable K corresponds to the difference between water-soluble K and K-NH<sub>4</sub>OAc. Wherein water-soluble K corresponds to K solubilized in an aqueous medium and K-NH<sub>4</sub>OAc corresponds to K extracted with 1 mol L<sup>-1</sup> acetate ammonium solution and 1:10, after stirring for 4 h on a shaking table at 300 rpm (Castilhos and Meurer, 2001; Mancuso *et al.*, 2014; Melo *et al.*, 2005; Villa *et al.*, 2004). The non-exchangeable K was determined by the difference between K-NH<sub>4</sub>OAc and K-HNO<sub>3</sub>, which K<sup>+</sup> defines extracted with 1 mol L<sup>-1</sup> HNO<sub>3</sub> boiling for 10 minutes (Castilhos and Meurer,

2001; Mancuso *et al.*, 2014; Melo *et al.*, 2005; Song and Huang, 1988; Villa *et al.*, 2004). Moreover, K-HNO<sub>3</sub> may also be represented by K released, which corresponds to the sum of water-soluble K and exchangeable K, and non-exchangeable K. The structural K is the difference between total K and K-HNO<sub>3</sub> (Castilhos and Meurer, 2001; Melo *et al.*, 2005; Song and Huang, 1988). The K<sup>+</sup> contents in the solutions were determined by flame atomic absorption spectrometry (FAAS).

Atomic absorption analyses were performed on a Varian spectrometer, SpectrAA-55B model. Operating conditions for potassium determination were a C<sub>2</sub>H<sub>2</sub>/air flame and a potassium hollow cathode lamp, with a wavelength 766.5 nm and a slit of 1.0 nm. Analytical solutions were prepared using ultrapure water obtained with a Milli-Q system, and all reagents used were analytical grade (PA).

## 2.5. Potassium leaching curve

Sequential extractions obtained samples for K leaching curves with 0.01 mol L<sup>-1</sup> citric acid and with the Mehlich-1 solution, which is formed by mixing 0.0125 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 0.05 mol L<sup>-1</sup> HCl. In addition, K leaching was also evaluated in an aqueous medium with ultrapure water (Milli-Q), following the procedures used in the literature (Castilhos and Meurer, 2001; Melo *et al.*, 2005; Song and Huang, 1988; Villa *et al.*, 2004). Such solutions are commonly used to evaluate the K availability (Araújo and Sampaio, 2010; Castilhos and Meurer, 2001; Silva, 2009; Silva *et al.*, 2012; Silva *et al.*, 2013; Teixeira *et al.*, 2012). Furthermore, citric acid is one of the acids produced by plants in the rhizosphere region (Castilhos and Meurer, 2001; Silva, 2009).

Successive extractions were carried out up to 1812 h. The rock and the extraction solution were mixed with a 1:10 weight ratio in plastic film-capped flasks, and these were stirred on an oscillating table at 150 rpm at room temperature. In the first extraction, the mixture (rock + extractor) was agitated for 2 h and then rested for a further 2 h for the deposition of the solid materials so that the total contact time of the mixture was 4 h. The supernatant solution was filtered at 0.45 microns membrane, and the K<sup>+</sup> present in the solution was determined by atomic absorption spectroscopy.

To the remaining material in the flask was added a new extraction solution. Then the

mixture was agitated for a variable time followed by 2 hours of rest, filtered, and analyzed for K<sup>+</sup> content. This procedure was repeated until 11 extractions (4; 22; 23; 22; 95; 69; 169; 167; 288; 377, and 576 contact time), resulting in 1812 hours total extraction.

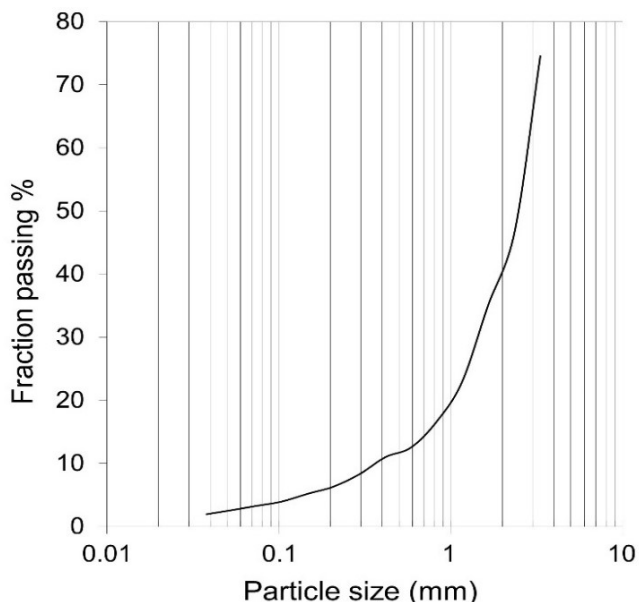
K released and the contact time accumulated correspond to the sum of the data obtained for each leaching stage.

### 3. RESULTS AND DISCUSSION

#### 3.1 Results

##### 3.1.1 Characterization of phonolite

The granulometric analysis of phonolite (Figure 1) showed the wide distribution of the particle size since about 8% of the particles are smaller than 0.3 mm, and less 2% of the particles are smaller than 0.038 mm. Besides, about 50% of the particles have a granulometry greater than 2.4 mm, and about 20% of the particles have granulometry greater than 1.0 mm.



**Figure 1.** Granulometric analysis of phonolite. Source: the author.

The rock chemical composition (Table 1) where indicated that it has an appreciable K content, about 7.1% K<sub>2</sub>O.

It was also verified that the phonolite has a high potential as a flux material with 15.4%

K<sub>2</sub>O+Na<sub>2</sub>O, and according to the chemical classification of igneous rock (Sah, 2005), this phonolite is classified as an intermediate rock since it has 55% SiO<sub>2</sub> content. Besides, it has nutrients necessary for plants, such as silicon, iron, calcium, manganese, and phosphorus, that favor its application as an alternative fertilizer. Highlight that Na<sub>2</sub>O content, about 8%, which can cause the accumulation of this element in poorly drained soils and to the formation of saline-sodic soils (Gheyi *et al.*, 2016).

**Table 1.** Chemical composition of phonolite. Source: the author.

Composition	% in weight
SiO <sub>2</sub>	55.6
Al <sub>2</sub> O <sub>3</sub>	21.6
Na <sub>2</sub> O	8.3
K <sub>2</sub> O	7.1
Fe <sub>2</sub> O <sub>3</sub>	4.1
CaO	1.6
MgO	0.29
MnO	0.20
Sulfite	0.17
TiO <sub>2</sub>	0.15
Chlorine	0.15
ZrO <sub>2</sub>	0.14
P <sub>2</sub> O <sub>5</sub>	0.07
Nb <sub>2</sub> O <sub>5</sub>	0.04
CuO	0.03
ZnO	0.02
Rb <sub>2</sub> O	0.01
Humidity (100 °C)	0.15
Fire assay (1000 °C)	1.40

By XRD (Figure 2A) was confirmed that the main mineralogical composition of this rock is alkaline feldspars and feldspathoids (Andrade *et al.*, 2005). The minerals found in phonolite are microcline and orthoclase, sanidine, and nepheline. These results corroborate the XRF since the rock is rich in Si, Al, Na, and K.

Analcime (Na,K[AlSi<sub>2</sub>O<sub>6</sub>].H<sub>2</sub>O) chemical composition from phonolite show K<sup>+</sup> and Na<sup>+</sup> miscibility which in natural analcime

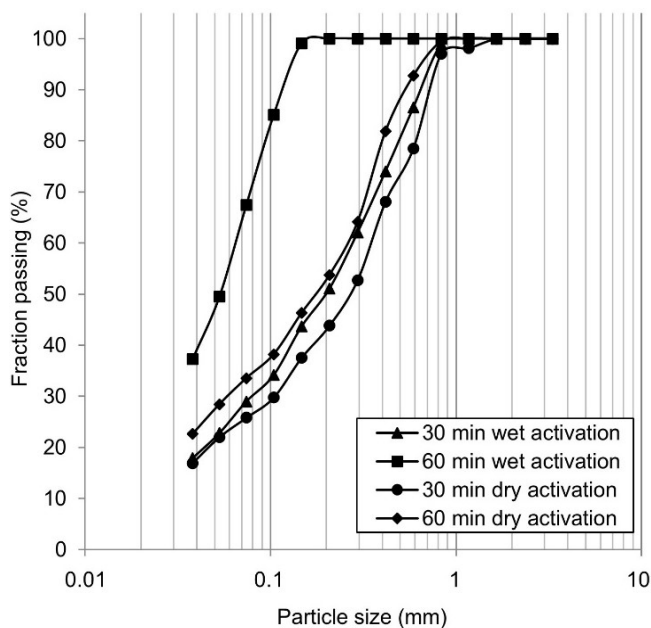
(Na[AlSi<sub>2</sub>O<sub>6</sub>].H<sub>2</sub>O) is 15-20% K<sup>+</sup> (Seryotkin and Bakakin, 2008).

FTIR spectra (Figure 2B) suggested that the main vibrations are related to the minerals of feldspar group. The vibration band at wavelength range between 3650 and 3300 cm<sup>-1</sup> correspond to the functional group OH stretch (Coates, 2000). Peak at 1635 cm<sup>-1</sup> indicates O-H deformation (Pekov *et al.*, 2007). The absorption band between 1200 to 900 cm<sup>-1</sup> are related to Si-O-(Si,Al) asymmetric stretch (d'Azevedo *et al.*, 2006; Wu *et al.*, 2008) and corroborate with the presence of silicon and aluminum oxides determined by XRF. Peaks of Si-O-Si symmetrical stretch and Al-O stretch octahedrally coordinated were shown at 765 and 721cm<sup>-1</sup> (Prud'homme *et al.*, 2011; Santos *et al.*, 2006). The peak at 583 cm<sup>-1</sup> indicates O-(Si,Al)-O deformations, microcline feldspar characteristic (Suresh *et al.*, 2011). The peak at 540 cm<sup>-1</sup> indicates O-Si-O deformation (Prud'homme *et al.*, 2011). Peaks at 464 and 430 cm<sup>-1</sup> correspond (Si,Al)-O deformation (Wu *et al.*, 2008).

SEM-EDS, Figure 2C, allowed identifying chemical homogeneity and irregular particle morphology with dimensions between 20 and 200 μm. Besides, chemical elements as Si, Al, O, Na, and K were identified by SEM-EDS in the chemical composition of representative particles that, according to the XRD, correspond the alkaline feldspar presence as the microcline, orthoclase, sanidine, and nepheline.

### 3.1.2 Characterization of samples mechanically activated

Granulometric distribution to the phonolite rock samples mechanically activated (Figure 3) showed a similar fraction passing curve to the samples activated for 30 and 60 min by dry mechanical activation. The wet mechanical activation, the sample activated for 60 min had a greater fine particle, approximately 85% of the particles had dimensions less than 0.1 mm, and 100% of the particles had dimensions less than 0.2 mm. However, samples mechanically activated for 30 min wet and 60 min dry had around 50% of the particles less than 0.2 mm, and to dry mechanical activation by 30 min had particle sizes less 0.3 mm. Besides, in this activation process, 100% of the particles had dimensions less than 1.0 mm, that is larger than the particles obtained in wet activation by 60 min.



**Figure 3.** Particle size distributions of phonolite after mechanical activation. Source: the author.

XRD for samples submitted to different mechanical activation conditions (Figure 4A) showed that the water in the mechanical activation process did not change the mineral composition; however, a reduction in the intensity of the diffraction peaks was observed around 27.5° for the sample with 60 min of wet activation.

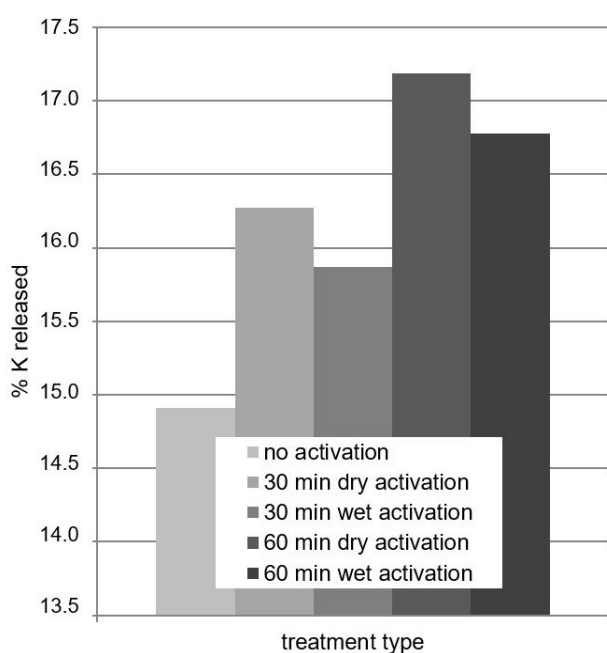
FTIR spectra of the samples after wet and dry mechanical activation (Figure 4B) showed the same behavior as unmilled rock, corroborating of the XRD results, since indicated maintenance of the mineralogical composition.

### 3.1.3 Potassium availability

Results to total K, water-soluble K, exchangeable K, non-exchangeable K and structural K obtained to the activated to the samples (Table 2) are shown, between brackets, as percent at the total K of each one of the samples rocks. The analysis shows that the water-soluble K in an aqueous medium is less than 0.1% of the total K contained in the rock, regardless of the time and mechanical activation mode. Regarding the exchangeable K, it was verified that mechanical activation increases the amount of potassium compared to the sample without mechanical activation. Among the results, the mechanical activation to dry for 30 min showed a lower exchangeable K content than the content obtained in the other samples

with mechanical activation. However, a low influence of time and the mechanical activation mode was observed since the percentage of exchangeable K in all activated samples had relatively low values, between 0.12 and 0.22%. These results corroborate with the data of XRD, once it was observed that the grinding mode did not interfere in the mineralogical composition of the rock. Regarding the results of non-exchangeable K, it was observed that the samples with mechanical activation for 60 min have a higher content than those activated for 30 min. However, samples activated for 60 min have a lower content of structural K than the samples activated for 30 min. In addition, samples with dry mechanical activation showed a higher amount of released K than wet activated samples. In the samples with dry mechanical activation, a higher increase of non-exchangeable K is observed, corresponding to K that is bound electrostatically to the minerals and is slowly released in the soil solution (Nascimento and Loureiro, 2004; Silva *et al.*, 2013; Straaten, 2007).

Results of K released, which corresponds to the sum of water-soluble K with exchangeable K and non-exchangeable K, reveal that the mechanically activated samples showed an increase in nutrient release compared to the non-activated samples (Figure 5). Since in the dry mechanical activation for 60 min, the released K increased by 15% in relation to the sample without mechanical activation.



**Figure 5.** K released percentage (relation to total K) of the phonolite mechanically activated. Source: the author.

### 3.1.4 Potassium leaching curve

The K leaching curves of the mechanical activation samples (Figure 6) showed an increase of the K released over time by extraction with 0.01 mol L<sup>-1</sup> citric acid and Mehlich-1 solutions.

Samples after wet or dry mechanical activation had similar K leaching curves. K released with the water extractor was very low, 62 mg kg<sup>-1</sup> after 235 hours of total contact time. While for other extractors, an initial stage with a higher K leached was identified. K leaching with Mehlich-1 solution was about 6000 mg kg<sup>-1</sup>, whereas the extraction with 0.01 mol L<sup>-1</sup> citric acid was almost 3500 mg kg<sup>-1</sup> after 235 hours of contact time. After 1812 hours, about 10000 and 7000 mg kg<sup>-1</sup> of K leaching was with Mehlich-1 and 0.01 mol L<sup>-1</sup> citric acid solutions, respectively, and corresponded 16 and 11% of total K in the sample.

For other forms of K in the mechanically activated samples, levels K leaching was 60 times greater than the exchangeable K after 1812 hours of sequential extraction with a citric acid solution. Therefore, evident that the extraction with 0.01 mol L<sup>-1</sup> citric acid solution leaches the water-soluble K and exchangeable K together a significant part of non-exchangeable K. For sequential extraction with Mehlich-1 solution was observed a K leaching 80 times greater than the exchangeable K after 1812 hours of extraction. This K leaching corresponds to 95% of the K released, the total between the water-soluble K and exchangeable K, and the non-exchangeable K.

## 3.2 Discussion

Characterization of the phonolite confirmed its potential as an alternative source of potassium fertilizer since it has about 7.1% K<sub>2</sub>O, and the main constituent minerals of the rock are from the class of alkaline feldspars (Andrade *et al.*, 2005). According to the literature, rocks with K<sub>2</sub>O levels above 6.0% and composed of minerals such as alkaline feldspars and micas can be used as an alternative source of potassium by means of the stonemeal method (Felix, 2014; Shirale *et al.*, 2019). On the other hand, the high Na<sub>2</sub>O content of the rock reinforces the importance of in-depth study of the

rock before its application in agriculture since the accumulation of this element in soils can cause the formation of saline-sodic soils (Gheyi et al., 2016) and reduce the benefits of rock-extracted  $K^+$  ion for crops in poorly drained soils.

Granulometric distribution behavior to the phonolite rock samples is considered common in cases of dry milling and can be explained by the agglomeration of structurally modified particles during milling (Kleiv and Thornhill, 2007). In wet mechanical activation, the obtaining of a material with a greater quantity of fine particles can be explained by the fact that water acts as a lubricant, which hinders the agglomeration of the particles. This reinforces the role of water in reducing the forces of attraction between tiny particles (Kleiv and Thornhill, 2007). From an agronomic point of view, the application of a material with very fine particles implies the need for special equipment, in addition to the loss of material by the wind.

The wet milling for 60 min produced finer particles indicating more intense changes in the activated rock particles that can be attributed to a greater reduction in the crystallinity of the minerals of this rock (Baláž et al., 2008; Kleiv and Thornhill, 2007; Pourghahramania and Akhgar, 2015; Temuujin et al., 2003).

Regarding the released K, it is reasonable to assume that dry activation causes a larger defect in the material, and in contrast, the energy supplied in wet mechanical activation is probably partially dissipated by water.

The increase of non-exchangeable K in samples with dry activation can be explained by the fact of that the mechanical activation causes damage to the structure of minerals, particularly in regions near the surface of the particles, making K more accessible to the extractor (Crusciol and Soratto, 2013). Similar results have been reported in the literature for high-intensity mechanical activation, and the K availability has been shown to be related to increased surface area and structural disorder (Kleiv and Thornhill, 2007). It should be noted that, in our study, a low-intensity mechanical activation (mill speed of 70 rpm) was performed, while in the literature, the high-intensity mechanical activation (with speeds of 500-900 rpm) is usually performed (Kleiv and Thornhill, 2007).

The released K increase by 15% in the sample after dry mechanical activation compared to the non-activated sample suggests that the phonolite rock should present an improvement in the  $K^+$  release efficiency when applied to the soil. Studies have shown that finely ground phonolite

rock promoted an increase in the production of long-term crops like KCl. In addition, the rock has the advantage of having a residual effect. However, the results were not so good in the case of short-term crops (Crusciol and Soratto, 2013; Franco *et al.*, 2013; Mancuso *et al.*, 2014; Soratto and Crusciol, 2013). Therefore, our results are an incentive to carry out new research on the mechanical activation of phonolite rock as an alternative source of potassium for short-term crops.

K leaching curve showed that the potassium forms weakly bound to the crystalline mineral structure were released at the first leach stage. Subsequently, the leaching process slowly since the potassium was strongly bound to the crystalline mineral structure (Castilhos and Meurer, 2001; Silva *et al.*, 2013; Plata *et al.*, 2021). The results suggest that regardless of the mechanical activation mode, the phonolite can be considered as a source of K slow-release, i.e., the phonolite rock refers to a material of the low aqueous solubilized however had K release continuously (Silva, 2009). The K leaching 80 times greater than the exchangeable K after 1812 hours of sequential extraction with Mehlich-1 solution confirms the potassium reserve of the mechanically activated rock can be continuously made available to plants (Melo *et al.*, 2005).

Thus, leaching curve results suggest that K released increases progressively at extractions with the longer contact time, and the agriculture application of the mechanically activated phonolite rock must present a residual effect, where the structural K would be slowly made available to the plants. This effect concords with the results of the application of the finely ground phonolite rock at successive crops of soybeans, wheat, and corn that showed a similar or superior efficiency of KCl in some cases (Soratto and Crusciol, 2013). Other studies have also confirmed the efficiency of phonolite rock finely ground at long-term cultivation (Franco *et al.*, 2013; Mancuso *et al.*, 2014). However, short-term crops were observed to have low efficiency when compared to KCl application (Soratto and Crusciol, 2013) which can be explained by the low-release water-soluble K.

It is important to result that citric acid solution is commonly found in the rhizosphere region, and it is widely used in sequential K leaching studies to simulate the conditions of the natural environment of plants (Castilhos and Meurer, 2001; Silva, 2009). The extraction solutions operate in the K leaching by the ion exchange reaction with  $H^+$ , and through the



complex formation of groups OH and COOH with solution cations. These processes favor the decomposition of the minerals structure (Crusciol and Soratto, 2013). The 1812 hours of sequential leaching corresponds to approximately 2.5 months, and according to literature (Melo *et al.*, 2005), two months is considered a satisfactory time to simulate the growth of the annual crop conditions. This way, results shown to K leaching curve indicate that the mechanical activation of phonolite rock may be a good alternative to improve the K release for long-term cultures.

## 4. CONCLUSIONS

After mechanical activation, results of phonolite rock from Poços de Caldas, Brazil, reveal the low influence of the time and process mode, dry or wet, at the change of the rock mineralogical composition at water-soluble K and exchangeable K content. However, activated samples showed a significant increase in non-exchangeable K content, corresponding to K<sup>+</sup> electrostatically bound to the rock-forming minerals. Activated samples by the dry mechanical process for 60 min showed the highest K released and the lowest structural K content; that is it, this activation mode is more efficient in creating structural defects compared with wet activation. Besides, the results obtained at the K leaching curves confirm the possibility of phonolite rock application as a slow-release fertilizer. It should be noted that the mechanical activation improved K release potential since it increased non-exchangeable K and reduced structural K content with 95% of the K released after 1812 hours of Mehlich-1 solution extraction. The slow and continuous K release favors the mechanically activated rock application at soils of circular and intensive agriculture, as it prevents the rapid loss of K released to aquatic systems.

## 5. DECLARATIONS

### 5.1. Study Limitations

The study is limited to the sample size.

### 5.2. Acknowledgements

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### 5.4. Competing Interests

The authors declare that they have no competing interests.

### 5.5. Open Access

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## 7. REFERENCES:

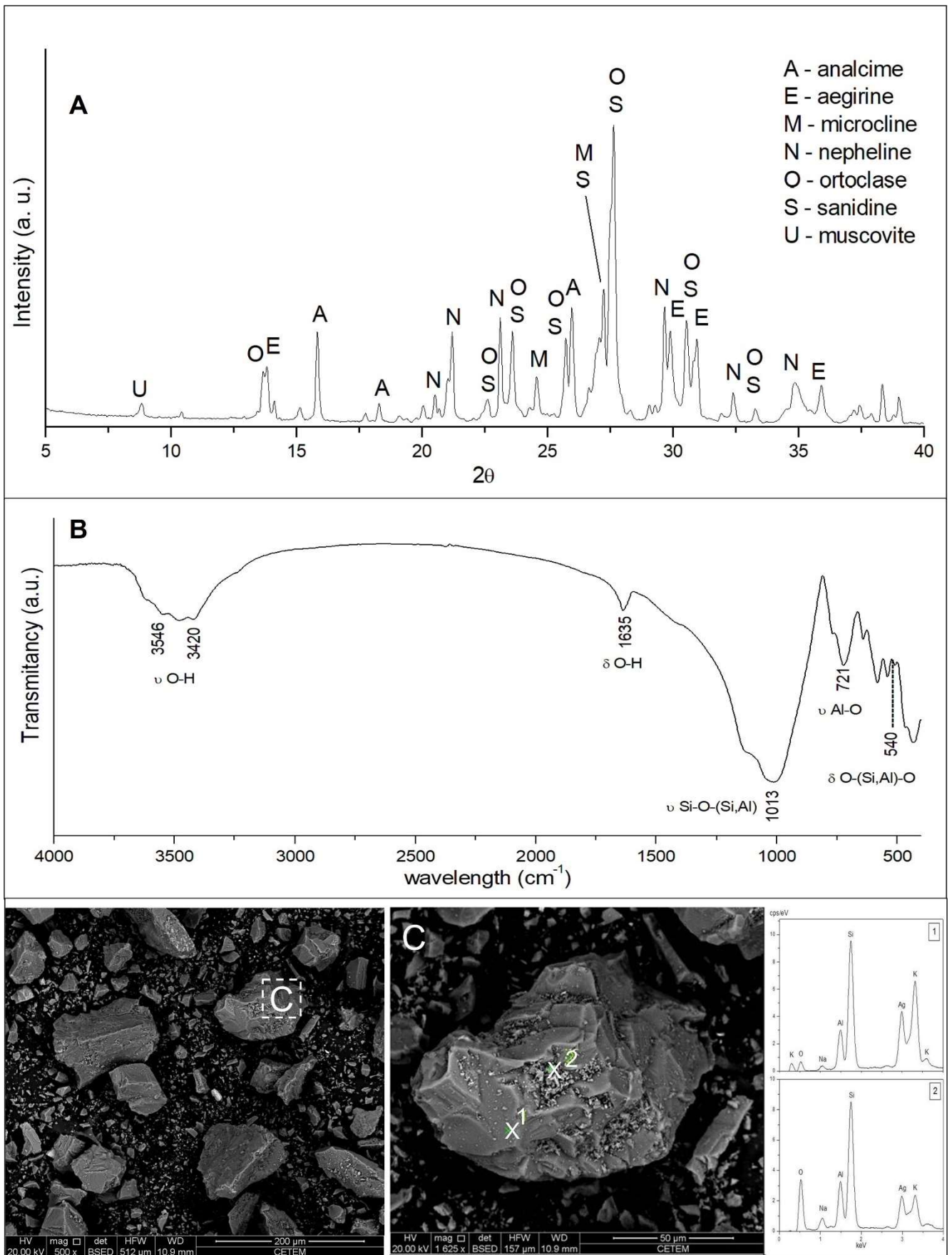
1. Andrade, P. M., Neto, H. S. N., Monteiro, S. N., & Vieira, C. M. F. (2005). Efeito da

- adição de fonolito na sinterização de argila caulínica. In *Cerâmica* (Vol. 51, Issue 320, pp. 362–371). FapUNIFESP (SciELO). <https://doi.org/10.1590/s0366-69132005000400010>
2. Araújo, M. S. ; Sampaio, J. A. (2010) Estudo do uso de rocha potássica como fertilizante de liberação lenta, In: Luz, A. B.; Baltar, C. A. M.; Bertolino, L. C. (Eds.), *II Simpósio de Minerais Industriais do Nordeste. Anais...*, CETEM/UFPE, Campina Grande, 2010, 145–152. ISBN: 978-85-61121-66-2
  3. d’Azevedo, C. A., Garrido, F. M. S., & Medeiros, M. E. (2006). The effect of mechanochemical activation on the reactivity in the MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system. In *Journal of Thermal Analysis and Calorimetry* (Vol. 83, Issue 3, pp. 649–655). Springer Science and Business Media LLC. <https://doi.org/10.1007/s10973-005-7405-1>
  4. Baláž, P., Turianicová, E., Fabián, M., Kleiv, R. A., Briančin, J., & Obut, A. (2008). Structural changes in olivine (Mg, Fe)<sub>2</sub>SiO<sub>4</sub> mechanically activated in high-energy mills. In *International Journal of Mineral Processing* (Vol. 88, Issues 1–2, pp. 1–6). Elsevier BV. <https://doi.org/10.1016/j.minpro.2008.04.001>
  5. Baláž, P., & Dutková, E. (2009). Fine milling in applied mechanochemistry. In *Minerals Engineering* (Vol. 22, Issues 7–8, pp. 681–694). Elsevier BV. <https://doi.org/10.1016/j.mineng.2009.01.014>
  6. Bhatti, T. M., Bigham, J. M., Vuorinen, A., & Tuovinen, O. H. (2011). Weathering of phlogopite in simulated bioleaching solutions. In *International Journal of Mineral Processing* (Vol. 98, Issues 1–2, pp. 30–34). Elsevier BV. <https://doi.org/10.1016/j.minpro.2010.10.004>
  7. Castilhos, R. M. V., & Meurer, E. J. (2001). Cinética de liberação de potássio em planossolo do estado do Rio Grande do Sul. In *Ciência Rural* (Vol. 31, Issue 6, pp. 979–983). FapUNIFESP (SciELO). <https://doi.org/10.1590/s0103-84782001000600010>
  8. Coates, J. (2000) Interpretation of infrared spectra, a practical approach, In: Meyers, R. A. (Ed.), *Encyclopedia of Analytical Chemistry*, Chichester: John Wiley & Sons Ltd., 2000, 10815–10837. ISBN:9780470027318
  9. Crusciol, C. A. C.; Soratto, R. P. (2013) Eficiência de rocha fonolito moída como fonte de potássio para as culturas do arroz, feijão, milho e soja, In: Theodoro, S. M. C. H.; Martins, E. S.; Fernandes, M. M.; Carvalho, A. M. X. (Eds.), *II Congresso Brasileiro de Rochagem, Anais...*, Poços de Caldas, MG: Suprema, 2013, 327–337. ISBN: 978.85.8179.061-9
  10. Erdemoğlu, M., & Baláž, P. (2012). An Overview of Surface Analysis Techniques for Characterization of Mechanically Activated Minerals. In *Mineral Processing and Extractive Metallurgy Review* (Vol. 33, Issue 1, pp. 65–88). Informa UK Limited. <https://doi.org/10.1080/08827508.2010.542582>
  11. Felix, A. A. S. (2014) Síntese e caracterização estrutural de minerais com liberação controlada de potássio. 134 p., Tese (Doutorado) Instituto de Química, UFRJ, Rio de Janeiro, 2014. <https://buscaintegrada.ufrj.br/Record/aleph-UFR01-000814892>
  12. Franco, D.; Yasuda, M.; Fukuda, L. A.; Ferracini, R. T. (2013) Avaliação do desempenho do fonolito via mineral em laranjeiras adultas, In: Theodoro, S. M. C. H.; Martins, E. S.; Fernandes, M. M.; Carvalho, A. M. X. (Eds.), *II Congresso Brasileiro de Rochagem, Anais...*, Poços de Caldas, MG: Suprema, 2013, 321–326. ISBN: 978.85.8179.061-9
  13. Gheyi, H. R.; Dias, N. S.; Lacerda, C. F.; Gomes Filho, E. (Eds.) (2016) Manejo da salinidade na agricultura: Estudo básico e aplicado, Fortaleza: INCTSal, 2016, 504 p. ISBN: 978-85-420-0948-4
  14. Guelfi-Silva, D. R.; Marchi, G.; Spehar, C. R.; Guilherme, L. R. G.; Faquin, V. (2013)

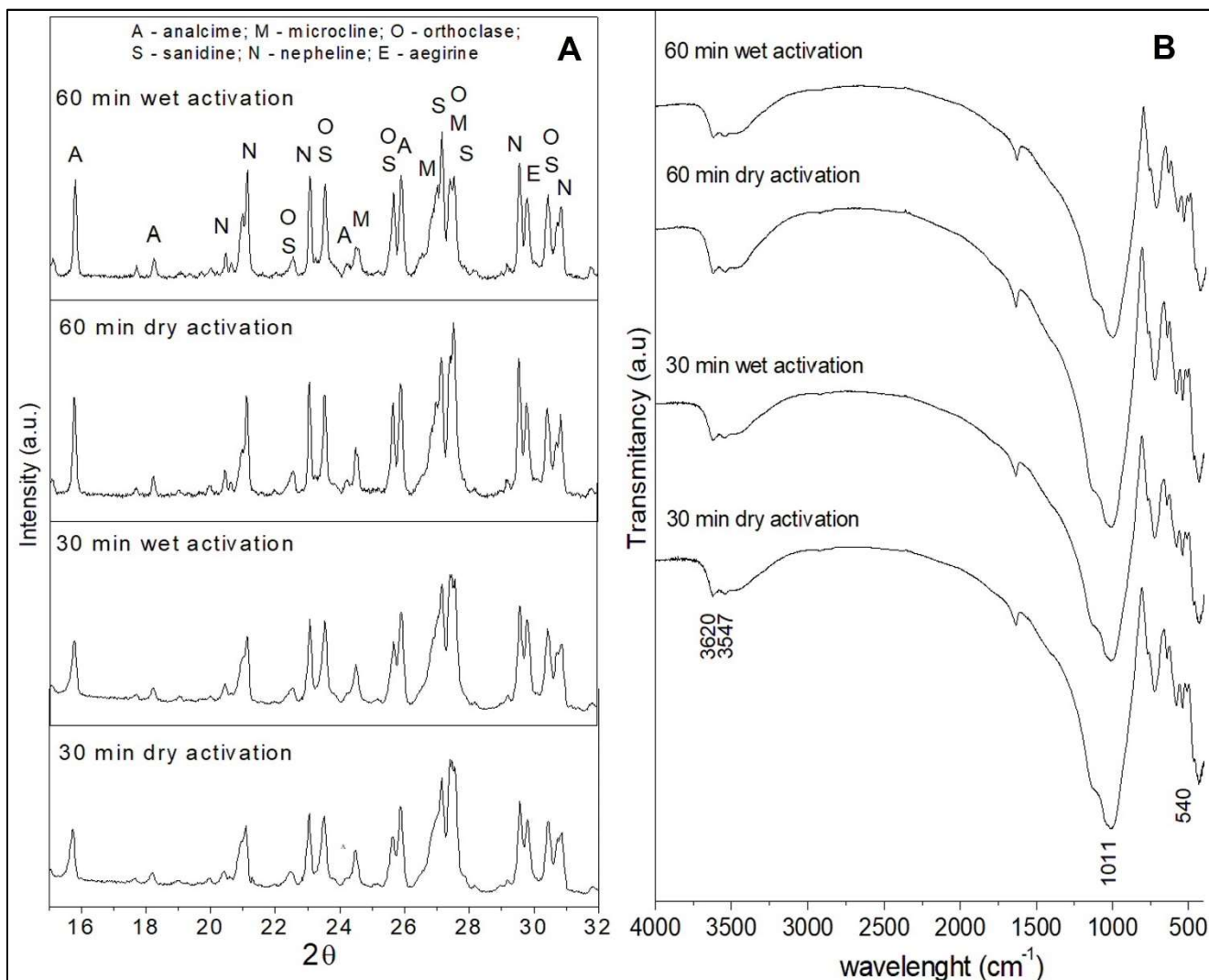
- Agronomic efficiency of potassium fertilization in lettuce fertilized: With alternative nutrient sources, *Rev. Cienc. Agron.*, 44, 2, 267–277. <http://ccarevista.ufc.br/seer/index.php/ccarevista/article/view/1944>
15. Jena, S. K. (2020). A Review on Potash Recovery from Different Rock and Mineral Sources. In *Mining, Metallurgy & Exploration* (Vol. 38, Issue 1, pp. 47–68). Springer Science and Business Media LLC. <https://doi.org/10.1007/s42461-020-00286-7>
  16. Kleiv, R. A., & Thornhill, M. (2007). Production of mechanically activated rock flour fertilizer by high intensive ultrafine grinding. In *Minerals Engineering* (Vol. 20, Issue 4, pp. 334–341). Elsevier BV. <https://doi.org/10.1016/j.mineng.2006.08.017>
  17. Mancuso, M. A. C., Soratto, R. P., Crusciol, C. A. C., & Castro, G. S. A. (2014). Effect of potassium sources and rates on arabica coffee yield, nutrition, and macronutrient export. In *Revista Brasileira de Ciência do Solo* (Vol. 38, Issue 5, pp. 1448–1456). FapUNIFESP (SciELO). <https://doi.org/10.1590/s0100-06832014000500010>
  18. Manning, D. A. C. (2010). Mineral sources of potassium for plant nutrition. A review. In *Agronomy for Sustainable Development* (Vol. 30, Issue 2, pp. 281–294). Springer Science and Business Media LLC. <https://doi.org/10.1051/agro/2009023>
  19. Melo, V. de F., Corrêa, G. F., Ribeiro, A. N., & Maschio, P. A. (2005). Cinética de liberação de potássio e magnésio pelos minerais da fração argila de solos do Triângulo Mineiro. In *Revista Brasileira de Ciência do Solo* (Vol. 29, Issue 4, pp. 533–545). FapUNIFESP (SciELO). <https://doi.org/10.1590/s0100-06832005000400006>
  20. Nascimento, M.; Loureiro, F. E. L. (2004) Fertilizantes e sustentabilidade: o potássio na agricultura brasileira, fontes e rotas alternativas. Rio de Janeiro: CETEM/MCT, 66 p. ISBN:8572272038
  21. Pekov, I. V., Chukanov, N. V., Dubinchuk, V. T., & Zadov, A. E. (2007). Middendorffite,  $K_3Na_2Mn_5Si_{12}(O,OH)_{36} \cdot 2H_2O$ , a new mineral species from the Khibiny pluton, Kola Peninsula. In *Geology of Ore Deposits* (Vol. 49, Issue 7, pp. 522–529). Pleiades Publishing Ltd. <https://doi.org/10.1134/s1075701507070069>
  22. Plata, L. G., Ramos, C. G., Silva Oliveira, M. L., & Silva Oliveira, L. F. (2021). Release kinetics of multi-nutrients from volcanic rock mining by-products: Evidences for their use as a soil remineralizer. In *Journal of Cleaner Production* (Vol. 279, p. 123668). Elsevier BV. <https://doi.org/10.1016/j.jclepro.2020.12.3668>.
  23. Pourghahramani, P., & Akhgar, B. N. (2015). Characterization of structural changes of mechanically activated natural pyrite using XRD line profile analysis. In *International Journal of Mineral Processing* (Vol. 134, pp. 23–28). Elsevier BV. <https://doi.org/10.1016/j.minpro.2014.11.005>
  24. Prud'homme, E., Michaud, P., Joussein, E., Clacens, J.-M., Arii-Clacens, S., Sobrados, I., Peyratout, C., Smith, A., Sanz, J., & Rossignol, S. (2011). Structural characterization of geomaterial foams — Thermal behavior. In *Journal of Non-Crystalline Solids* (Vol. 357, Issue 21, pp. 3637–3647). Elsevier BV. <https://doi.org/10.1016/j.jnoncrysol.2011.06.033>
  25. Ramos, C. G., de Mello, A. G., & Kautzmann, R. M. (2014). A preliminary study of acid volcanic rocks for stonemeal application. In *Environmental Nanotechnology, Monitoring & Management* (Vols. 1–2, pp. 30–35). Elsevier BV. <https://doi.org/10.1016/j.enmm.2014.03.002>
  26. Sabah, E., Özdemir, O., & Koltka, S. (2013). Effect of ball mill grinding

- parameters of hydrated lime fine grinding on consumed energy. In *Advanced Powder Technology* (Vol. 24, Issue 3, pp. 647–652). Elsevier BV. <https://doi.org/10.1016/j.apt.2012.12.001>
27. Sah, S. L. (2005) Petrography: Chemical and quasi-chemical classification, In: Sah, S. L. (Ed.), *Encyclopaedia of Petroleum Science & Engineering*, Delhi, India: Kalpaz Publications, 2005, 91–96. ISBN: 81-7835-355-5 (vol. 8)
  28. Sampaio, J. A.; França, S. C. A.; Braga, P.F.A. (2007) Tratamento de minérios: práticas laboratoriais, 1 Ed., Rio de Janeiro: CETEM/MCT, 2007, 570 p. ISBN: 9788561121020
  29. Sandvik, K. L., Kleiv, R. A., & Haug, T. A. (2011). Mechanically activated minerals as a sink for CO<sub>2</sub>. In *Advanced Powder Technology* (Vol. 22, Issue 3, pp. 416–421). Elsevier BV. <https://doi.org/10.1016/j.apt.2010.06.004>
  30. Santos, P. T. A.; Freitas, N. L.; Gama, L.; Jesus, A. A.; Andrade, H. M. C.; Costa, A. C. F. M. (2006) Síntese via reação de combustão de catalisadores de NiAl<sub>2</sub>O<sub>4</sub> para a reação de deslocamento de vapor d'água, *Rev. Eletrôn. de Mat. e Process.*, 1, 2, 46–54. ISSN 1809-9797
  31. Sanz Scovino, J. I., & Rowell, D. L. (1988). The use of feldspars as potassium fertilizers in the savannah of Colombia. In *Fertilizer Research* (Vol. 17, Issue 1, pp. 71–83). Springer Science and Business Media LLC. <https://doi.org/10.1007/bf01050458>
  32. Seryotkin, Yu. V., & Bakakin, V. V. (2008). The thermal behavior of secondary analcime as leucite derivate and its structural interpretation. In *Russian Geology and Geophysics* (Vol. 49, Issue 3, pp. 153–158). GeoScienceWorld. <https://doi.org/10.1016/j.rgg.2007.06.014>
  33. Shirale, A. O., Meena, B. P., Gurav, P. P., Srivastava, S., Biswas, A. K., Thakur, J. K., Somasundaram, J., Patra, A. K. & Rao, A. S. (2019). Prospects and challenges in utilization of indigenous rocks and minerals as source of potassium in farming. In *Journal of Plant Nutrition* (Vol. 42, Issue 19, pp. 2682–2701). Taylor & Francis. <https://doi.org/10.1080/01904167.2019.1659353>
  34. Silva, A. A. S. (2009) Caracterização de flogopitito da Bahia para uso como fertilizante alternativo de potássio. 88 p., Dissertação (Mestrado) Instituto de Química, UFRJ, Rio de Janeiro, 2009. <https://buscaintegrada.ufrj.br/Record/ale-ph-UFR01-000731521>
  35. Silva, A. A. S., Medeiros, M. E., Sampaio, J. A., & Garrido, F. M. S. (2012). Verdete de cedro do abaeté como fonte de potássio: caracterização, tratamento térmico e reação com CaO. In *Matéria* (Rio de Janeiro) (Vol. 17, Issue 3, pp. 1061–1073). FapUNIFESP (SciELO). <https://doi.org/10.1590/s1517-70762012000300004>
  36. Silva, A. de A. S. da, Sampaio, J. A., Luz, A. B. da, França, S. C. A., & Ronconi, C. M. (2013). Modeling Controlled Potassium Release from Phlogopite in Solution: Exploring the Viability of using Crushed Phlogopitite Rock as an Alternative Potassium Source in Brazilian soil. In *Journal of the Brazilian Chemical Society. Sociedade Brasileira de Química (SBQ)*. <https://doi.org/10.5935/0103-5053.20130173>
  37. Silva, F. A. N. G., Barbato, C. N., Santos, R. D., Almeida, D. S. G. de, Sampaio, J. A., Medeiros, Marta. E., & Garrido, F. M. S. (2012). Mechanochemical Activation to Bauxite. In *Light Metals 2012* (pp. 27–32). John Wiley & Sons, Inc. <https://doi.org/10.1002/9781118359259.ch5>
  38. Song, S. K., & Huang, P. M. (1988). Dynamics of Potassium Release from Potassium-Bearing Minerals as Influenced by Oxalic and Citric Acids. In *Soil Science Society of America Journal* (Vol. 52, Issue 2, pp. 383–390). Wiley. <https://doi.org/10.2136/sssaj1988.03615995005200020015x>
  39. Soratto, R. P.; Crusciol, C. A. C. (2013) Eficiência residual de rocha fonolito moída nas sucessões de culturas soja-

- trigo-milho e milho-milheto-soja, In: Theodoro, S. M. C. H.; Martins, E. S.; Fernandes, M. M.; Carvalho, A. M. X. (Eds.), *II Congresso Brasileiro de Rochagem, Anais...*, Poços de Caldas, MG: Suprema, 2013, 312–320. ISBN: 978.85.8179.061-9
40. Suresh, G., Ramasamy, V., Meenakshisundaram, V., Venkatachalapathy, R., & Ponnusamy, V. (2011). A relationship between the natural radioactivity and mineralogical composition of the Ponnaiyar river sediments, India. In *Journal of Environmental Radioactivity* (Vol. 102, Issue 4, pp. 370–377). Elsevier BV. <https://doi.org/10.1016/j.jenvrad.2011.02.003>
  41. Teixeira, A. M. dos S., Garrido, F. M. S., Medeiros, M. E., & Sampaio, J. A. (2012). Caracterização e classificação quanto ao risco ambiental do estéril da mina de cromita do município de Andorinha, Bahia. In *Química Nova* (Vol. 35, Issue 9, pp. 1794–1799). FapUNIFESP (SciELO). <https://doi.org/10.1590/s0100-40422012000900017>
  42. Teixeira, A. M. dos S., Garrido, F. M. dos S., Medeiros, M. E., & Sampaio, J. A. (2015). Effect of thermal treatments on the potassium and sodium availability in phonolite rock powder. In *International Journal of Mineral Processing* (Vol. 145, pp. 57–65). Elsevier BV. <https://doi.org/10.1016/j.minpro.2015.07.002>
  43. Teixeira, A. M. dos S., Sampaio, J. A., Garrido, F. M. dos S., & Medeiros, M. E. (2012). Technological Characterization of Phonolite Rock to be Applied as Source of Nutrients to the Brazilian Agriculture. In *EPD Congress 2011* (pp. 81–86). John Wiley & Sons, Inc. <https://doi.org/10.1002/9781118495285.ch10>
  44. Teixeira, A. M. D. S., Sampaio, J. A., Garrido, F. M. dos S., & Medeiros, M. E. (2012). AVALIAÇÃO DA ROCHA FONOLITO COMO FERTILIZANTE ALTERNATIVO DE POTÁSSIO. In *HOLOS* (Vol. 5, p. 21). Instituto Federal de Educacao, Ciencia e Tecnologia do Rio Grande do Norte (IFRN). <https://doi.org/10.15628/holos.2012.1102>
  45. Temuujin, J., Okada, K., Jadambaa, T. S., MacKenzie, K. J. D., & Amarsanaa, J. (2003). Effect of grinding on the leaching behaviour of pyrophyllite. In *Journal of the European Ceramic Society* (Vol. 23, Issue 8, pp. 1277–1282). Elsevier BV. [https://doi.org/10.1016/s0955-2219\(02\)00297-2](https://doi.org/10.1016/s0955-2219(02)00297-2)
  46. Theodoro, S. H., & Leonardos, O. H. (2006). The use of rocks to improve family agriculture in Brazil. In *Anais da Academia Brasileira de Ciências* (Vol. 78, Issue 4, pp. 721–730). FapUNIFESP (SciELO). <https://doi.org/10.1590/s0001-37652006000400008>
  47. Van Straaten, P. (2006). Farming with rocks and minerals: challenges and opportunities. In *Anais da Academia Brasileira de Ciências* (Vol. 78, Issue 4, pp. 731–747). FapUNIFESP (SciELO). <https://doi.org/10.1590/s0001-37652006000400009>
  48. Van Straaten, P. (2007). *Agrogeology: the use of rocks for crops*. 1. Ed. Guelph: Enviroquest Ltd., 426 p. ISBN:978-09-68012-35-2
  49. Vdović, N., Jurina, I., Škapin, S. D., & Sondi, I. (2010). The surface properties of clay minerals modified by intensive dry milling — revisited. In *Applied Clay Science* (Vol. 48, Issue 4, pp. 575–580). Elsevier BV. <https://doi.org/10.1016/j.clay.2010.03.006>
  50. Villa, M. R., Fernandes, L. A., & Faquin, V. (2004). Formas de potássio em solos de várzea e sua disponibilidade para o feijoeiro. In *Revista Brasileira de Ciência do Solo* (Vol. 28, Issue 4, pp. 649–658). FapUNIFESP (SciELO). <https://doi.org/10.1590/s0100-06832004000400007>
  51. Wu, D., Lu, Y., Kong, H., Ye, C., & Jin, X. (2007). Synthesis of Zeolite From Thermally Treated Sediment. In *Industrial & Engineering Chemistry Research* (Vol. 47, Issue 2, pp. 295–302). American Chemical Society (ACS). <https://doi.org/10.1021/ie071063u>



**Figure 2.** Characterization of phonolite. (A) X-ray diffraction, Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). (B) Spectra FTIR, range 4000 at 400 cm<sup>-1</sup>. (C) SEM-EDS images. Source: the author.

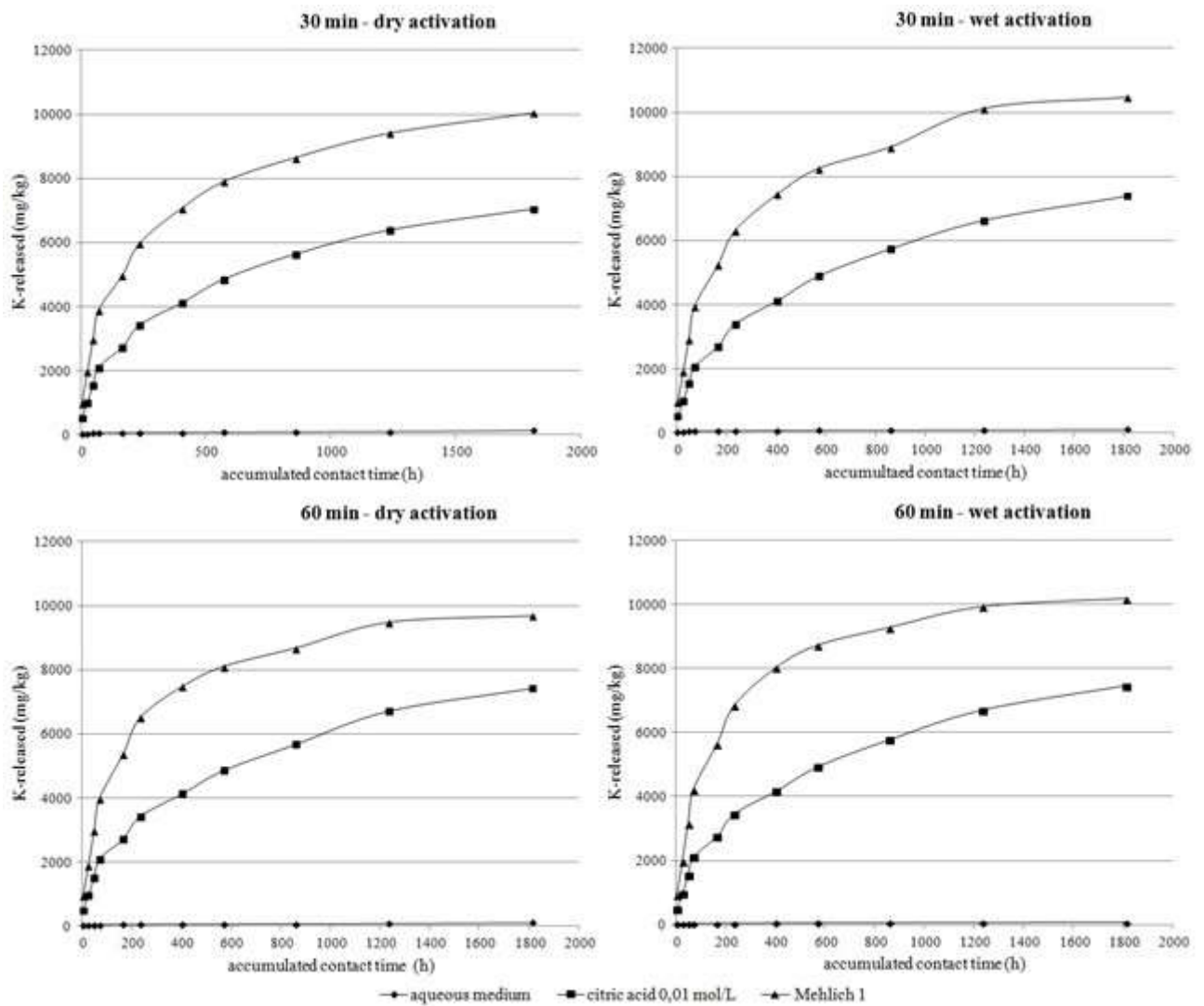


**Figure 4.** Characterization of the mechanically activated phonolite. (A) X-ray diffraction, Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). (B) Spectra FTIR, range 4000 at  $400 \text{ cm}^{-1}$ . Source: the author

**Table 2.** K forms in phonolite before and after mechanical activation. Source: the author

Treatments	K <sub>t</sub>	K <sub>sol</sub>	K <sub>exc</sub>	K <sub>non</sub>	K <sub>rel</sub>	K <sub>str</sub>
	----- mg kg <sup>-1</sup> -----					
	----- (%) -----					
No activation	64000.00 (100.00)	17.97 (0.03)	47.65 (0.07)	9477.33 (14.84)	9542.95 (14.91)	54457.06 (85.09)
30 min wet activation	63100.00 (100.00)	29.95 (0.05)	139.24 (0.22)	9846.01 (15.60)	10015.20 (15.87)	53084.81 (84.13)
60 min wet activation	64950.00 (100.00)	16.96 (0.03)	129.84 (0.20)	10753.17 (16.56)	10899.97 (16.78)	54050.03 (83.22)
30 min dry activation	65933.00 (100.00)	21.44 (0.04)	77.25 (0.12)	10626.34 (16.12)	10725.03 (16.27)	55208.30 (83.73)
60 min dry activation	63680.00 (100.00)	27.63 (0.04)	113.84 (0.18)	10806.71 (16.97)	10947.58 (17.19)	52731.82 (82.81)





**Figure 6.** Cumulative K<sup>+</sup> leaching curve as a function of contact time with the extraction solution, for the samples after mechanical activation wet and dry for 30 to 60 min. Source: the author.