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# Analysis of Structural Modifications of Phlogoptite from Bahia/Brazil as an Alternative Source of Potassium in Agriculture

## *Análise das Modificações Estruturais da Flogoptita da Bahia/Brasil como Fonte Alternativa de Potássio na Agricultura*

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Brazil has an enormous agricultural potential, but crop yields can be hampered by the lack of some nutrients in soil. Potassium is one of the main macronutrients needed for plant development. The low content of potassium available in soil makes it necessary to apply fertilizers, mainly imported. In order to promote the development of the sector, phlogoptite rock was studied, from Pindobaçu region, Bahia, which contains 8.26% of $K_2O$ in its chemical composition. Two structural modification methods were applied. The first was the samples calcination with 10% w/w of CaO at different temperatures. The second involved mechanochemical activation by 10% of CaO for 30, 60 and 90 min followed by calcination at different temperatures. In both cases, the samples were submitted to extraction tests with citric acid 0.1 $mol.L^{-1}$. At the end of the tests, it was observed an increase in the nutrient solubility, going from 0.450 $g.L^{-1}$ in the unprocessed rock to 4.14 $g.L^{-1}$ in the sample calcined at 1,200 °C after addition of 10% w/w of CaO and to 25.1 $g.L^{-1}$ in the sample subjected to mechanochemical activation for 90 minutes with 10% w/w of CaO, calcined at 1,000 °C.

**Keywords:** Structural modification; solubility; mechanochemical activation; calcination.

## 1. Introduction

Agribusiness sector has a great importance to Brazilian economy. According to Center for Advanced Applied Economic Studies (CEPEA),[1] the sector accounted for about 21.4% of the country's GDP in 2019, an increase of 3.81% percent over the previous year. This increase came from the animal husbandry segment, since there was a decline of the crops quantity harvested, accompanied by higher costs.

This decline of production and increase of costs can be directly attributed to Brazilian soil fertility. The soil has the function of providing a substrate for plants, storing water and supplying nutrients, in the last case associated with soils chemical characteristics.

Potassium (K) is the macronutrient present in greatest quantity in plants. It has the functions of catalyzing various reactions; synthesizing carbohydrates, proteins, and adenosine triphosphate (ATP); and performing osmotic regulation and enzymatic activation associated with photosynthesis and respiration, thus promoting resistance to pests and diseases (Karimi, R.).[2] Plants can absorb potassium from the soil when it is in the form of potassium ions. However, between 90 and 98% of the potassium present in soil is associated with the crystalline structure of minerals and cannot be absorbed by plants. Hence, the availability of K is directly related to soil physicochemical characteristics (Zörb *et al.*).[3]

Due to potassium low availability in the soil and its great importance to crops development, approximately 95% of global production of K is used in fertilizers, and in 90% of these fertilizers it is in potassium chloride (KCl) form (Oliveira, L. A. M.).[4] Brazilian soils typically have low concentrations of minerals containing potassium in their structures, and low capacity to retain cations, favoring the leaching of K. Therefore, Brazil is responsible for the consumption of 7% of the world production of fertilizer. About 38% of the fertilizer applied in Brazil contains KCl, of which 95% is imported (Richetti, P.).[5]

KCl, the most used potassium fertilizer, contains a 52% concentration of $K^+$ and when applied in the soil dissolves readily, releasing potassium ions. This raises the potential for leaching, causing a large loss of applied K, making repeated fertilizer applications necessary (Valdez *et al.*).[6]

Thus, research is needed to find alternative sources of potassium-rich fertilizers, to improve the country's agricultural productivity and reduce production costs (Santos *et al.*).[7] Among the studies carried out in this regard are those that investigate the stonemeal process, which denotes soil fertilization by direct application of powdered rock to promote remineralization. (Dalmora *et al.*; Van Straaten )[8,9.]

According to Van Straaten (2010)[9] the weathering rate of rocks with a high potassium content is quite slow to replenish the potassium consumed by plants and the release of this nutrient contained in the crystalline lattice is insignificant and unavailable. Stonemeal would make it possible to carry out low-cost and high-efficiency techniques for releasing potassium from methods for physical (mechanical activation), physical-chemical (thermal process) and chemical (acidulation with organic acids) modifications. One of the major advantages of using powdered rock as fertilizer is the slow nutrient release. Studies of the stonemeal process have indicated that in general 4 to 5 metric tons of powdered rock needs to be applied per hectare, which can be in a single application or spread out over a period of up to 5 years (Theodoro & Almeida)[10].

Biotite mineral, present in shale and selenite rocks, is characterized by a high potassium release rate when in contact with plant roots. The study carried out by Karl *et al.*, 2022,[11] evaluated the availability of nutrients in samples of shale biotite and syenite biotite for corn cultivation. According to the results, the rocks provided the nutrients K, Ca, Mg, Fe and Mn. On the other hand, the work carried out by Pereira and Gomes, 2021,[12] obtained better results of potassium release when the biotite was submitted to processes that promoted its structural modification.

Syenite is a rock classified as an alkaline feldspar with an identical chemical and mineralogical composition regardless of the different intrusions origin. However, it has different crystallization forms, causing distinct degrees of $K^+$ leaching. Cícere *et al.*[13] conducted a petrographic study of a set of syenite samples and found that those with finer particles of potassic feldspar and greater fracture degree had faster leaching kinetics, indicating the importance of the grinding process on the availability of potassium to crops.

Glauconite has been applied as an alternative to supply potassium to sunflower (Torqueti *et al.*)[14] In that study, 4 glauconite samples were tested, with varied granulometry and presence of organic matter, and the results were compared with those obtained through traditional potassium fertilizer (KCl) application. The results were promising regarding replacement of traditional fertilizers. Although the results with KCl were slightly better than those with the calcined rock, the glauconite sample with finer granulometry and containing organic matter stood out for yielding more durable flowers after harvest and larger stalk height.

Phlogopitite from Pindobaçu region, Bahia, is a byproduct of emeralds extraction. It is composed mainly of phlogopite, a mineral classified as a mica. The term mica comes from the Latin word *micare* (to glitter) and is used to designate minerals composed of hydrated silicates of aluminum, iron, potassium, sodium and magnesium, having different chemical compositions, with the physical properties of easy cleavage into thin layers, low thermal and electrical conductivity and resistance to high temperatures (Said *et al.*)[15]. It has a 2:1 lamellar structure, where two tetrahedral layers of $SiO_2$ sandwich an octahedral layer of $Al_2O_3$. When the $Si^{4+}$ is isomorphically substituted by $Al^{3+}$, an excessive negative charge is generated that is compensated by cations such as $K^+$ (Fanning *et al.*)[16]. The chemical composition of phlogoptite contains 8.26% of $K_2O$ due to the presence of the mineral phlogopite [$KMg_3(AlSi_3O_{10})(OH)_2$], which has a crystalline phase rich in $K^+$ , enabling its use as an alternate source of $K^+$ for agriculture.

Felix 2014[17] reported that rocks with $K_2O$ levels above 6.0% can be used as alternative sources of potassium by means of the stonemeal method. The rocks normally used for this purpose are composed of minerals such as alkaline feldspars and micas (Shirale *et al.*).[18]

Marchi *et al.*,[19] study the application of agrominerals, among them phlogoptite, in lettuce and rice cultivation soils, as an alternative source of Zn, Cu and Ni micronutrients. The soil containing agrominerals showed a greater availability of plants micronutrients, increasing the production of the region. This can be considered as a good indication of phlogoptite rock application as an alternative source of potassium macronutrient.

This study follows in the footsteps of previous studies by our research group (Felix,[17]; Dias[20]; Fontoura,[21]) and analyzes the structural modifications of phlogoptite rock aiming its use as an alternative source of potassium in agriculture.

## 2. Experimental

The experimental procedures employed in this study consisted of the following steps: ore dressing, chemical and mineralogical characterization, and thermal treatment, with or without mechanochemical activation, to promote structural changes in phlogoptite to release the potassium contained in the crystalline lattice, determined by means of extraction tests with acid solutions.

### 2.1. Ore dressing

10 kg of phlogopitite from Pindobaçu, Bahia, was processed was processed in a jaw crusher in a closed circuit with passage through a 2.38 mm mesh. The crushed rock was homogenized and divided by means of a conical and prismatic pile for 1 kg aliquots removal. Then these were submitted to wet grinding using a suspension with 50% solids in a mill with 10 stainless steel rods having 20 mm diameter, for 30 min at 75 r.p.m.

The ground samples were submitted to wet granulometric analysis in a vibrating screen separator at 945 r.p.m., utilizing a set of sieves with mesh from 1,200 mm to 150 µm. The fractions were dried in an oven at 60 °C for 24 h. The fraction smaller than 150 µm was disaggregated and divided with a Jones riffle splitter, and the resulting aliquots were sent for characterization and use in the structural modification tests.

### 2.2. Technological characterization

The crystalline structure of the phlogoptite was characterized by X-ray powder diffraction (XRD), infrared vibrational spectroscopy (IR), X-ray fluorescence spectrometry (XRF) and scanning electron microscopy (SEM).

The *in natura* samples and submitted to mechanochemical activation, calcination and extraction for 48 and 96 h were obtained with a Bruker-D4 Endeavor diffractometer (Karlsruhe, Germany), under the following operating conditions: Cu Kα radiation (40 kV/40 mA), goniometer speed of 0.02° (2θ) per pass, with counting time of 0.5 s *per* pass and collection from 4 to 80° (2θ), with a LynxEye position sensitive detector. The samples submitted to mechanochemical activation, calcination and extraction for 24 h were obtained with a Bruker-D8 diffractometer (Karlsruhe, Germany) under the following operating conditions: Co Kα (40 kV/25 mA), goniometer speed for 0,01° (2θ), per pass, with counting time for 92 s *per* pass collection from 5 to 80° (2θ). The qualitative interpretations of the diffractograms were carried out by comparison with standards contained in the PDF02 database in the Bruker DiffracPlus software.

The infrared spectra of the samples were obtained with a Thermo Nicolet 6700 Fourier-transform infrared spectrometer (Thermo Fisher Scientific, USA), with diffuse reflectance accessory. Spectra in the range of 4,000 to 500 $cm^{-1}$ were obtained by co-addition of 64 scans with resolution of 4 $cm^{-1}$. The samples were mixed with potassium bromide (KBr) (1:10) and homogenized in an agate mortar and pestle to produce pellets for analysis.

The X-ray fluorescence spectrometry was performed with a Malvern Panalytical mAX-Advanced spectrometer (Almelo, Nethrlans). The loss due to calcination was measured using a sample mass of 0.2000 g in a porcelain crucible, which was weighed before and after calcination for 16 h in a muffle furnace at 1,000°C. The resulting sample was dried in an oven at 100°C for 24 h and then 0.3000 of the binder boric acid was added to 30,000 g of sample. After disaggregation of the sample, a pellet was formed using boric acid in a VANEOX model 20 mm press with a series of three pressures (10, 15 and 20 tons).

Scanning electron microscopy (SEM) was performed with an FEI Quanta 25 FEG microscope (Thermo Fisher Scientific, USA), operating at 25.00 K. The samples were previously metallized with a Leica EM ACE600 sputter coater.

### 2.3. Structural modification of the potassium

Two methods were used to promote the structural change of the rock samples. The first was the addition of CaO (Sigma-Aldrich) without mechanochemical activation, followed by calcination, while the second was mechanochemical activation in a rod mill with CaO followed by calcination.

### 2.4. Calcination in the presence of CaO

Samples of phlogopitite with grain size smaller than 150 µm (*in natura*) were submitted to calcination tests for 4 h in a muffle furnace at temperatures of 600, 900 and 1,200 °C with and without addition of 10% w/w of CaO (Sigma-Aldrich). After 4 h, the samples were removed from the furnace and submitted to thermal shock by immersion in distilled water at room temperature, so that the defects promoted by the calcination process would remain in the mineral structure.

### 2.5. Mechanochemical activation with CaO followed by calcination

In the mechanochemical activation step, the samples *in natura* were placed in a stainless-steel mill bar with 10 bars with diameter of 10 mm, in the presence of 10% w/w of CaO, using a total mass of 500 g, in a rock:water ratio of 1:1. The mechanochemical activation times were 30, 60 and 90 min at 75 r.p.m.. After activation, the samples were dried and calcined for 4 h at temperatures of 600, 800 and 1,000 °C.

### 2.6. Extraction and quantification of potassium

The samples were submitted to extraction tests using an orbital shaker table operating at 200 r.p.m. while in contact with a citric acid (Sigma-Aldrich) solution ($C_6H_8O_7$) at 0.1 mol.$L^{-1}$ in a ratio of 1:10 (calcined sample: $C_6H_8O_7$), with 5 g of sample and 50 mL of solution for 24, 48 and 96 h.

The soluble potassium content in the solutions was quantified by flame atomic emission spectrometry (FAES), using an Analyser model 910M flame photometer (São Paulo, Brazil). The remaining solids were characterized by XRD and IR.

## 3. Results and Discussion

### 3.1. Technological characterization

XRD was used to evaluate the mineralogical composition of the samples. This showed that the *in natura* sample was composed mainly of the mineral phlogopite – $KMg_3(AlSi_3O_{10})(OH)_2$ – but also contained magnesium talc ($Mg_3Si_4O_{10}(OH)_2$) and magnesium-ferri-hornblende

($Ca_2(Mg_4Fe)Si_7AlO_{22}(OH)_2$), which was revealed by the presence of the respective crystalline phases characteristic peaks, at 2.00, 3.35, 5.00, 10.10 Å for phlogopite, 3.12, 9.41 Å for talc and 2.53, 8.45 Å for hornblende, as shown by the diffractogram of Figure 1. This composition is characteristic of the rocks found in the mining region of the state of Bahia (Silva *et al.*),[22] origin of the rock used in this study.

Table 1 reports the chemical composition of *in natura* sample, determined by X-ray fluorescence.

Note that the *in natura* sample was composed mainly of silica, magnesium and alumina (39.9% 17.5% and 10.1%, respectively), which was expected since the rock was classified as an aluminosilicate. These concentrations are in line with those determined for other samples of phlogoptite (Macedo *et al.*,[23] and Sreenivasan *et al.*,[24]). The high content of MgO confirms the presence of magnesium talc mineral, as was also ascertained by XRD. The iron content can be explained by mineral hornblende ($Ca_2(Mg_4Fe)Si_7AlO_{22}(OH)_2$) occurrence (Figure 1) and by the isomorphic substitutions of phlogopite structures - $Si^{4+}$ by $Al^{3+}$ and $Fe^{3+}$ at tetrahedral sites and $Mg^{2+}$ and $Fe^{3+}$ at octahedral sites (Niu *et al.*, [25]). The chemical analysis results corroborate with those of the mineralogical analysis (XRD), since the high content of $K_2O$ (8.26%) is explained by the presence of phlogopite, the main constituent of the sample. This is very important for the purposes of this study since the release of potassium ions by phlogopite occurs more easily than from feldspar minerals. The reason for this faster release is that the ions occupy the interlayer position of the 2:1 structure, only stabilizing weak bonds, which allows the substitution by $Na^+$, $Mg^{2+}$ and $Ca^{2+}$ cations during the weathering process (Teixeira, *et al.,* [26]).

Infrared spectra were used to complement the data obtained by XRD. The IR spectrum obtained for the phlogoptite is presented in Figure 2.

The IR spectrum contained bands characteristic of phlogopite [$KMg_3(AlSi_3O_{10})(OH)_2$] (Silva *et* al.,[22] ; Bigham *et al.*,[27]) as presented in Table 2. Since the spectrum presented is in the range from 4000 to 500 $cm^{-1}$.

The band in the region of 3,719 $cm^{-1}$ refers to the stretching of O-H bond of Mg(OH) group. This band is typically observed in the 3,704 – 3,712 $cm^{-1}$ range of natural phlogopites. The spectra of samples also shows bands in the 3,500 $cm^{-1}$ region, referring to the axial stretch of OH group; a band at 1,072 $cm^{-1}$ is characteristic of Si-O-Si bond; the band at 942 $cm^{-1}$ is attributed to the vibrations of Al-OH bond; bands in the 660-730 $cm^{-1}$ region refer to the vibration of Al-Si-O bond; the band at 817 $cm^{-1}$ is characteristic Al-O vibration bond of the $AlO_4$ group and the band at 1,620 $cm^{-1}$, which is attributed to adsorbed water molecules. (Silva *et al.*,[22]; Silverstein,[28]; Bigham *et al.*[27]). All these bands are characteristic of the mineral phase of phlogopite, which is the main constituent of the rock under study.

We used scanning electron microscopy (SEM) to observe the morphology of the samples. The images in Figure 3

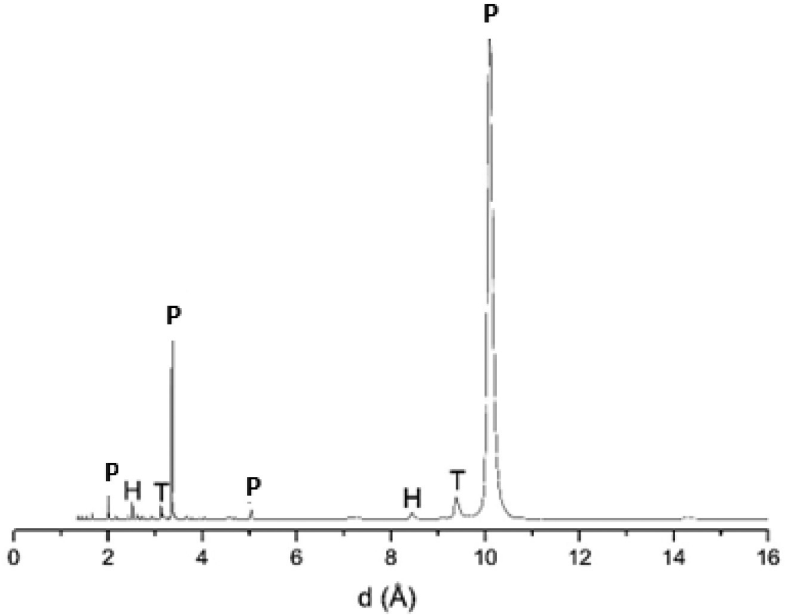

**Figure 1.** X-ray diffractogram (Cu(Kα)) of the *in natura* sample. P = Phlogopite ($KMg_3(AlSi_3O_{10})(OH)_2$), T= magnesium talc ($Mg_3Si_4O_{10}(OH)_2$ ) and H= hornblende ($Ca_2(Mg_4Fe)Si_7AlO_{22}(OH)_2$)

**Table 1.** Chemical composition of *in natura* sample

| Oxide | $SiO_2$ | $Al_2O_3$ | MgO | $Fe_2O_3$ | $K_2O$ | CaO | $Cr_2O_3$ | MnO | NiO | LOI* |
|---|---|---|---|---|---|---|---|---|---|---|
| **Content (%)** | 39.9 | 10.1 | 17.5 | 8.60 | **8.26** | 0.54 | 0.51 | 0.18 | 0.14 | 12.0 |

*Loss on ignition.

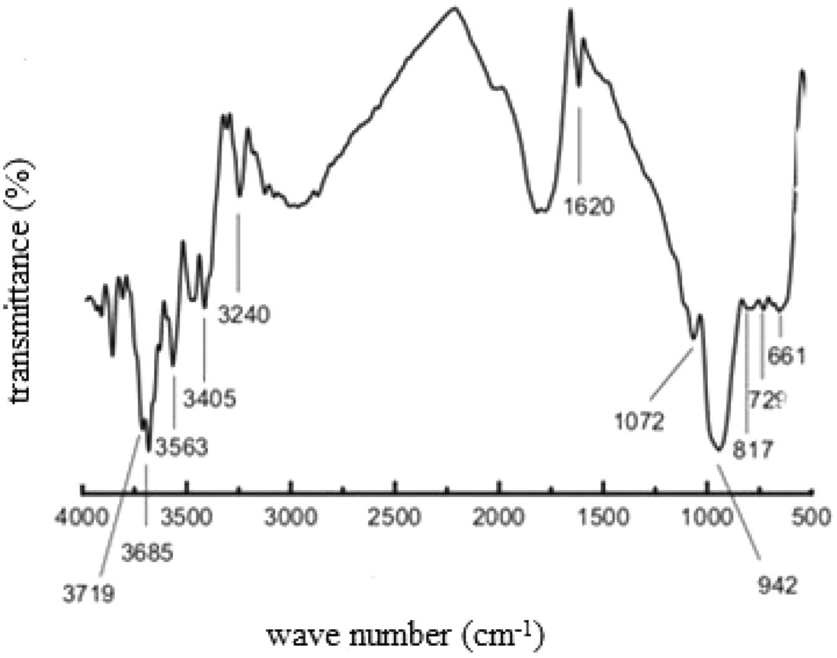

**Figure 2**. Infrared spectrum of the *in natura* sample Reprinted from Publication Journal of the Brazilian Chemical Society 2013, 24(8), 1366-1372, Silva, A. A. S.; Sampaio, J. A.; Luz, A. B.;França, S. C. A.; Ronconi, C. M.; Modeling controlled potassium release from phlogopite in solution: exploring the viability of using crushed phlogopitite rock as an alternative potassium source in Brazilian soil; doi:10.5935/0103-5053.20130173, with permission from JBCS, PubliSBQ Editorial Manager

**Table 2.** Vibrations characteristic of the bonds referring to the elements of the phlogoptite sample obtained by IR spectrometry

| Vibrational modes | Wavenumbers (cm$^{-1}$) |
|---|---|
| O-H | 3,700 |
| Si-O-Si | 1,072 |
| Al-OH | 942 |
| Al-O-Si | 660-729 |
| Al-O | 817 |
| Water molecules | 1,620 |

show that the rock has a lamellar structure, characteristic of minerals of the mica group, to which the mineral phlogopite belongs (Rizzo *et al.*).[29] This structure is present because the crystalline unit characteristic of this class is formed by two tetrahedral layers of silicon and one octahedral layer of aluminum in the center, in a 2:1 lamellar arrangement.

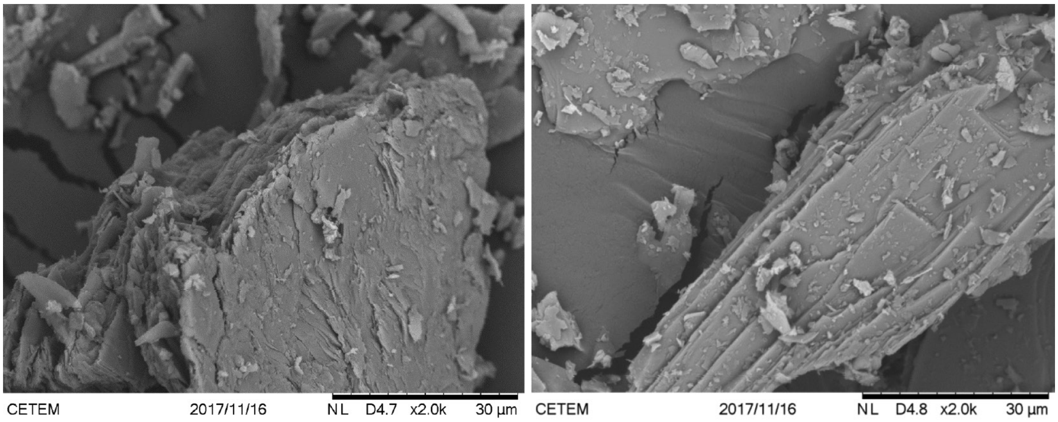

**Figure 3.** SEM images of the *in natura* sample

The data in Table 1, obtained by XRF, indicate that the phlogoptite sample is composed of 8.26% of $K_2O$. However, not all this potassium is available for release into the soil. With the objective of quantifying how much of this nutrient is available for release, tests of release were carried out from acid solutions by flame atomic emission spectrometry (FAES). The results indicated that in the *in natura* sample, 0.450 g.L$^{-1}$ of potassium contained in the rock was in soluble form, equivalent to a 0.54% potassium concentration (82.6 g.L$^{-1}$).

### 3.2. Structural modification tests

To increase the content of soluble potassium, calcination with and without a fluxing agent and mechanochemical activation followed by calcination were applied. These techniques, which were developed and consolidated by our research group, aiming to promote structural modifications in the sample by inserting new cations in the structure and by thermal treatment.

In the calcination tests, CaO was used as the fluxing agent, which also is a good modifier of the glass network (Silva *et al.*)[30]. In this respect, the objective of applying CaO in the calcination step was to form new stable crystalline phases with the presence of $Ca^{2+}$ and to increase the solubility of any glass structures formed (Felix)[17]. To assure maintenance of the changes promoted during the calcination process, the samples were submitted to thermal shock by direct contact with distilled water at room temperature, since slow cooling can favor the formation of chemical bonds with the inserted potassium.

After the addition of CaO and conclusion of the calcination tests, the samples were submitted to extraction with $C_6H_8O_7$ at 0.1 mol.L$^{-1}$ during the three-time intervals previously determined, and the concentration of potassium was measured by flame atomic emission spectroscopy (FAES). The results are reported in Table 3.

Among the results obtained, of particular interest are those of the tests with calcination at 1,200 °C in the presence of CaO and extraction during 24, 48 and 96 h. The levels of soluble $K^+$ were 4.14 g.L$^{-1}$ for the sample extracted for 24 h, 2.25 g.L$^{-1}$ for 48 h, and 1.25 g.L$^{-1}$ for 96 h. These contents represent 5.01%, 2.72% and 1.51% of the potassium present in the rock, respectively.

The initial increase in nutrient solubility and the decrease of potassium extraction with extraction time increase can be explained based on the XRD and IR results of phlogoptite samples after the structural modification and extraction steps. Figure 4 depicts the X-ray diffractograms of the samples calcined for 4 h at 1,200 °C and submitted to extraction tests for 24, 48 and 96 h. The increase in the intensity of phlogopite peak with the increase of extraction time indicates that potassium has been reincorporated into the crystalline structures.

The diffractograms of the samples calcined at 1,200 °C show the absence of new crystalline phases with the incorporation of potassium and decreased intensity of the peaks of the calcined phlogopite in comparison with the diffractogram of the *in natura* sample. In this respect, analysis of the data in Table 3 shows that the initial increase in the release of potassium is related to the reduced intensity of the peak characteristic of phlogopite, indicating that at this moment partial rupture of the phlogopite structure occurred, favoring the access of the extraction solution to the potassium ions composing the mineral (Niu *et al.*)[25]. Therefore, the decreased intensity of the peaks referring to phlogopite and the absence of formation of new mineral phases containing potassium explain the increase of its solubility (Santos *et al.*)[31].

The data in Table 3 show that increasing extraction time was associated with a progressive decline in the quantity of potassium released. This result was opposite to what was expected, which was that the increase of contact time would be accompanied by a greater quantity of potassium in solution.

Equation 1 presents the equilibrium that should have been obtained when a solution containing different cations ($M^+$) than the original contra-ions of the phlogopite ($K^+$) is placed in contact with the mineral.

$$KMg_3\left(AlSi_3O_{10}\left(OH\right)_2\right)_{(s)} + M^+_{(aq)} \rightleftarrows MMg_3\left(AlSi_3O_{10}\left(OH\right)_2\right)_{(s)} + K^+_{(aq)} \qquad (1)$$

Therefore, it can be considered that the equilibrium obtained when using an acid solution is represented by Equation 2:

$$KMg_3\left(AlSi_3O_{10}\left(OH\right)_2\right)_{(s)} + H^+_{(aq)} \rightleftarrows HMg_3\left(AlSi_3O_{10}\left(OH\right)_2\right)_{(s)} + K^+_{(aq)} \qquad (2)$$

Thus, as the contact time of the phlogopite with the acid solution progressed, we expected the mineral to dissolve

**Table 3.** Results of available $K^+$ from the extraction tests of phlogoptite rock powder with granulometry smaller than 150 μm, submitted to structural modification without mechanical activation.

| **Experimental Conditions** | | **Soluble $K^+$ (g.L$^{-1}$)** | | | | | |
|---|---|---|---|---|---|---|---|
| **Calcination 4 h** | | **Without CaO** | | | **With CaO 10% w/w** | | |
| **Temperature (ºC)** | | 600 | 900 | 1200 | 600 | 900 | 1200 |
| **Extraction Time (h)** | 24 | 0.351 | 0.225 | 0.530 | 0.625 | 0.614 | **4.14** |
| | 48 | 0.246 | 0.340 | 0.361 | 0.666 | 0.299 | **2.25** |
| | 96 | 0.118 | 0.404 | 0.112 | 0.425 | 0.444 | **1.25** |

*Level of available $K^+$ from phlogoptite *in natura* = 0.450 g.L$^{-1}$

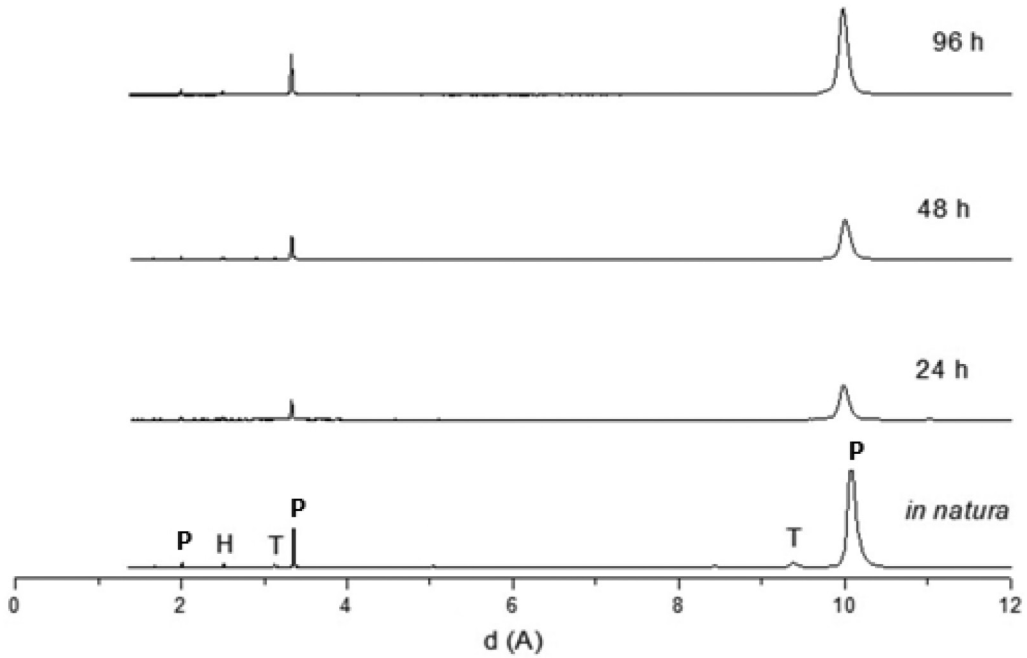

**Figure 4.** X-ray diffractograms obtained from phlogoptite *in natura* (Cu(K$\alpha$)) and calcined at 1,200 ºC for 4 h with 10% w/w CaO and submitted to extraction with $C_6H_8O_7$ at 0.1 mol.L$^{-1}$ for 24, 48 and 96 h (Co(K$\alpha$)). P = Phlogopite ($KMg_3(AlSi_3O_{10})(OH)_2$) T= Magnesium talc ($Mg_3Si_4O_{10}(OH)_2$) and H= Hornblende

according to Equation 2, and consequently for the quantity of potassium in the aqueous solution to increase. The data in Table 3 show that with extraction for 24 h, the expected increase occurred. These data together with Figure 4 indicate a relative decrease in the intensity of the peak characteristic of phlogopite after extraction for 24 h, and no formation of any other potassium-rich phase. This confirms phlogopite dissolution with consequent potassium release in solution.

However, with longer extraction time, there was a decrease of the quantity of potassium released. These data on potassium release together with the X-ray diffractograms indicate that with increase in time, the intensity of the peaks related to phlogopite also increased. This situation leads us to believe that after the dissolution of potassium reaches a specific saturation level, reversal of the chemical equilibrium possibly occurs, to the reaction represented by Equation 2, and restoration of the structure of the phlogopite. This is a possible motive to explain the reduction in the quantity of potassium in solution.

The rearrangement of the phlogopite phase was also confirmed by the IR spectra of the samples (Figure 5). A reduction of the intensity of the band near 3,500 cm$^{-1}$, which is characteristic of the O-H bonds present in the crystalline phase, was identified, in line with the finding reported by Corno *et al.*[32] This further contributes to the hypothesis of structural rearrangement during calcination.

Another method applied for structural modification of the rock was mechanochemical activation. In this process, the mineral is submitted to mechanical forces that cause distortions in its crystalline lattice, enabling some chemical reactions that do not occur with thermal activation alone (Azevedo *et al.*)[33]. When mechanochemical activation is performed followed by calcination, the objective is to promote the disorder of the minerals crystalline structure, transforming it into an amorphous structure (Kumar *et al.*)[34]. The results of the samples submitted to extraction with citric acid ($C_6H_8O_7$) at 0.1 mol.L$^{-1}$ after mechanochemical activation and calcination are presented in Table 4.

Among the results in Table 4, the most relevant are those of the samples submitted to mechanochemical activation for 90 min, calcined at 1,000 °C and subjected to extraction for 24, 48 and 96 h. In these cases, the soluble potassium contents were 22.9 g.L$^{-1}$ for the sample after extraction for 24 h, 25.1 g.L$^{-1}$ for 48 h, and 13.9 g.L$^{-1}$ for 96 h. These contents respectively represented 27.7%, 30.4% and 16.8% of the total potassium present in the samples, very significant values compared with the 0.54% of soluble K$^+$ in the unprocessed sample (*in natura*).

The 56-fold increase in potassium solubility can be explained by the XRD patterns and IR spectra of the samples. The diffractograms of the samples that were submitted to mechanochemical activation for 90 min and then calcined for 4 h at 1,000°C and extracted for 24, 48 and 96 h are presented in Figure 6.

Analyzing Figure 6, it can be observed that X-ray diffractograms profile is quite similar, both for in-nature sample and for treated samples. However, despite the similarity between these figures there is a fundamental difference between them, the intensity of the peaks relative to phlogopite mineral ($KMg_3(AlSi_3O_{10})(OH)_2$). Relating this event to the increase in the release of potassium we can say that there was a destabilization of the crystalline structure of the phlogopite when the samples are mechanically activated and extracted for 24, 48 and

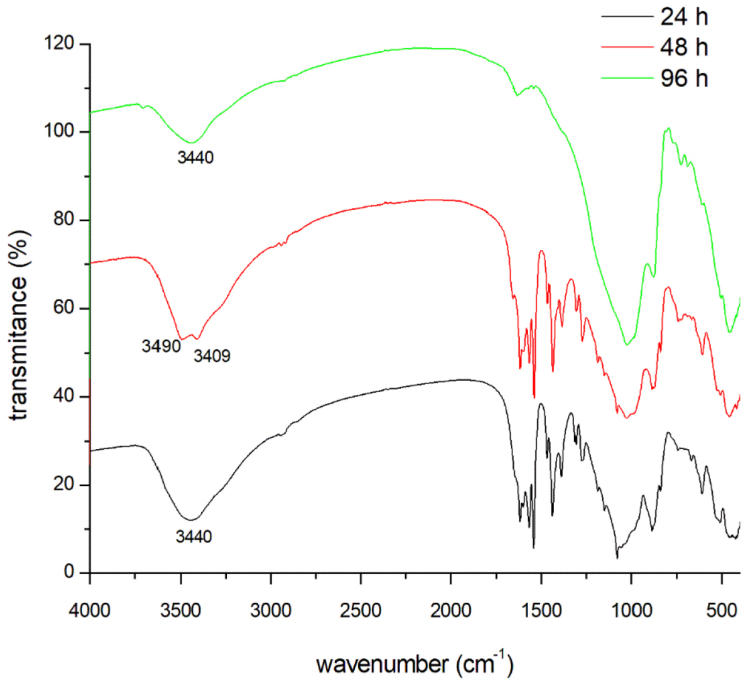

**Figure 5.** Infrared (IR) spectra obtained for the samples of phlogopite calcined at 1,200 °C for 4 h with 10% w/w of CaO and submitted to extraction with $C_6H_8O_7$ at 0.1 mol.L$^{-1}$ for 24, 48 and 96 h. Reduction of the band at 3,440 cm$^{-1}$ characteristic of phlogopite

**Table 4.** Results of available $K^+$ from the tests of extraction from powdered phlogoptite rock with granulometry smaller than 150 µm, submitted to structural modification and mechanochemical activation with 10% w/w of CaO.

| **Experimental Conditions** | | **Soluble $K^+$ / (g L$^{-1}$)** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Calcination 4h** | | **Activation 30 min** | | | **Activation 60 min** | | | **Activation 90 min** | | |
| **Temperature (°C)** | | 600 | 800 | 1,000 | 600 | 800 | 1,000 | 600 | 800 | 1,000 |
| **Extraction time (h)** | 24 | 0.243 | 0.232 | 8.07 | 0.250 | 0.180 | 10.6 | 0.171 | 0.180 | **22.9** |
| | 48 | 0.171 | 0.136 | 9.11 | 0.310 | 0.180 | 20.8 | 0.197 | 0.154 | **25.1** |
| | 96 | 0.258 | 0.197 | 9.64 | 0.267 | 0.145 | 10.6 | 0.206 | 0.145 | **13.9** |

96 h. This fact suggests that potassium ions, constituents of the structure of phlogopite, are more available for ionic exchange, thus justifying the considerable increase in the release of potassium in these treatment conditions. The X-ray diffractograms of the sample extracted for 48 h has the least intense peak, so the destabilization of phlogopite is higher, consequently higher potassium content is released. We can also see that the efficiency in the release of potassium in times of 24 and 48 h is practically the same. These results corroborate with the corresponding diffractograms to these samples since the intensity of the phlogopite peaks in these diffractograms is similar. The sample extracted for 96 h has the most intense peak of phlogopite, indicating a lower destabilization of the mineral, which culminated in the lower potassium content released the activated samples. Besides this, a stable crystalline phase was formed by the insertion of $K^+$. Finally, a peak appeared referring to diopside ($CaMgSi_2O_6$), a phase rich in $Ca^{2+}$ and $Mg^{2+}$ (Pereira *et al.*)[35]. Taken together, these results indicate that the promotion of chemical reactions through application of mechanical energy during the mechanochemical activation was efficient.

The infrared spectra of the samples activated mechanochemically and calcined (Figure 7) confirm the destabilization of phlogopite and the formation of another mineral phase during the activation and thermal treatment. In these spectra, it is possible to observe the reduced transmitance (%) of the band in the region of 3,500 cm$^{-1}$, referring to O-H bond. Moreover, this band was broader, further supporting the possible structural destabilization of the phlogopite. Comparing IR spectra of the activated versus the non-activated samples shows the different profiles of these bands, explaining the considerable increase in potassium release from the activated samples, because the disruption of the phlogopite was more evident due to the broadening of these bands.

## 4. Conclusion

The content of soluble $K_2O$ in the unprocessed phlogoptite was 0.450 g.L$^{1}$, representing 0.54% of the

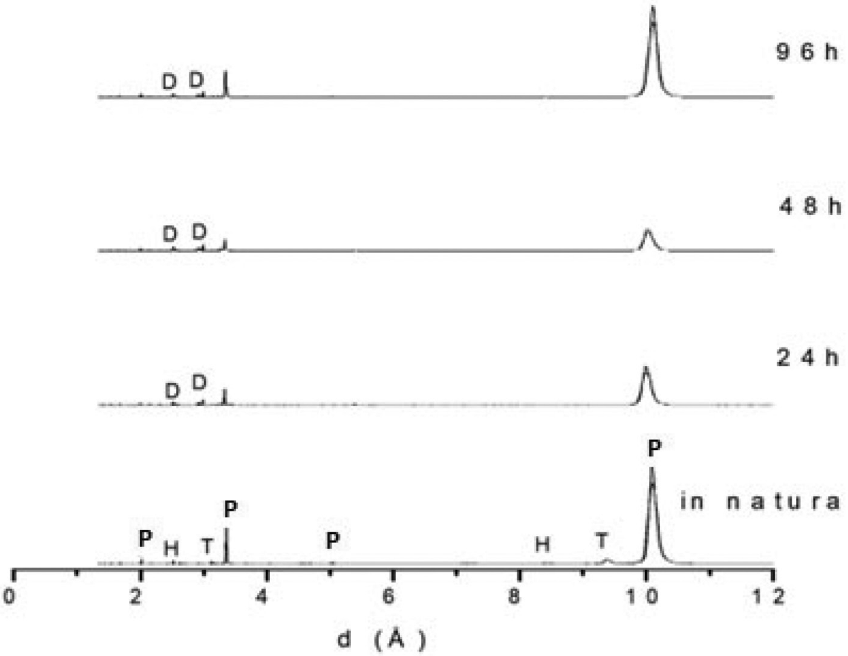

**Figure 6.** X-ray diffractograms obtained for the *in natura* sample (Cu(Kα)) and submitted to mechanochemical activation (MA) with 10% of CaO for 90 min, calcined at 1,000 °C for 4 h and extracted with $C_6H_8O_7$ at 0.1 mol.L$^{-1}$ for 24 (Co(Kα)), 48 and 96 h (Cu(Kα)). P = Phlogopite ($KMg_3(AlSi_3O_{10})(OH)_2$), D = Diopside ($CaMgSi_2O_6$), T= Magnesium talc ($Mg_3Si_4O_{10}(OH)_2$) and H = Hornblende ($Ca_2(Mg_4Fe)Si_7AlO_{22}(OH)_2$)

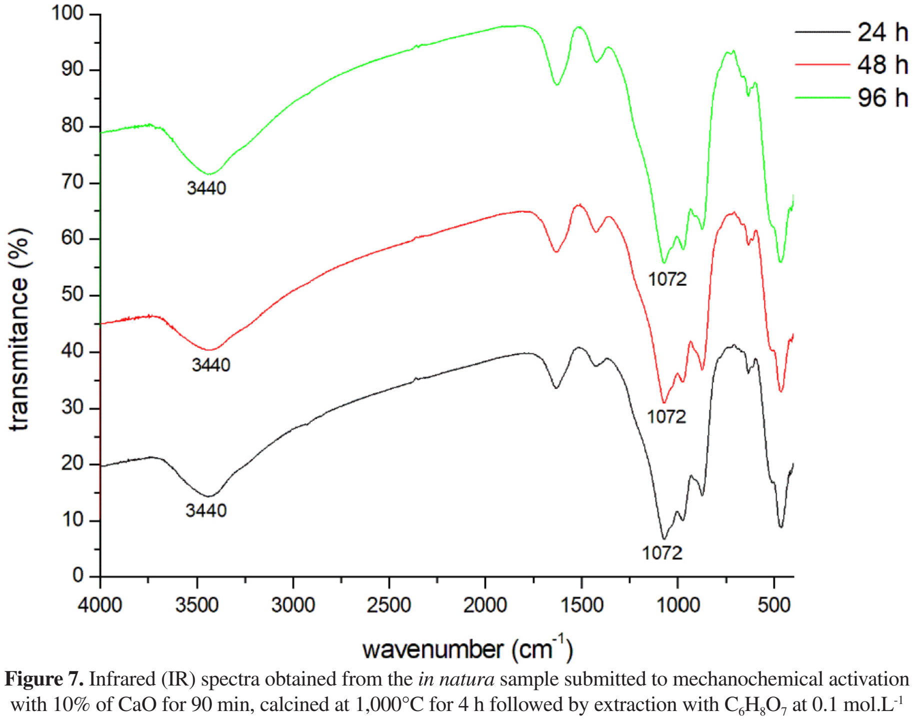

**Figure 7.** Infrared (IR) spectra obtained from the *in natura* sample submitted to mechanochemical activation with 10% of CaO for 90 min, calcined at 1,000°C for 4 h followed by extraction with $C_6H_8O_7$ at 0.1 mol.L$^{-1}$ for 24, 48 and 96 h. Reduction of the band at 3,440 cm$^{-1}$, characteristic of phlogopite, and emergence of bands in the 1,100 cm$^{-1}$ region referring to the glass network rich in silica and modified by CaO

82.6 g.L$^{-1}$ of $K^+$ present in the rock. After thermal treatment at 1,200 °C for 4 h with addition of 10% w/w of CaO and submission to extraction with citric acid at 0.1 mol.L$^{-1}$ for 24 h, the content of soluble $K_2O$ increased to 4.14 g.L$^{-1}$, 5.01% of all the potassium present. When the powdered rock was subjected to mechanical activation with 10% of CaO for 90 min, followed by calcination for 4 h at 1,000 °C and extraction for 48 h with the citric acid solution at 0.1 mol.L$^{-1}$, the content of soluble potassium was 25.1 g.L$^{-1}$, representing 30.4% of the total content.

Therefore, we can conclude that the treatment of phlogoptite was satisfactory with respect to potassium solubility increase, reaching a 9-fold increase of soluble $K^+$ for the samples submitted to mechanical addition of CaO and a 56-fold increase in the level of soluble potassium for the sample submitted to mechanochemical activation.

The increase of the content of soluble potassium was directly associated with the alterations of the mineral structure during the activation process. This was demonstrated by the diffractograms of the samples, in which there was a decrease in the intensity of phlogopite mineral peak compared to the peak of the unprocessed sample and the emergence of a diopside crystalline phase, rich in $Ca^{2+}$ and $Mg^{2+}$. The structural rearrangement was confirmed by the infrared spectra of the samples, in which there was a decrease in transmitance of the band in the region of 3,500 $cm^{-1}$, referring to phlogopite O-H bond.

Both modification methods applied produced an increase of exchangeable potassium content. The mechanochemical activation method was more efficient in promoting reactions in the solid state by means of fractures in the crystalline structure and the mechanical energy applied to the system. These reactions were enhanced when the process was followed by thermal activation (calcination).

The promising results obtained in this study associated with the low complexity of the tests and the good solubility of the potassium enable the application of phlogoptite in agriculture as an alternative source of potassium. This is particularly important due to the possibility of substituting expensive imported fertilizers to supplement the low level of this nutrient in typical Brazilian soils.

According to the results obtained, the prospective future of this research will be evaluate the influence of climatic conditions (dry and rainy periods) on the extraction of other ionic phases and the use of characterization techniques such as capacity exchange cationic and textural analysis (BET and B.J.H.) of treated samples in order to corroborate with the elucidation of structural changes after the extraction process.

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## References

1. Centro De Estudos Avançados Em Economia Aplicada (CEPEA); *PIB do agronegócio*. Available at: <www.cnabrasil.org.br>. Accessed on: 5 th March 2022.
2. Karimi, R.; Potassium-induced freezing tolerance is associated with endogenous abscisic acid, polyamide and soluble sugars changes in grapevine. *Scientia Horticulturae* **2017**, *215*, 184. [Crossref]
3. Zörb, C.; Senbayram, M.; Peiter, E.; Potassium in agriculture-Status and perspectives. *Journal of Plant Physiology* **2014**, *171*, 656. [Crossref]
4. Oliveira, L. A. M.; Sumário Mineral. Brasília: Departamento nacional de produção Mineral – DNPM. Available at: <http://www.anm.gov.br/dnpm/publicacoes/serie-estatisticas-e-economia-mineral/sumario-mineral>. Accessed on: 5th September 2022.
5. Richetti, P.; Tendências da produção de fertilizantes no Brasil. Available at: <http://www.cenarioagro.com.br/tendencias-da-producao-de-fertilizantes-no-brasil/>. Acessed on: 5th September 2022.
6. Valdez, S. K.; Abregu, B. A.; Orce, A.; Kwok, L. H.; Alternatives for the Production of Potassium Fertilizers in Argentina. *Journal of Agricultural Science and Food Research* **2020**, *11*, 270. [Link]
7. Santos, W. O.; Mattiello, E. M.; Vergutz, L.; Costa, R. F.; Production and evuluation of potassium fertilizers from silicate rock. *Journal of Plant Nutrition and Soil Science* **2016**, *179*, 421. [Crossref]
8. Dalmora, A. C.; Ramos, C. G.; Oliveira, M. L. S.; Oliveira, L. F. S.; Schneider, I. A. H.; Kautzmann, R. M.; Aplication of Andesite rock as a clean source of fertilizer for eucalyptus crop: Evidence of sustainability. *Journal of Cleaner Production* **2020**, *256*, 120432. [Crossref]
9. Van Straaten, P.; Distribuition of agromineral resources in space and time-a global geolocial erpective. P*esquisa Agropecuária Brasileira* **2022**, 57 [Crossref]
10. Theodoro, S. H.; Almeida, E.; Agrominerais e a construção da soberania em insumos agrícolas no Brasil. *Agriculturas* **2013**, *10*, 22. [Link]
11. Krahl, L. L.; Valadares, L. F.; Sousa-Silva, G; M.; Martins, E. S.; Increase in cátion Exchange capacity by the action of maize rhizosphere on Mg or Fe biotite-rich rocks. *Pesquisa Agropecuária Brasileira* **2022**, *57*, 01467. [Crossref]
12. Pereira, A. C.; Gomes, M. R. S.; Biotita e flogopita como fonte alternativa de potássio para fertilizante: Extração hidrometalúrgica. *Geociências* **2021**, *71*, 786. [Link]
13. Cicere, D.; Oliveira, M.; Stokes, R. M.; Skorina, T.; Allanore, A.; Characterization of potassium agrominerals: Correlation between petrographic features, comunnition and leaching of ultrapotassic syenites. *Minerals Engineering* **2017**, *102*, 42. [Crossref]

14. Torqueti, S. T. S.; Boldrin, K. V. F.; Nascimento, A. M. P.; Paiva, P. D. O.; Neto, A. E. F.; Luz, I. C. A.; Alternative potassium source for the cultivation of ornamental sunflower. *Ciência e Agrotecnologia* **2016**, *40*, 257. [Crossref]
15. Said, A.; Hu, H.; Liu, Y.; Zhang, H.; Qu, J.; Mehcanochemical activation of phlogopite to enhance its capacity as absorbent for the removal of heavy metal ions. *Water, Air, & Soil Pollution volume* **2021,** *232*, 15. [Crossref]
16. Fanning, D. S.; Keramidas, V. Z.; El-desoky, M. A.; Em *Micas In Minerals in Soil Environments*, Dixon, J. B.; Weed, S. B. (Eds.); 2nd Edition, 1989, cap. 12. [Crossref]
17. Felix, A. A. S.; *Tese de doutorado,* Universidade Federal do Rio de Janeiro, 2014. [Link]
18. 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.; Prospecti and challenges n utilization of indigenous rocks and minerals as source of potassium in farming rocks and minerals as source of otassium. *Journal of Plant Nutrition* **2019**, *42*, 2682. [Crossref]
19. Marchi, G.; Guelfi-Silva, D. R.; Malaquias, J. V.; Guilherme, L. R. G.; Spehar, C. R., Martins, E. de S.; Solubility and avalability of micronutrients extracted from silicate agrominerals. *Pesquisa Agropecuária Brasileira* **2020**, *55*, 1. [Crossref]
20. Dias, R. S. S.; *Trabalho de conclusão de curso*, Universidade Federal do Rio de Janeiro, 2014. [Link]
21. Fontoura T. C. S.; *Trabalho de conclusão de curso*, Universidade Federal do Rio de Janeiro, 2017. [Link]
22. Silva, A. A. S.; Sampaio, J. A.; Luz, A. B.; França, S. C. A.; Ronconi, C. M.; Modeling controlled potassium releases from phlogopite in solution: Exploring the viability of using crushed phlogopite rock as na alternative potassium source in brazilian soil. *Journal of the Brazilian Chemical Society* **2013**, *24*, 1366. [Crossref]
23. Macedo, H. A. O.; Giustina, M. E. S. D.; Oliveira, C. G.; Praxedes, I. F.; The São Luis de Montes Belos vermiculite deposit, central Brazil: Hydrothermal mineralization associated with intracontinental strike slip zone. *Journal of South American Earth Sciences* **2018**, *88*, 459. [Crossref]
24. Sreenivasan, H.; Kinnunen, P.; Heikkinein, E. P.; Illikainen, M.; Caracterização de flogopita para processamento de filtros cerâmicos porosos pelo método de replica. *Minerals Engeenering* **2017**, *113*, 47. [Crossref]
25. Niu, H.; Kinnunen, P.; Sreenivasan, H.; Adesanya, E.; Illikainen, M.; Structural collapse in phlogopite mica-rich mine tailings induced by mechanochemical treatment and implications to alkali activation potential. *Minerals Engeenering* **2020,** *151*, 106331. [Crossref]
26. Teixeira, A. M. S.; Garrido, F. M. S.; Medeiros, M. E.; Sampaio, J. A.; Estudo do comportamento térmico da rocha fonolito com fins à produção de fertilizantes. *Holos* **2015**, *5*, 52. [Crossref]
27. Bigham, J. M.; Bahtti, T.; Vourionen, A.; Toouvinen, O. H.; Dissolution and structural alteration of phlogopite mediated by proton attack and bacterial oxidation of ferrous iron. *Hydrometallurgy* **2001**, *59*, 301. [Crossref]
28. Silversteins, R. M.; Bassler, G. C.; Morril, T. C.; Em *Espectroscopia no infravermelho. Identificação espectrométrica de compostos orgânicos,* 5th edition, 1994, cap 3.
29. Rizzo, G.; Piluso, E.; Morten, L.; Phlogopite from the Serre ultramafic rocks, Central Calabria, Southern Italy. *European Journal Mineralogy* **2001**, *13*, 1139. [Crossref]
30. Silva, A. A. S.; Medeiros, M. E.; Sampaio, J. A.; Garrido, F. M. S.; Verdete do cedro de abaté como fonte de potássio: caracterização, tratamento térmico e reação com CaO. *Matéria* **2012,** *17*, 1061. [Crossref]
31. Santos, W. O.; Mattiello, E. M.; Pacheco, A. A.; Vergutz, L.; Souza-filho, L. F. S.; Abdaka, D. B.; Thermal treatment of a potassium-rich metamorphic rock in formation of soluble K forms. *International Journal of Mineral Processing* **2017**, *159*, 16. [Crossref]
32. Corno, M.; Pedone, A.; Dovesi, R.; Ugliengo, P.; B3LYP simulation of the full vibrational spectrum of the 45S5 bioactive silicate glass compared to v-silica. *Chemistry of Materials* **2008**, *20*, 5610. [Crossref]
33. Azevedo, C. A. D.; Garrido, F. M. S.; Medeiros, M. E.; The effect of the mechanochemical activation oon the reactivity in the $MgO-Al_2O_3-SiO_2$ system. *Journal of Thermal Analysis and Calorimetry* **2006**, *83*, 649. [Crossref]
34. Kumar, G.; Tanvar, H.; Pratap, Y.; Dhawam, N.; Thermal and mechanical activation of sericite for recorvery of potash values. *Transactions of the Indian Institute of Metals* **2019**, *72*, 17. [Crossref]
35. Pereira, A. C.; Gomes, M. R. S.; Rocha, S. D. F.; Glauconita como fonte alternativa de potássio para a produção de fertilizante de liberação lenta. *Genomos, CPMTC-UFMG* **2019**, *27*, 32. [Crossref]