Nutrient release from K-feldspar ore altered in hydrothermal conditions

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Abstract
The development of potash materials from local K-bearing resources such as aluminosilicate minerals is desirable to overcome reliance on imported fertilizers in tropical countries. However, the nutrient release from such materials follows a time-dependent profile that is not well-understood and that is significantly different if probed at agronomic or geological timescales. This work investigates the nutrient release from a calcium–aluminum–silicate–hydrate (C–A–S–H) material obtained via hydrothermal alteration of K-feldspar ore and CaO. The C–A–S–H hydrothermal material is subjected to sequential leaching cycles with diluted HNO3 (initial pH = 5), renewing the leaching solution at every cycle. X-Ray Powder Diffraction (XRD) is used to monitor changes in the material mineralogy as the leaching progresses, showing a relative increase of calcite (up to 7 wt%) and amorphous phase (up to 23 wt%). Inductively Coupled Plasma Mass Spectrometry (ICP-MS) of the leachates is used to monitor the release of K, Ca, Si and Al, and shows that the material releases K nutrient at every leaching cycle. The pH of the leachates shows that as the content of calcite in the material increases a buffering capacity at pH ≈ 9.6 is developed by the material. The mineralogy, nutrient release, and pH results presented in this study suggest a potential application of the material as a slow release fertilizer when compared to KCl. Experimental results also imply that kinetic parameters rather than solubility are more suited to describe the fertilizer value of silicate materials.

Keywords Calcium–aluminum–silicate–hydrate (C–A–S–H) • K-feldspar • Hydrothermal processing • Potash • Slow release fertilizers

Introduction
Traditionally, K fertilizers (potash) have been obtained from KCl, which is mined profitably in the Northern hemisphere as evaporitic ore. However, in the tropics the development of a new generation of fertilizers is required due to the fertilizer high price at the farmer’s gate, increasing demand deriving from increasing population and quest for reduction in agricultural yield gaps. Recent research has demonstrated the importance of K-bearing rocks for agriculture (Van Straaten 2006; Manning 2010; Liu et al. 2015; Ciceri et al. 2017a). Silicate minerals such as K-feldspar (KAlSi3O8) and micas may be used as potassium (K) feedstock alternative to imported KCl (Ciceri et al. 2017b). A review of geological deposits of alkaline rocks can be found elsewhere (Woolley 1987; Kogarko et al. 1995; Woolley 2001).

Chemical processing can enhance the rate of nutrient release and the fertilizing properties of these silicate minerals. As an example, alkaline hydrothermal alteration of K-feldspar with CaO has been shown to be an option to engineer fertilizers from local and affordable raw materials (Ciceri et al. 2017a, 2019).

Currently, key chemical properties used to describe the agricultural value of potash are the nutrient content (K2O wt%), the salt index and the solubility, which are not necessarily suited to describe the properties of alternative resources such as raw or processed K-feldspar powders (Supplementary Table S1). The residual effect, i.e. the favorable response of crops to the major nutrients applied to a previous crop, may also be used to evaluate fertilizers, but it has not been investigated sufficiently for potash materials (Cook 2017a).

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Nutrient content is critical because fertilizer guidelines are generally based on the nutrient offtake, i.e., the amount of fertilizer material needed for the new agricultural season should match, at minimum, the amount of K_2O nutrient removed by the crops of the previous season (Supplementary Table S1).

Salt index (SI) is the ratio between the increase in osmotic pressure of the soil solution resulting from fertilizer addition to a given soil, and that resulting by addition of the same pressure of the soil solution resulting from fertilizer addition (Chou and Wollast 1985; Wilson 2004; Crudewell 2015a, b; Skorina and Allanore 2015; Ciceri and Allanore 2015). The resulting feldspar dissolution rate determined in the laboratory is considered too slow for fertilizer purposes (10^{-10} to 10^{-13} mol K^+ m^{-2} s^{-1}), but conflicting agronomic results demonstrate that the key issue is determining if the actual dissolution rate in soil could be synchronized with the rate of crop uptake, which in turn is not known with accuracy (Drew and Nye 1969; Drew et al. 1969; Bakken et al. 1997; Manning 2010; Ciceri et al. 2017b; Manning et al. 2017).

A kinetic understanding of fertilizer materials becomes important also to elucidate the reactivity of potential alternatives, such as the hydrothermal material obtained as a result of the alteration process of K-feldspar by CaO (Ciceri et al. 2017a, 2019). Such a material was shown to contain at least three distinct K-bearing components (Ciceri et al. 2017a). The first was likely a carbonate or a mixture thereof (K_2CO_3, K_2Ca(CO_3)_2), presumed to dissolve fast with respect to the 24 h timescale of the dissolution experiment investigated. The second component was a mixture of K-incorporating C–A–S–H phases such as hydrogроссular (Ca_3Al_2(SiO_4)_3-x(OH)_4x), α-dicalcium silicate hydrate (Ca_2SiO_4(OH)_2), tobermorite (Ca_5Si_6O_16(OH)_2·4H_2O) and a Calcium-Silicate-Hydrate (C–S–H) amorphous phase, all presumed to release K at a moderate-to-slow rate. The third component was altered K-feldspar, i.e., a K reservoir for release over the long-term at a slow rate. Additional time-dependent properties of the material were envisaged, including the ability to regulate soil pH and to release concurrently more than one nutrient (e.g., K and Ca) as partially corroborated for similar materials (Liu et al. 2015, 2017a, b). A key problem is how the dissolution rate of such a material is being defined both in terms of timescale and probed physical quantity (Supplementary Material).

In this contribution, the key objective is to demonstrate that due to its complex mineralogy the material obtained via hydrothermal alteration of a K-feldspar ore releases K continuously over sequential contacts with an aqueous media. Results from leaching tests performed in sequential steps, renewing the leaching solution at each step, show indeed a pH- and time- dependent multi-nutrient release of the hydrothermal material, a behavior that is in sharp contrast with that of conventional soluble salt fertilizers. Our findings imply that solubility is not a relevant parameter to describe the property of potential rock-based fertilizers that may serve as an alternative to KCl in tropical countries.
Experimental

Materials

The hydrothermal material investigated in this work was the same presented previously by Ciceri et al. (2017a). The material is synthesized through hydrothermal processing of ultrapotassic syenite in the presence of CaO. Briefly, syenites are alkali-feldspar-bearing intrusive igneous rocks. The adjective ultrapotassic refers to the exceptionally high K<sub>2</sub>O content in the rock. Here, the rock used as the raw material was sample MCA41 described by Ciceri et al. (2017b), with a K<sub>2</sub>O content of 14.3 wt%. The rock and CaO (reagent grade, Alfa Aesar) were milled jointly for 1 min in dry and CO<sub>2</sub>-free conditions with stainless–steel balls. The Ca:Si molar ratio in the milled mixture was 0.23. Water was added in a 4:1 weight ratio to such a mixture, and the slurry was processed in autoclave at autogenic pressure for 5 h at 200 °C (Parker, EZE-Seal<sup>®</sup>, 300 mL, USA). The processed slurry was dried at 90 °C and atmospheric pressure yielding a solid that was ground with pestle in an agate mortar. The resulting powder was labelled “hydrothermal material”. As discussed by Ciceri et al. (2017a), XRD mineralogy provides only a partial description of the material, which contains an altered form of K-feldspar, K-substituted C–A–S–H phases (hydrogros- sular, Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>–x(OH)<sub>x</sub>; α-dicalcium silicate hydrate, Ca<sub>2</sub>SiO<sub>3</sub>(OH)<sub>2</sub>; tobermorite, (Ca<sub>5</sub>Si<sub>6</sub>O<sub>16</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O), a K-substituted C–S–H and a mixture of carbonates such as K<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub> in concentrations below detection limit. An overview of the XRD mineralogy before and after leaching of the hydrothermal material is given in Fig. 1.

Leaching tests

The elemental release from the hydrothermal material was assessed through leaching tests performed with a solution of HNO<sub>3</sub> at initial pH = 5. The initial pH was chosen to simulate the acidic conditions encountered in many tropical soils. The stock leaching solution was prepared by appropriate dilution of standardized HNO<sub>3</sub> 0.1 M (Alfa Aesar) in the available water (Ricca Chemical Company<sup>®</sup>, ACS reagent grade) followed by degassing under vacuum. In each test, a given amount of hydrothermal material and the leaching solution were contacted at a mass ratio 1:10 to form a slurry that was rotated continuously for a given amount of time. Then, the slurry was filtered under vacuum (Whatman<sup>®</sup> Nuclepore Track-Etched Membranes, 0.05 µm). A portion of the clear leachate was used for pH and conductivity measurements and a portion was immediately diluted 1:100 by volume in standardized 0.1 M HNO<sub>3</sub> (Alfa Aesar), and analyzed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the concentration of K, Al, Si and Ca in the diluted leachate (ICP-MS, Agilent Technologies, 7700x). The instrument used an Octopole Reaction System (ORS) that was run in “He mode” (He = 4.0 mL min<sup>−1</sup>) except for Ca, which was determined in “no–gas mode”. A solution at 1 ppm of In (Sigma Aldrich, TraceCERT<sup>®</sup>) was used as the internal standard. Here, the final elemental concentrations are reported as ppm in the undiluted leaching solution rather than ppm in the leached material reported earlier (Ciceri et al. 2017a).

Fig. 1 Relative change in mineralogy of the hydrothermal material in sequential leaching steps. Time enclosed in parentheses is the cumulative contact time; bar at the 24 h mark is the mineralogy for leaching in a single 24 h step. Compare with Fig. 2 for pH conditions.
Leaching occurred in four sequential steps of 15 min each, with addition of one final step of 23 h. The experimental protocol allows to discriminate the fraction of immediately available K from that available over a longer term, testing the hypothesis that solubility is not an adequate parameter to describe the K release from the hydrothermal material. Each experiment was run in triplicates, and the solid fractions originating from each of the triplicates were reunited on a glass watch, dried over a warm surface, and homogeneously mixed before XRD analysis and re-splitting for the following leaching step (Supplementary Material). Loss of a minimal part of the material was unavoidable from step to step.

The pH of all solutions after filtering was measured with a calibrated pH meter (Hanna, HI4222). Standard buffers used for calibration were at pH = 4.00 (Ricca Chemical Company®), pH = 7.00 (Ricca Chemical Company®) and used for calibration were at pH = 12.46 (Thermo Fisher Scientific). The conductivity of all solutions after filtering was measured with a calibrated conductivity meter (Oakton CON2700). Calibration standards were 15 µS cm⁻¹ and 1300 µS cm⁻¹ (Hamilton). The cell constant was 0.62 cm⁻¹. The conductivity meter featured a thermometer that permitted recording the temperature during conductivity measurements.

X-Ray powder diffraction (XRD)

After each leaching step, the samples of hydrothermal material were ground with mortar and pestle, loaded into a Panalytical X’Pert MPD diffractometer using Cu Kα radiation at 45 kV and 40 mA. Scans were run over the range of 5°–90° with a step size of 0.0131° and an accumulated counting time of 250 s per step. Minerals were identified with the Powder Diffraction File of the International Centre for Diffraction Data, and quantified with a Rietveld refinement. Inorganic Crystal Structure Database (ICSD) numbers used in the refinement were as follow: “altered K-feldspar” determined as the sum of orthoclase (#159347) and microcline (#34790); hydrogrossular determined as plazolite (#31250); α-dicalcium silicate hydrate (α-C₂S) (#75277); 11 Å tobermorite (#40048); albite (#16744); panunzite (#30951); calcite (#40107). For all samples, a few small peaks contributing to 1% or less of the overall diffraction pattern could not be identified and were ignored.

For each sample, a 25 wt% fraction of Si powder (NIST SRM 640) was thoroughly mixed with the sample. The samples were then loaded into a sample cup and a second X-ray scan was performed under the same conditions of the initial scan. Once the patterns had been collected, a refinement for this mixture of “sample plus Si” is performed allowing a comparison, adjusted for differences in scattering power between the integrated intensity of the Si peaks and the integrated intensity of the known crystalline phases determined in the initial analysis. The difference between these values as a portion of the total represents the estimated amorphous content of the sample. The crystalline components are the result of the initial Rietveld refinement adjusted to incorporate the estimated amorphous content from the second refinement. As per our previous study, samples required extensive manual fitting, which was exacerbated by addition of Si. Like in our early study, quantitation should be considered an estimate (Ciceri et al. 2017a). The hydrothermal material as such (not leached) was from the same batch discussed earlier, but XRD quantitation revealed a slightly different composition than the previous determination (Ciceri et al. 2017a). This may be due to XRD analytical uncertainty, inhomogeneous sampling or possible evolution of the amorphous over time.

Results

The mineralogical change over sequential leaching steps is shown in Fig. 1.

Because the absolute mass of sample from step to step was not monitored, changes in phase content can be evaluated only relative to each other. The comprising mineral phases of the hydrothermal material before leaching were K-feldspar (altered), hydrogrossular, α-dicalcium silicate hydrate, tobermorite, albite, panunzite and amorphous. After leaching, the relative weight of hydrogrossular is approximately constant (10–7 wt%), confirming its stability under a range of alkaline chemical conditions. α-Dicalcium silicate hydrate is completely dissolved after the second leaching step, whereas tobermorite decreases slightly (7–4 wt%). The relative content of amorphous phase detected via XRD increases upon increasing the number of leaching steps, which is matched by a corresponding decrease in the altered K-feldspar. The composition of the hydrothermal material leached in a single 24 h step is similar to that of the original non-leached sample, although an increase in the amorphous component and the formation of CaCO₃ are observed. A key feature for both sequential- and single-step leaching experiments is the formation of 2–7 wt% of CaCO₃.

The release of K and other nutrients in the sequential-steps experiment is shown in Fig. 2a. Experimental data demonstrate that within the given time resolution of 15 min, the hydrothermal material exhibits a non-negligible K release upon the renewal of the leaching solution, which plateaus at a value of ~33 ppm of K (Fig. 2a). From XRD results (Fig. 1), the potential sources of K are altered K-feldspar and K-incorporating phases such as K-tobermorite and the amorphous phase (Ciceri et al. 2017a). An additional K-bearing carbonate phase not detected by XRD was also shown to exist in the hydrothermal material (Ciceri et al. 2017a).
The release of Al is substantially negligible at any leaching step sequential to the first one (Fig. 2b). The potential sources of Al are altered K-feldspar, hydrogrossular, Al-tobermorite and the amorphous phase, although traces of Al were determined in α-dicalcium silicate hydrate too (Ciceri et al. 2017a). XRD showed that the concentration of hydrogrossular was relatively constant, suggesting that such a phase is not a significant source of Al (Fig. 1). The amorphous phase may change its composition in sequential leaching steps, and its relative stability with respect to the surrounding chemical environment may also change. However, given that no significant amount of Al is being released other than in the first step, which is at higher pH, it is inferred that the amorphous phase does not release Al. A single-step 24 h leaching experiment yielded more Al in solution than sequential-steps leaching. This may be explained by both the higher solubility of Al at pH ~ 12 in the 24 h experiment (Fig. 2b) and the time required by Al(OH)₃ to reach equilibrium in solution. For at least gibbsite, which is not necessarily a proxy for the mineral phases investigated here, this equilibrium time was shown to be longer than 15 min (May et al. 1979).

The amount of Si released decreases at any sequential leaching step (Fig. 2c). The cumulative amount of Si is comparable to that obtained in a single-step 24 h experiment. Si is subjected to a higher analytical error due to interferences in the ICP-MS plasma torch, and similarly to Al, its concentration may be dictated by the aqueous pH: the lower the pH the lower the solubility of siliceous species in solution (Iler 1979). Because in the sequential leaching experiment the pH is decreasing progressively, then the concentration of total Si is also decreasing.

Fig. 2 Elemental release (left axis) from the hydrothermal material in sequential leaching steps for, a K, b Al, c Si, and d Ca. Time enclosed in parentheses is the cumulative contact time; shaded bar at the 24 h mark is the concentration for leaching in a single 24 h step. Dotted line is the cumulative concentration assuming constant volume. The pH of the filtrate after each step (right axis) is shown as empty circle for sequential leaching and as a filled circle for 24 h leaching. For all experiments: initial pH = 5 (HNO₃), mₛ:mₖ = 1:10, room temperature. Compare with Fig. 1 for changes in mineralogy.
Additionally, in Fig. 1 it is shown that α-dicalcium silicate hydrate dissolves completely at the beginning, and may constitute a major source of Si in the first two steps. Finally, the amount of Ca released is relatively constant, which suggests a saturation state independent from pH, although the release in the first 15 min is higher than in sequential steps. Similarly to Si, in the first step a major contribution to the Ca concentration may come from the complete dissolution of α-dicalcium silicate hydrate. For sequential steps, the concentration of Ca of ~35 ppm (Fig. 2d) is much higher than the value expected if it were to be regulated by the $K_{sp}$ of CaCO$_3$, which would be equivalent to 2.2–2.7 ppm of Ca (Butler 1982). That implies that an additional phase(s) other than CaCO$_3$ must determine the concentration of Ca. Such a phase is likely to be the C–S–H in either crystalline (e.g., tobermorite) or amorphous (reported to contain up to ~26 wt% of CaO (Ciceri et al. 2017a) forms. The amorphous C–S–H solid has a different composition than that obtained after a single 24 h leaching experiment.

The conductivity of the leaching solution after each step is shown in Fig. 3a. Conductivity data confirm the overall trend of decreasing elemental concentration per sequential leaching step, as observed in Fig. 2. Ca, which is the only species present in relatively constant concentration at each leaching step is likely to give a minor contribution to the total conductivity ($A^{0}_{1/2 \text{Ca}^{2+}} = 59.47 \times 10^{-4} \text{m}^2 \text{S} \text{mol}^{-1}$; $A^{0}_{\text{K}^+} = 73.48 \times 10^{-4} \text{m}^2 \text{S} \text{mol}^{-1}$; $A^{0}_{\text{OH}^-} = 198 \times 10^{-4} \text{m}^2 \text{S} \text{mol}^{-1}$) (Haynes 2016).

The Salt Index (SI) measured over a period of 30 days is reported in given in Fig. 3b, showing a net increase over that time period. As anticipated in Supplementary Table S1, a single salt-index value cannot be identified for this reactive system, because a complex series of dissolution and re-precipitation reactions occur concurrently, and do not necessarily reach equilibrium within the timescale of the experiment.

**Discussion**

The data on mineralogy (Fig. 1), elemental release (Fig. 2) and conductivity (Fig. 3) presented in this work are in sharp contrast with the chemical behavior of KCl or comparable soluble salts fertilizers, both in terms of pH and nutrient release dynamics (Fig. 4).

First, the hydrothermal material shows time-dependent pH properties. The initial pH of the leaching solution is 5, but it is shown that the hydrothermal material raises such value and buffers it in the alkaline range. The pH value measured at the first leaching steps of ~12 is higher than that calculated for a solution of K$_2$CO$_3$ that generates the concentration of K shown in Fig. 2a ($\times1$, 15 min, $K_{2 \text{CO}_3 \text{equivalent}} = 14.3 \text{mM}$, pH$_{\text{expected}} = 11.2$). One possibility to justify the experimental pH at the first step is that further to K$_2$CO$_3$ minor amounts of KOH are also present in the dried hydrothermal material, but no experimental evidence supported that hypothesis. Residual Ca(OH)$_2$ may also be

**Fig. 3**  
(a) Conductivity of the leaching solution in contact with the hydrothermal material in sequential leaching steps. Time enclosed in parentheses (bottom axis) is the cumulative contact time; open triangle at 24 h mark is the conductivity after a single 24 h leaching. Leaching conditions as in Fig. 2 with $T = 21.8 \pm 0.8 \degree C$. (b) Salt Index (SI) determined as the ratio of the measured conductivity of a 1 g L$^{-1}$ solution of hydrothermal material in distilled water (max 0.056 $\mu$S cm$^{-1}$) and 1.08 mS cm$^{-1}$, which is the extrapolated conductivity of a solution of NaNO$_3$ 1.0 g kg$^{-1}$ at 25 $\degree C$ (Haynes 2016). SI is measured over a period of 30 days with $T = 23.6 \pm 0.7 \degree C$, pH variation between 9.3 and 10.3 over the 30 days period is not shown for clarity. Dotted and dashed lines are shown exclusively to guide the eye.
present in the material and, if so, this would be the pH-determining species in both the first step of sequential leaching and the 24 h leaching (Eq. 1). In the first step of sequential leaching the [Ca] matches that of an under-saturated solution of Ca(OH)$_2$ that would generate ~70 ppm of Ca as shown in Fig. 2d (×1, 15 min, Ca(OH)$_{2\text{equivalent}}$ = 1.75 mM, pH$_{\text{expected}}$ = 11.6). However, in the 24 h leaching due to the longer equilibration time the concentration of Ca is lower and the pH does not match that expected based solely on a Ca(OH)$_2$ equivalency (24 h, Ca(OH)$_{2\text{equivalent}}$ = 0.98 mM, pH$_{\text{expected}}$ = 11.3), but that of Si is higher than in the first step. The XRD results (Fig. 1) show that more amorphous phase is formed during the 24 h leaching. In this case, the measured pH may be regulated by the newly formed C–S–H. Then, a possible chemical pathway during 24 h leaching sees α-dicalcium silicate hydrate and/or other C–S–H phases undergoing hydrolysis generating Si, Ca and OH$^-$ upon contact with the aqueous solution and then part of the Ca re-precipitating as a new C–S–H phase (Chen et al. 2004) and/or CaCO$_3$ (Eqs. 2 and 3).

$$\text{CaO}_{(s)} + \text{H}_2\text{O}_{(l)} = \text{Ca(OH)}_{2\text{aq}} = \text{Ca}^{2+}_{\text{aq}} + 2\text{OH}^-_{\text{aq}} \quad (1)$$

$$\text{Ca}_2\text{SiO}_3\text{(OH)}_{2\text{aq}} + \text{H}_2\text{O}_{(l)} = 2\text{Ca}^{2+}_{\text{aq}} + \text{SiO}_3^{2-}_{\text{aq}} + 2\text{OH}^-_{\text{aq}} = \text{C} - \text{S} - \text{H}_{(s)} \quad (2)$$

During the re-precipitation process evidenced by XRD, the amount of carbonate appears to be the limiting factor. As the leaching progresses through sequential steps, the mineral substrate that is being leached changes its chemical composition and CaCO$_3$ precipitates (Fig. 1). Accordingly, the pH plateaus at ~9.6, which is the expected pH of a saturated solution of CaCO$_3$ that is not in equilibrium with atmospheric CO$_2$ (Butler 1982). With the current setup, atmospheric CO$_2$ could not equilibrate with the system because the vial in which the experiment takes place is entirely filled with degassed leaching solution.

Second, unlike KCl, the dissolution behavior of the hydrothermal material is not straightforward (Fig. 4). Given the experimental protocol used in this study one could foresee two key scenarios for K release, depending on the chemical nature of the K source. To describe these scenarios, we use the qualitative terms “fast” and “slow”, which need to be considered with respect to the probed leaching time of 15 min. Additionally, we base our reasoning on concentration rather than dissolution rate, because such a rate depends on the chosen timescale (Supplementary Data), and because the desired rate of nutrient uptake by crops is not known. In the first scenario, K originates from an excess of a fast-dissolving species such as 

$$\text{Ca}^{2+}_{\text{aq}} + 2\text{OH}^-_{\text{aq}} + \text{CO}_2^{(g)} \rightleftharpoons \text{CaCO}_3(s) + \text{H}_2\text{O}_{(l)} \quad (3)$$
as KCl, which reaches the solubility limit promptly, nearly instantaneously. Then, a concentration plateau would be observed, because such a solubility limit would be met consistently. However, the same fast-dissolving species could be in defect with respect to the solubility limit. Then, for any leaching step after the first one, no K would be detected in solution. This is shown to occur arbitrarily in leaching step III of Fig. 4a. In the second scenario, a slow-dissolving K compound (or a mixture of a fast- and slow-dissolving compounds) is responsible for releasing K in the soil solution. Then, a certain concentration of K would be detected at any leaching step (Fig. 4b), similarly to what observed in Fig. 2a. Overall, experimental data do not allow to resolve if in the hydrothermal material the K–liberating species is a salt (e.g., K$_2$CO$_3$), a silicate phase that incorporates K (e.g., (K)C–S–H) or a mixture of the two (Ciceri et al. 2017a), nor allow to determine the kinetic profile within the individual leaching step. However, the second scenario is likely a more accurate representation of the physical reality of the hydrothermal material. Some possible reactions that release K upon contact of the hydrothermal material with water at the given pH are the following:

\[
\text{KAlSi}_3\text{O}_8(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + 6\text{OH}^-\text{(aq)} \rightleftharpoons \text{Al(OH)}_3\text{^-aq} \quad + 3\text{H}_2\text{SiO}_3\text{^-aq} + \text{K}^+\text{aq} (4)
\]

\[
\text{(K)C–A–S–H} \rightarrow \text{K}^+\text{aq} + \text{C} - (\text{A} - \text{S}) - \text{H}_2\text{O} \quad \text{(5)}
\]

where (K)C–A–S–H indicates a calcium-aluminum silicate-hydrate heavily enriched in K. Indeed, the concentration of K observed over sequential leaching cycles (Fig. 2) is not compatible with the presence of a salt-like compound alone.

Within experimental error, the cumulative amount of K released in 24 h from sequential leaching steps is in excellent agreement with the amount obtained in a single step for the same time span, suggesting that the overall rate of K release (fast + slow component) is independent of pH or other chemical conditions, at least in the range investigated here. Figure 4 shows that the hydrothermal material has potential for enhanced residual effect upon sequential exposures to water, for example a rainfall. However, conversely to the most common controlled release fertilizers, the K release observed here for the first time is an inherent and active property of the material, as illustrated in Fig. 2. The slow nutrient release is the result of hydrothermal processing, which redistributes K from the aluminum–silicate framework of K-feldspar to secondary mineral phases. For traditional controlled release fertilizers, the slow nutrient release is achieved by coating soluble compounds with engineered resins or other polymers.

Third, upon leaching Ca dissolves into the solution, where the chemical conditions are such to allow the precipitation of CaCO$_3$ (Fig. 1). The possible sources of carbon are: (i) the carbonaceous fraction that was already present in the non-leached material, although not detected by XRD (Ciceri et al. 2017a) (ii) the CO$_2$ solubilized in the leaching solution (likely negligible) and (iii) atmospheric CO$_2$ that reacts with the material during filtering operations. The amount of K$_2$CO$_3$ that supplies enough CO$_3^{2-}$ to justify the 2 wt% of CaCO$_3$ measured in the material after the first leaching step corresponds to 2.76 wt%, which in turn is equivalent to 1560 ppm of K expected in the leaching solution. The observed experimental value of 1117 ppm of K (Fig. 2a) is slightly lower than expected, which indicates that K$_2$CO$_3$ alone does not provide enough carbonate ion for calcite precipitation and, therefore, the material may absorb CO$_2$ during evaporation of the residual leaching solution between a leaching step and the sequential one, a hypothesis that would explain why the content of CaCO$_3$ in the leached material tends to increase at each leaching step. Although the determination of carbonates in the hydrothermal material at such low concentration has been elusive, experimental data suggest they play a pivotal role in regulating the pH, whichever origin they may have. Na as well as other elements that were not monitored (e.g., Mg and Fe) may also exist as carbonates in the material.

The reactivity evidenced by Figs. 1 and 2 shows that solubility is a parameter that is not adequate to characterize the hydrothermal material, because of its intrinsic chemical reactivity operating over a range of timescales. Key observations from Fig. 1, e.g. consumption of α-dicalcium silicate hydrate and the formation of CaCO$_3$, highlight the key role of phase re-precipitation with a potentially lower rate of nutrient release. Figure 2 highlights the high alkalinity of the material that will benefit tropical soil, which are generally acidic. Additionally, the re-precipitation of CaCO$_3$ and the multi-nutrient release are also highlighted. A quantitative discrimination of the K contribution from each of the comprising mineral phases will be necessary to forecast the nutrient release from the material in the soil environment.

Conclusions

The development of affordable K fertilizers (potash) from feedstocks alternative to KCl will greatly benefit tropical agriculture. An example of such fertilizers is the material obtained from hydrothermal alteration of K-feldspar ore with CaO. Overall, this work demonstrates that the traditional concept of solubility does not apply to such a hydrothermal material, which contains mineral components that releases K progressively and is likely to benefit crop growth.
over several agronomic cycles. Development of alternative fertilizers that release plant nutrients in slow and/or controlled manner requires development of indexes and standard parameters beyond solubility. A key aspect is defining dissolution rates under a specified set of physicochemical soil conditions.

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Compliance with ethical standards

Conflict of interest Advanced Potash Technologies, a commercial company, provided funding for this research in the form of salaries for the authors, equipment, and materials. The funder had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript. The funder is developing a commercial product based on the research presented in this article. The funding of this work was subjected to the terms set forth by the Office of Sponsored Programs at the Massachusetts Institute of Technology (http://osp.mit.edu).

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