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Fertilizer derived from alkaline hydrothermal alteration of K-feldspar: a micrometer to nanometer-scale investigation of K in secondary reaction products and the feldspar interface

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Key words: alkaline hydrothermal alteration, potassium fertilizer from feldspars, coupled interfacial dissolution-reprecipitation (CIDR), analytical transmission electron microscopy (TEM), energy filtered TEM (EFTEM), field emission SEM (FESEM), FESEM-EDXS, chemical phase mapping, fluid-rock interaction, solid-fluid interfaces

Abstract Global food security concerns have spurred increasing demand for locally sourced and produced K-fertilizers. Various processes have been explored for more than a century; one promising solution is based on the alkaline aqueous alteration of feldspar-rich rocks at elevated temperatures. However, knowledge of the overall physico-chemical reactions comprising dissolution of feldspar and precipitation of secondary phases is still rudimentary, in particular how the feldspar structure evolves at the nm-scale during hydrolysis at alkaline conditions. Here we report on the results of a study aimed at converting potassium feldspars to K-rich fertilizer based on the alteration of sanidine and microcline samples at 190 °C in pH 12 $\text{Ca}(\text{OH})_2$ solutions for 24 hours. Based on X-ray diffraction and Rietveld refinement, the secondary authigenic minerals that precipitated are primarily composed of Ca-carbonate (calcite, vaterite), and Ca-(Al)-silicates, such as tobermorite and hydrogrossular. Short-term bench top leaching experiments in water prove that the hydrothermal product releases up to two orders of magnitude more K than the unaltered K-feldspar starting material, pointing to its application as a ready-to-use fertilizer for K-deficient soils. Detailed chemical mapping and energy dispersive X-ray spectroscopy (FESEM- and TEM-EDXS) analyses of the precipitates at the μm to nm-scale show that the distribution of K associated with the secondary phases is very heterogeneous, both spatially and in terms of concentrations. Using various analytical transmission electron microscopy (TEM) techniques, e.g., HRTEM, TEM-EDXS, EFTEM, to investigate the structure and chemistry of the feldspar interface, we find no evidence for a change in chemistry or structure at the nm-scale, even though dissolution continuously decreases the volume of each grain. Our observations also show the existence of an amorphous surface altered layer (SAL) of variable thickness (10 to ~ 100 nm) forming at the feldspar interface. Nanometer-scale chemical measurements show that this amorphous SAL is rich in K, and therefore may also be an important reservoir of easily leachable K. We hypothesize that it forms continuously and in situ at the expense of the feldspar by a coupled interfacial dissolution-precipitation process (CIDR).

1. Introduction

An ever-burgeoning world population continues to increase pressure on land and water resources, leading to warnings of an impending global food supply crisis (IPCC, 2019). Climate change, extreme weather events, and land conversion count among the most important factors that are exacerbating the situation. The IPCC report emphasizes the need for environmentally sound development to mitigate the diminution of fertile soils due to erosion, desertification, and land degradation. Sustainable land

management practices to increase food security continue to be a sought-after goal. One widely accepted practice has been based on increasing crop yields and agricultural productivity via the application of NPK (nitrogen, phosphorous, potassium) fertilizers to soils. However, the over-use of fertilizers has also had negative environmental consequences, in particular due to nutrient-rich water runoff from fertilized soils- this has in fact become a global problem. With respect to potassium fertilizer, the majority is derived from soluble potassium-rich salts that are sourced in northern hemisphere countries, e.g., Belarus, Russia, Canada, Germany (Jasinsky, 2019). Because of the prohibitive costs and environmental impacts of long-distance maritime transport, there has been increasing interest in localized and sustainable production of K-fertilizers, in particular in subtropical and tropical countries. Soils in these areas of the world are often low in fertility due to climate, over intensive and non-sustainable agricultural practices, and high rainfall. The latter can lead to a too rapid release of K from fertilizer salts and its depletion by rainwater runoff.

Despite the enduring commercial predominance of K-bearing salts, the extraction of K from K-rich silicate rocks had been explored early on, starting with early work by Tilghmann (1847)- see also Supp Info. 1. For over a century now, industrial and scientific work has been carried out on the extraction of potassium from K-feldspars, via either aqueous chemical processes or heat treatment (Ciceri et al., 2015). Interest in K-feldspars is chiefly due to their high K-content and ubiquitous occurrence in the Earth's crust (Klein and Philpotts, 2017). Recent research on this topic reveals the unabated interest in aqueous hydrothermal alteration of K-feldspars as a means for obtaining K-fertilizer that is both environmentally sustainable and economical. The secondary phases produced during chemical alteration, as well as left over grains of unreacted K-feldspar, constitute what can be termed as the 'hydrothermal product'. Aside from use as a K-fertilizer, the hydrothermal product can also be employed for its acid neutralization properties, the mitigation of abiotic stress in plants, and soil remediation (Supp. Info. 2).

Until now, the identification of secondary authigenic products has been the central theme of the majority of recent studies. This is obviously a first and important step in understanding the overall process. However, from a basic research point of view, much remains unknown concerning the mechanism that controls how a primary K-feldspar mineral is structurally and chemically decomposed during alkaline hydrothermal alteration. Some studies have attempted to clarify the mechanism, and not surprisingly, this has resulted in many opposing points of view. Perhaps one reason has been the application of poorly suited analytical methods. In addition, not much is known about the fate of K once it is released from the feldspar structure, as very little research has been committed to quantifying the concentrations of K associated with the crystalline and amorphous secondary phases produced during alteration. Closely related to this is the need to measure the kinetics of K release from secondary phases when exposed to near-neutral pH aqueous fluids at ambient conditions- these conditions characterize typical soil pore fluids. The K-release behavior from the hydrothermal product to the soil when in contact with water (i.e. soil pore fluids, precipitation) is in essence what controls the performance of any K-

fertilizer. Even though hydrothermal products can be used ‘as-is’, it is also possible to transform them further into various soluble K-salts, see e.g., Ma et al., 2015.

As detailed further on, both recent and current studies have explored the aqueous extraction of potassium from K-feldspars based on chemical processes at hydrothermal temperatures (≤ 250 °C). Because K-feldspars are chemically robust minerals and dissolve very slowly, their alteration kinetics can be dramatically increased at elevated temperatures and at pH conditions that are either strongly acidic or alkaline (Blum and Stillings, 1995; Bandstra et al., 2008; Hellmann, 1994; Yuan et al., 2019). While some studies have altered K-feldspars at acid pH conditions, most have favored using strongly alkaline solutions, in large part due to green chemistry arguments (e.g., Ciceri et al., 2017a, Ma et al., 2015). For example, limestone, a common sedimentary rock type, can serve as raw material for producing an alkaline solvent (i.e., $\text{CaCO}_3 (\text{s}) \rightarrow \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$; $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$). A hybrid process, based on the calcination of limestone together with K-feldspar at $T = 1050$ °C, followed by hydrothermal decomposition of the heat-treated K-feldspar, has been reported by Liu et al., 2020- apparently this process significantly increases the efficacy of the hydrothermal product.

2. Previous work and goals of present study

Over the past thirty years only a few studies have been dedicated to the alkaline hydrothermal alteration of alkali feldspars. One of the earlier ones concerns the far-from-equilibrium hydrothermal alteration of pure albite, $\text{NaAlSi}_3\text{O}_8$, in a flow reactor (Hellmann, 1995) at $\text{pH}_{25^\circ\text{C}} = 10.0, 11.0, 12.0$ and $T = 100, 200$ and 300 °C. The study by Hellmann (1995) shows that the fluid composition was non-stoichiometric with respect to the solid, pointing to the mobility of Na and Al right from the onset of fluid contact with albite. The author interpreted the aqueous results in terms of preferential cation release (Na, Al) within the context of leached layer theory. This interpretation can now be questioned, since it is generally acknowledged that stand-alone aqueous stoichiometric measurements do not lend themselves to an unambiguous interpretation of the dissolution mechanism, but rather require high-resolution solid-state observations of the interfacial region of the reacted parent phase (see e.g., Hellmann et al., 2003, 2012, 2015).

The extraction of potassium from K-feldspars has been a focus of several research laboratories in China. A study by Liu and co-workers (2015) revealed that K-feldspars reacted between $160\text{--}220$ °C in NaOH, KOH, and $\text{Ca}(\text{OH})_2$ solutions had different reactivities, a finding based on the amount of secondary phases formed. Basic pH solutions using $\text{Ca}(\text{OH})_2$ were by far the most reactive solvent. The authors ascribe this to ion exchange at the surface between 2K^+ and Ca^{2+} , which was postulated to lead to the formation of a transitional compound: $[\text{Ca}^{2+} \equiv 2\text{AlSi}_3\text{O}_8^- \equiv x\text{OH}^-]$. This compound in turn transforms to crystalline phases such as hydrogarnet and CSH phases. Hydrogarnet (hydrogrossular) has the formula: $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ ($x = 0\text{--}3.0$). The prominent CSH phase was tobermorite,

$\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Overall, the net reaction can be thought of as dissolution of the primary feldspar and classical precipitation of secondary phases. In related studies at similar conditions, Liu et al. (2018, 2019) postulated that the initial dissolution of primary feldspar is progressively slowed down by the formation of secondary phases on the surface ($\sim t > 20$ hours), which ultimately results in a diffusion-controlled alteration process. The formation of hibschite, katoite, and tobermorite was universal in these studies (Liu et al., 2015, 2018, 2019). The former two phases are Ca-Al-silicate hydrate minerals (CASH), whereas tobermorite is a Ca-silicate hydrate (CSH). In addition, the studies by Liu et al. (2015, 2018, 2019, 2020) also noted the significant formation of carbonate phases, such as CaCO_3 , K_2CO_3 , and $\text{K}_2\text{Ca}(\text{CO}_3)_2$. Another study (Su et al., 2015) presents data from hydrothermal alteration of K-feldspars in NaOH solutions at 240 and 280 °C. The main secondary phases that formed were kalsilite (KAlSiO_4) and hydroxycancrinite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$). The authors postulated that OH⁻-mediated dissolution of the K-feldspar structure results in the congruent (i.e., stoichiometric) release of elements, followed by classical precipitation of secondary phases from an oversaturated bulk solution. This is the same mechanism as proposed by Liu et al. (2015), but without the formation of a transitional surface species.

Recent experiments by Ciceri et al. (2017a) altered not pure K-feldspar, but rather a K-feldspar-rich intrusive rock, ultrapotassic syenite. The alteration conditions were based on a very high pH $\text{Ca}(\text{OH})_2$ solution (pH unspecified) at 200 °C for 5 hours. Among the secondary phases that they measured by XRD-Rietveld are 11 Å tobermorite, albite, hydrogrossular, α -dicalcium silicate hydrate ($2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$), amorphous material (18.2%), panunzite ($(\text{K},\text{Na})\text{AlSiO}_4$). The amorphous material was described to be composed of ‘severely altered’ K-feldspar, very small (i.e., nanometer-sized) crystalline particles, and truly amorphous compounds. Of all the secondary phases in that study, one dominates at 66.5 wt %: ‘altered’ K-feldspar. It is, however, not clear from their work exactly what this phase is or what it represents. As in the study by Su et al. (2015), they also envisaged an OH⁻-mediated hydrolytic attack of the feldspar structure. However, their scenario differs from others in that they evoke the idea of incorporation of Ca atoms deep into the feldspar framework via exchange of K⁺ for Ca²⁺ ions. This process can be interpreted in terms of leached layer theory, where cation exchange is controlled by interdiffusion (for leached layer theory applied to feldspar dissolution, see e.g., Hellmann et al. 1989, 1990; Hellmann, 1999a, b; see also reviews in Hellmann et al. 2003, 2012, 2015). Their idea of Ca insertion via K⁺-Ca²⁺ exchange was primarily based on electron probe microanalysis (EPMA) of altered grains. Even though this technique has low elemental detection limits, it has the distinct disadvantage of a large beam footprint (in μm -range), which limits the spatial resolution of the analyses.

The present study is a part of a pilot program designed to evaluate the feasibility of converting alkali (potassic) feldspars into K-rich fertilizer. To achieve this goal, certain igneous rock types were chosen that are particularly rich in K-feldspars. For this reason, commonplace granites were not used as a source of K-feldspar. Our research work is based on the alkaline hydrothermal alteration of 7 different

potassic feldspars: one sanidine and 6 microcline samples. The immediate goals of this research were to: a) identify the phases present in the hydrothermal product, b) measure at the μm to nm-scale the levels of K associated with the authigenic phases, c) investigate at the nm-scale the chemical and structural evolution of the post-reaction feldspar interface, d) carry out short-term leaching tests of the hydrothermal product in acid and neutral pH aqueous solutions. While point *a* has certainly been carried out by nearly all previous studies in this field, to the best of our knowledge points *b* and *c* have not been done before in any detailed and systematic manner, and point *d* in only a few studies. The combination of points *a-d* is what constitutes the originality of the present research.

While recognizing that a detailed micrometer-scale structural characterization of our raw samples undoubtedly would have been important for understanding differences in the dissolution kinetics of the original feldspar samples and the partitioning of secondary product phases, this was not a goal of our study. It is well established that microstructural properties (e.g. dislocation density, exsolution lamellae) can significantly affect the kinetics of mineral-fluid interactions, both in the laboratory and the field (see e.g., Lee and Parsons, 1995 and Lee et al., 1998; see also Ciceri et al., 2017b).

3. Materials and methods

3.1. Feldspar sample localities

Six microcline samples and 1 sanidine sample were collected from 5 different localities in China. The localities represent diverse geological environments and ages. Microcline samples LS-1 and LS-2 originated from a granitic pegmatite vein occurring within a large potash feldspar deposit in Lingshou County, Hebei Province. The granitic pegmatite is associated with the Yanshanian orogen from the middle-Jurassic (Quan et al., 2009). Sample SX-1 is from the Xiong'ershan region in Song County, Henan Province. The sample was extracted from a granite porphyry that has been dated to the late early Proterozoic (Cui et al., 2010). Late Permian granites (Guo, 2019) in the Taiyanggou Fe-Sn-W polymetallic mining area, Suoboriga Sumu, Bairin Right Banner, Chifeng City, Inner Mongolia is the locality for samples TYG-3 and TYG-4. The sample WLST-1 is from a quartz porphyry associated with the Weilasituo polymetallic deposit in Bayinchagan Sumu, Keshiketeng (Hexigten) Banner, Chifeng City, Inner Mongolia. The age of the quartz porphyry is estimated to be early Cretaceous (Zhang et al., 2019). The sole sanidine sample, FHS-1, is from an ultra-hypabyssal quartz porphyry located 50 km distant on the westward side of Fenghuo Mountain, Kekexili Region, eastern Xinjiang Province. The porphyry has been assigned an early Miocene age (Wu et al., 2007).

3.2. Sample preparation

Each feldspar sample was dry-ground with a mortar and pestle. The crushed grains were first sorted under an optical microscope, and further removal of extraneous phases was done with heavy liquid

separations. Sieving isolated the $< 74\text{-}\mu\text{m}$ grain fraction that was used in the experiments. No attempt was made to remove surface fines. Representative scanning electron microscope (SEM) images of the unaltered grains are shown in Fig. S1a-g (note: this article contains an extensive electronic Supplementary Information file containing additional material, always designated by *S*, e.g. Fig. Sx, Table Sy). The average chemical compositions of the 7 unaltered samples are reported in terms of component oxides in Table 1a. Even though their overall chemical compositions are quite similar, there are two samples that have much higher $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios than the rest: microcline TYG-3 and sanidine FHS-1 (0.32 and 0.37). The chemical compositions were determined using a standard X-ray fluorescence (XRF) methodology with a Shimadzu 1500 XRF instrument. Table 1b lists elemental atomic ratios of the unaltered samples in terms of $(\text{Na}+\text{K})/\text{Si}$, K/Si , Al/Si . In addition, Table 1b also lists the same elemental ratios (based on nominal mineralogical formulas) for the 4 dominant authigenic crystalline phases that formed upon hydrothermal alteration: calcite, tobermorite, hibschite, and katoite. This facilitates comparison between the elemental ratios of the secondary products, determined by FESEM-EDXS and TEM-EDXS analyses, and the primary K-feldspars.

3.3. *Experimental protocol*

The protocol that we used to hydrothermally alter each sample, and the detailed solid-state and aqueous chemistry characterizations that followed alteration, are graphically shown in a flow chart in Fig. 1. This alteration protocol follows closely ones previously published in the literature (Liu et al., 2015; Ciceri et al., 2017a). Even though we did not run replicate experiments on any one particular sample, two sets of samples (LS-1 & LS-2; TYG-3 & TYG-4) did afford us the possibility of qualitatively determining the differences that arise between samples, while not identical, were close in composition, and most probably also similar in terms of their crystallographic structure.

Each experiment commenced by mixing 1 g of ground feldspar grains with 1 g of fresh CaO powder, to which 10 mL of pure water was added. The BET surface areas of the powders were on the order of $1\text{ m}^2\text{ g}^{-1}$ (Table 2). The immediate action of water converted the CaO to $\text{Ca}(\text{OH})_2$. The slurry was well stirred for 5 minutes- this was followed by a measurement of pH, which generally ranged from 12.3 to 12.5. Because the solubility of CO_2 increases dramatically as a function of pH at alkaline conditions, we assume that a non-negligible amount of dissolved CO_2 was a part of the initial solvent. The slurry mixture was then sealed in a 100 mL teflon-lined autoclave and placed in a pre-heated oven at $190\text{ }^\circ\text{C}$ and left for 24 h. After removal from the oven, the autoclave was allowed to cool down over ~ 6 hours. In order to drive off any remaining liquid, the slurry underwent a heat treatment step in an open vessel for an additional 12 hours at $105\text{ }^\circ\text{C}$. The dry altered powders that were recovered are composed of secondary authigenic phases that precipitated both during the hydrothermal alteration step, as well as the subsequent

drying stage at elevated temperature. The altered powder cake, also referred to as ‘hydrothermal product’, also contains abundant remnants of K-feldspar grains.

The dried hydrothermal product was then reground in order to obtain a size fraction of grains < 74 μm . The hydrothermal product was then subject to solid-state analyses, such as N_2 -BET surface area analysis (Table 2) and X-ray powder diffraction (XRD). A small quantity of each reacted powder served to make polished grain mounts. The mounts were fabricated by resin impregnation of powder in a liquid carbon-based epoxy resin (Struers). Once hardened, each mount was mechanically polished using SiC-coated abrasive disks and ultrapure water- polishing terminated at 5- μm granulometry. Even though water was used, we saw no evidence of any neo-formed etch pits or other dissolution features with respect to both the primary feldspar grains and the secondary products. This implies that the resin sufficiently protected the altered powders.

3.4 XRD

The unaltered feldspars were characterized by standard XRD techniques using powders with a grain size < 1 μm . The XRD patterns and the corresponding reference patterns for unreacted microcline and sanidine are reported in Figs. S2A, S2B. The diffraction patterns were collected using a Pananalytical X’Pert Pro diffractometer using $\text{CuK}\alpha$ radiation at 40 kV and 40 mA over a 2θ range of 10-90° using a 0.0167° step size.

The altered powders were analyzed using $\text{CuK}\alpha$ radiation at 40 kV and 40 mA with a Bruker D5000 powder diffractometer equipped with a SolX Si (Li) solid-state detector. Diffraction intensities were recorded from 5-90° (2θ) at 0.026° intervals with a 5 s counting time per step. The ICDD powder diffraction database was the primary tool for identifying the crystalline phases in the altered powders, which were comprised of authigenic minerals, amorphous material, and unaltered K-feldspar grains. The quantification limit for our XRD results is approximately 0.5-1.0 mass %, depending on the nature of the diffraction peak. The codes Profex (Döbelin and Kleeberg, 2015) and BGMN (Bergmann, 2005) were used to execute the Rietveld refinements of the XRD data. During each refinement iteration, we purposely excluded minor phases in order to constrain the final results to include only phases with concentrations ≥ 1 mass %. We did not analyze the amorphous content of the reacted powders.

3.5. FESEM imaging, FESEM-EDXS analyses, FESEM-EDXS chemical phase mapping

Two high-resolution field emission scanning electron microscope (FESEM) instruments were used in this study. The first is a Zeiss Ultra Plus, housed at the PISA Facility, GFZ. Aside from standard secondary electron (SE) and backscattered electron (BSE) detectors, it is equipped with a Thermo Fisher Scientific UltraDry SDD EDXS detector. The standard operating conditions we used were an accelerating voltage of 20 kV with a 120- μm aperture. The second FESEM is a Zeiss GeminiSEM 500 located at the

CP2M facility, Univ. Aix-Marseille. It is equipped with SE and BSE detectors for imaging, and an EDAX SDD 30 mm² EDXS detector. This instrument was operated at 0.5-20 kV with a 120- μ m aperture.

Polished grain mounts of all 7 altered samples were thoroughly characterized by FESEM. In addition, one altered microcline sample (LS-2C) was also examined ‘as-is’ by sprinkling loose powder from the hydrothermal product onto an SEM stub with double-faced tape. Secondary electron and BSE imaging by FESEM were used to characterize the morphology of the secondary phases and their spatial relation to the remaining feldspar grains. Energy dispersive X-ray spectroscopy (EDXS) was used to obtain single element chemical maps and chemical spectra of specific spot areas on the secondary alteration products and the interfacial region of the original feldspars. The measured spectra are based on standard *K*-lines for the elements pertinent to our study: Si, Al, O, K, Na, Ca, and C. The EDXS spot analyses are background and ZAF-corrected, and can be considered to be semi-quantitative. Due to the ubiquitous presence of the C-based resin, measured C concentrations should be evaluated with great care. The single-element chemical maps are based on raw net counts after background subtraction. See Supp. Info. 3 for details on FESEM-EDXS.

The EDXS chemical mapping results we report here are based on the ‘smart phase mapping’ feature of the EDAX TEAM™ software suite that is integrated with the EDAX-EDXS system of the Zeiss Gemini FESEM 500 instrument. The individual colors on the maps correspond to ‘chemical phases’ that represent objects or areas with similar chemical compositions, as determined by individual EDX spectra- see details in Supp. Info. 4. As detailed in Supp. Info. 3, both the FESEM-EDXS and FESEM smart phase mapping results should be interpreted with care, as the electron excitation volume at depth far exceeds the size of the electron beam foot print on the surface.

3.6 FIB

Focused ion beam (FIB) milling was used to prepare 2 to 3 electron transparent ultra-thin lamellae of each reacted sample. Suitable grains embedded within a grain mount were chosen for vertical FIB cuts, such that at each selected location, the vertical cut provided a cross sectional slice of an intact feldspar grain, the interfacial region, and secondary precipitates forming a lateral reaction rim. The FIB lamellae were prepared at GFZ using a FEI Helios G4 UC dual beam (SEM-FIB) instrument. A standard procedure was followed to prepare each FIB lamella (see Wirth, 2009). Very briefly, the procedure consists of deposition of a Pt strap at the desired location on the polished grain surface, followed by FIB milling with a Ga ion beam with a 30 kV accelerating voltage and 47 nA beam current, which is progressively decreased to 9 nA. The milling serves to cut trenches and then to free the sides and the bottom of the lamella from the matrix. Using an in situ transfer technique, the lamella is then welded to a single post on a TEM grid, where it undergoes further thinning with a 30 kV and 41 pA Ga beam. When the final thickness is achieved, the beam voltage is only 5 kV. Approximate dimensions of a typical FIB

lamella are 15 μm (length) x 5 μm (height) x 150 nm (thickness). FIB lamellae are generally moderately wedge-shaped in cross section, so there will be some variation in the thickness. One of the drawbacks of the FIB technique is Ga implantation into the sample, as well as amorphization of crystalline material at the surfaces of the lamella. Argon ion nano-milling is a common technique that can be used to gently remove implanted Ga (e.g., Leonard and Hellmann, 2017: see Supp. Info. therein), but this technique was not available to us in the present study.

3.7 TEM

The transmission electron microscope (TEM) we used in this study is a FEI Tecnai G2 F20 X-twin FEG TEM operating at 200 kV, and housed at GFZ. This instrument is equipped with bright field (BF), dark field (DF), and scanning TEM-high angle annular dark field (STEM-HAADF) detectors for routine medium and high-resolution imaging applications. In addition, analytical chemistry measurements are possible by TEM-EDXS, based on an EDAX EDX spectrometer equipped with a Si-Li detector.

The FIB lamellae for all 7 samples were investigated in various TEM imaging modes in order to characterize the secondary phases that formed during the overall hydrothermal alteration process. In particular, we were interested in the documenting at medium and high resolution the nature of the precipitated phases, the interfacial region of the original feldspar grains, and the spatial relation between the two. Elemental spectra obtained by scanning TEM-EDXS measurements provided chemical compositional data of small rectangular regions at the interfacial region and on the secondary precipitates. This was in particular pertinent to measuring K, where the goal was to better constrain concentrations and identify which secondary phases were associated with elevated K concentrations. The STEM-EDXS results are semi-quantitative; see Supp. Info. 5.

Electron energy loss spectroscopy (EELS) is the second type of analytical TEM technique that we used to investigate the chemistry of the interfacial region and the secondary precipitates. The Tecnai TEM we used is equipped with a post-column Gatan Tridiem energy filter. EELS is a powerful method that can provide both detailed information on chemical environments of individual elements, as well as chemical maps with nm-scale spatial resolution. EELS is based on measuring the energy loss of electrons due to inelastic scattering as they pass through the sample. Each element has specific energy edges where energy loss events occur, and thus by choosing specific energy ranges corresponding to element-specific edges, quantitative information on an element's concentration can be obtained. Detailed background information on EELS and its applications can be found in, e.g., Grogger et al., 2003 or Williams and Carter, 2009.

In this study, we used energy filtered TEM (EFTEM) to generate nm-scale chemical maps of Ca and Si in interfacial regions. In TEM-EELS spectrum mode, we recorded the Ca $L_{2,3}$ and Si $L_{2,3}$ edges of interfacial regions in order to construct 2-window jump ratio EFTEM maps. With this technique, a post-edge and a pre-edge image are recorded, and the jump ratio map is then obtained by dividing the post-

edge image by the pre-edge image. A jump ratio map, which is not quantitative, gives the distribution of the elements chosen, i.e., Ca and Si in our case. The slit widths and filter energies were pre-determined by the Gatan software. With all EFTEM maps, element concentrations are qualitatively represented in terms of a gray scale, with white indicating a high concentration, and conversely, black indicating depletion. Certain pertinent elements, such as K, could not be mapped by EFTEM. This is due to the fact that the K $L_{2,3}$ edge is too close in energy to the C K edge, making it technically very difficult to deconvolute their spectra. More details on the EFTEM technique can be found in Supp Info 6.

3.8 Aqueous leaching of hydrothermal product

Each of the seven reacted powders was subjected to short-term bench top leaching trials in order to test and quantify its reactivity in two types of aqueous fluids at ambient temperature: pure water (pH ~ 5.7); 0.5 mol L⁻¹ HCl-H₂O (pH ~0.3). We have assumed that both solutions were roughly in equilibrium with atmospheric CO₂. As graphically shown in Fig. 1 (starting at the oval ‘0.5 g altered powder’ symbol), each hydrothermal product was added to 50 mL of either near-neutral pH water or acid solution, and then shaken vigorously over a 1-hour period at ambient temperature. A 2 mL filtrate was extracted from each mixture and then diluted with 48 mL of pure water. In addition to the above leaching tests, we also did the same type of tests, but in this case using the unaltered K-feldspar powders. This permitted us to directly compare the leaching behavior of the same solids, before (i.e. unaltered K-feldspar) and after hydrothermal alteration and heat treatment. For all experiments, the resultant solutions were analyzed to determine the concentrations of K, Al, and Si by inductively coupled plasma-optical emission spectroscopy (ThermoFisher Scientific ICP-OES instrument) using matrix-matched standards.

4. Results and discussion

4.1. XRD and Rietveld refinement

The partitioning of the crystalline phases making up the hydrothermal product following alteration of 1 sanidine and 6 microcline samples is shown in Figs. 2a-g. The individual XRD patterns and Rietveld fits for each hydrothermal product are shown in Fig. S3. Grains of the original microcline make up between 7.9 and 25.3 % of the total, for sanidine the amount is 18.9 % (in section 4.1, all phase amounts are reported as mass %). This indicates that the experimental protocol converted a minimum of 75 % of the original feldspar. The most prevalent secondary crystalline phase is calcium carbonate, represented by the polymorphs calcite (22.7 - 49.8 %) and vaterite (0 - 15.6 %). The precipitation of carbonates is due to the Ca-rich solvent (Ca(OH)₂ + H₂O) and the adsorption of atmospheric CO₂ before the start of each experiment, and to a lesser degree, during the heat treatment step. At the start of the experiment (pH =

12.3-12.5), aqueous CO₂ exists exclusively as the CO₃²⁻ ion, which kinetically favors the reaction Ca²⁺ + CO₃²⁻ → CaCO₃.

Secondary CASH (Ca-Al-silicate-hydrate) and CSH (Ca-silicate-hydrate) phases make up the rest of the crystalline product in each experiment. Their overall proportions, shown in the bar graph in Fig. 2h, range from 40.0 to 56.8 %, with one outlier registering only 24.9 % (sample WLST-1C). Overall, katoite 1 and 2 (1 and 2 represent differing degrees of hydration) represent between 3.6 – 12.2 %, and hirschildite ranges from 5.8 – 15.9 %. These two phases are a part of the grossular mineral series: Ca₃Al₂(SiO₄)_{3-x}(OH)_{4x}: anhydrous grossular, x = 0; hirschildite, x = 0.2-1.5; katoite, x = 1.5-3.0. We group hirschildite and katoite together under the term ‘hydrogrossular’. The CSH phase tobermorite Ca₅Si₆O₁₆(OH)₂·4H₂O is comprised of 11 Å tobermorite and a minor amount of 9 Å clinotobermorite; they represent, respectively, 0-25.8 % and 0-8.6 % (if both phases are summed together, they amount to 7.7-34.1 % of the total). Synthetic Al-substituted tobermorite is known to exist, which is due to the combined substitution of Al³⁺ and Na⁺ for Si⁴⁺. Its potential presence in the hydrothermal product could not be verified in our analyses, as their XRD patterns are very similar (e.g., Mostafa et al., 2009). The minor presence of sylvite in one sample is likely due to contamination, or a fitting error. Other minor phases are also present (< 1 %) in the reaction products, but were purposely excluded during the Rietveld refinements (see section 3.4).

We did not determine the amorphous components in the 7 samples. However, in a study that investigated the alkaline hydrothermal decomposition mechanism of orthoclase (unpublished results), one sample altered at the same conditions had an amorphous component of ~16 % in the hydrothermal product. We make the reasonable assumption that a roughly similar value of amorphous material is present in the 7 hydrothermal products in the present study. Furthermore, in other similar K-feldspar alteration studies, amorphous components representing 18 % (Ciceri et al., 2017a), 5-11 % (Liu et al., 2018), and 5-30 % (Liu et al., 2019) of the hydrothermal product have been reported. Thus, hydrothermal alteration products can contain a relatively important percentage of amorphous material, which includes materials that are purely amorphous, poorly crystalline, and nanocrystalline.

The variability in the proportions of crystalline phases making up the hydrothermal products is relatively pronounced, as shown in Figs. 2a-h. In addition, there are also important differences in the amounts of unreacted microcline. Even though no replicates were run in this study, two sets of samples lend themselves for comparison. Samples LS-1C and LS-2C, which were sourced from the same pegmatite vein and have very similar chemical compositions (Table 1a), display nearly the same degree of microcline dissolution, with respectively only 7.9 and 8.2 % remaining in the product. In addition, their combined CASH and CSH proportions are in good agreement: 56.8 vs. 53.6 %, respectively. In comparison, TYG-3 and TYG-4, even though from the same general locality, are characterized by larger differences in the amount of remaining microcline, and also a more heterogeneous mix of CASH and CSH phases (Figs. 2d,e). An in-depth analysis of the myriad factors potentially responsible for the

heterogeneous nature and variability of the reaction products, including the amount of unreacted K-feldspar, was beyond the scope of this study, however.

4.2. Leaching tests of hydrothermal product

By exposing the 7 hydrothermal powders to short 1-hour aqueous leaching tests, we sought to investigate and compare their reactivity in pure water (pH ~5.7) and in acid solution (pH ~0.3). This yielded indices on which phases might readily release associated K to a soil pore solution. Even though the pH of the acid solution was very low, its use served to illustrate the kinetic behavior of the hydrothermal product at conditions (i.e., very high $[H^+]$) conducive to enhanced dissolution rates of all phases, in particular silicates. All of the chemical measurements that appear in Figs. 3a-c are reported in Table S1.

The first leaching test was done in pure water (pH ~5.7) at ambient temperature. This test served to elucidate how the hydrothermal product would perform when exposed to rainwater and/or pore fluids in soils. The concentrations of the 3 elements follow the order: $K > Si > Al$ (Fig. 3a). This first observation indicates that the powder is not only enriched in K, but it is also a very labile element that is readily released to a near-neutral pH solution. The concentrations of released K vary by a factor of ~2 among the 7 samples, Si varies by a factor of up to ~5. The sanidine-derived sample (FHS-1C) released less K and Si than nearly all of the other samples. Regarding just K release, samples TYG-3C and FHS-1C had the lowest concentrations, which may reflect that these samples also had the lowest amount of K in the original unaltered powders (Table 1a). The Al concentrations were most likely controlled by the very low solubility of Al-oxyhydroxide phases at near-neutral pH. The overall results of this leaching test show that the hydrothermal powders can be considered as an efficient K-fertilizer that could readily enrich a soil pore fluid with K^+ cations.

Figure 3b shows the degree of conversion for all 7 samples in terms of the same 3 elements, in pure water and in acid solution. The percentage conversion for each sample is calculated from the ratio of each element's mass in the fluid to its mass in the unaltered powder: $(\text{mass element } i)_{\text{leachate}} / (\text{mass element } i)_{\text{K-feldspar powder}}$, where $i = K, Al, \text{ or } Si$. Figure 3b reveals that in water, the degree of conversion of K is elevated, and one and two orders of magnitude greater than Si and Al, respectively. This suggests that K release to water occurs preferentially from soluble secondary phases rather than the less soluble (alumino)silicates. Authigenic soluble phases include carbonates and amorphous material; the latter can include poorly crystalline material and nanoparticles. As expected, the conversions for K, Si, and Al in all samples at acid pH are distinctly higher than in water: K increases by a modest amount (~20-30 %), whereas Si and Al increase by 2 and 3 orders of magnitude, respectively. Potassium associated with (alumino)silicate phases (authigenic CSH, CASH; remaining K-feldspar grains) is predictably less labile, and requires an aggressive solvent to rapidly liberate a significant amount of K.

The third series of tests explored the leaching behavior of the fresh starting materials with their altered counterparts. Samples TYG-4 (unaltered microcline) and TYG-4C (hydrothermal product) were chosen *ad hoc*. Leaching of these powders was carried out in both pure water and acid solution, and the results are portrayed in terms of Si, Al, and K concentrations in Fig. 3c. Element leaching into water increases 1 to 2 orders of magnitude due to alteration; the same holds for leaching in acid solution. Ciceri et al. (2017a) reported a similar result: a two orders-of-magnitude increase in elemental leaching (hydrothermal powder vs. fresh ultrapotassic syenite) at near-neutral pH.

One obvious explanation is based on the BET-measured specific surface areas of the materials. As shown in Table 2, each sample showed an important gain in surface area after alteration, ranging from 0.6 to 1 order of magnitude; for TYG-4C, the difference is roughly one of order of magnitude. As shown further on, the hydrothermal product is composed of an amalgam of secondary phases that are much smaller than the original feldspar grains. This in itself is sufficient to explain an increase in specific surface areas. In the same study already mentioned, Ciceri et al. (2017a) measured a significant increase in the population of smaller particles, which confirms our findings. However, the increase in surface areas most likely does not explain the entire difference in the leaching behavior. We make the reasonable assumption that all of the secondary phases that precipitated are simply more reactive than the original feldspar grains. It is well known that K-feldspars are very robust minerals and thus slow to dissolve, in particular at near-neutral pH (Bandstra et al., 2008).

4.3. Correlations: hydrothermal product phases, K-release

There are several useful correlations between the various phases present in the hydrothermal product that can be explored, in particular between the secondary phases and remaining K-feldspar. The amount of remaining K-feldspar can be reformulated in terms of the mass % of K-feldspar dissolved (1-mass fraction K-feldspar remaining). Thus, the degree of microcline and sanidine dissolution, which is also a measure of reaction progress, appears to play a direct role in the precipitation of authigenic phases. Figure 4a shows that the amount of authigenic calcite decreases in a linear fashion ($R = 0.92$) with increasing degree of dissolution of the primary K-feldspars. Interestingly, when calcite and vaterite are considered together, the carbonate-K-feldspar relation results in a much poorer correlation ($R = 0.58$; graph not shown). Plotting the mass % of CSH (11 Å tobermorite and clinotobermorite) and CASH (hibschite and katoite) phases as a function of K-feldspar dissolution show two positive linear correlations ($R = 0.81$ and $R = 0.93$, respectively) with different slopes (Fig. 4b). These two trends indicate that the dissolution of feldspar provides, as expected, the necessary elements (i.e., Al, Si, O) that kinetically favor the precipitation of tobermorite and hydrogrossular phases. From the above relations, it is also possible to deduce that the precipitation of Ca-carbonates is inhibited by the formation of CASH and CSH phases, as borne out by a negative linear relation ($R = 0.87$) shown in Fig. 4c. This suggests that progressive Ca

incorporation during tobermorite and hydrogrossular precipitation reactions removes free Ca cations from solution, thereby hindering the precipitation of calcite and vaterite.

The data presented in Fig. 3b can be used to further explore the relation between the normalized amount of K-released in pure water with the mass % of crystalline phases present in the hydrothermal product. To recall, K that is released from the hydrothermal product is derived from two sources: primarily authigenic secondary phases, and to a lesser extent, remaining K-feldspar grains. A graph showing the dependence of K conversion on the amount of remaining K-feldspar grains, shown in Fig. 5a, very surprisingly indicates a poorly correlated ($R = 0.68$) negative correlation. This relation can be interpreted to mean that the original feldspar grains do not readily dissolve and release K to water. Potassium-conversion as a function of carbonate content (calcite and vaterite) shows an even poorer correlation ($R = 0.27$, Fig. 5b) with a weak negative slope. It is debatable, however, whether there is any meaningful correlation between the two. In contrast, K-conversion as a function of tobermorite + hydrogrossular content shows a positive linear relation, with $R = 0.59$ (Fig. 5c). Given the overall poor quality of these correlations, this underscores the complex behavior of K during the alteration process.

4.4. FESEM-EDXS chemical phase and element mapping

Using both chemical phase and single element mapping, we investigated various areas at multiple scales on all polished grain mounts. Below we present representative results for one sanidine (FHS-1C) and one microcline sample (SX-1C). All EDXS element compositions and derived ratios are reported in terms of atom %, this allows for a straightforward comparison with nominal stoichiometric ratios of relevant primary and secondary phases.

Figure 6a is a low magnification BSE image showing primary sanidine grains that are surrounded by a medium grey matrix of much finer grains composed primarily of authigenic secondary precipitates. The sanidine grains are easily distinguishable by their large size, angular shape, and light color. Figure 6b is a chemical phase map characterized by 7 distinct phases; the dominant red phase is C-based resin. The pie chart and the corresponding proportions (aerial %) of each phase are shown in the two insets; their chemical compositions are reported in Table 3a. In most cases, the chemical phase compositions do not match those of the pure secondary phases determined by XRF (Table 1b)- this illustrates the limitations of chemical phase mapping of a complex amalgam of precipitates.

The salmon-colored grains in Fig. 6b represent sanidines that have preserved their original composition (i.e., no surface precipitates present- e.g., arrowed grain). Other large sanidine grains are colored blue, indicating a substantial surface veneer of Ca-rich precipitates. Considering the phases making up the fine-grained groundmass (yellow, purple, fuchsia, green, blue pixels), the blue and green pixels correspond to phases with the highest K concentrations. Overall, K concentrations in the groundmass range from 0.1 to 0.4 %- this compares to 3.2 % in the arrowed sanidine grain. Figure 6c, a

single element K map, shows a generalized, roughly homogeneous presence of K throughout the fine groundmass, with some obvious K-enriched areas. Companion single element maps for Ca, Si, and Al are shown in Figs. 6d-f.

Figure 7 zooms in on the arrowed sanidine grain from the previous figure. The BSE image in Fig. 7a reveals that the grain is surrounded by a rind composed primarily of authigenic phases with different morphologies, such as blades, fibers, spheres, and small non-descript grains in the sub- μm range. The sanidine grain edges are very distinct, except for localized fragmentation, e.g., bottom right. The origin of the major cracks running through the grain cannot be ascertained, but some large cracks were also present in the unaltered grains (Fig. S1a-g). A chemical phase map, with accompanying pie chart and phase proportions, is shown in panel Fig. 7b; compositions are listed in Table 3b. The blue sanidine grain is characterized by $(\text{Na}+\text{K})/\text{Si}$ and $\text{Al}/\text{Si} = 0.3$, which corresponds to the nominal composition of unaltered sanidine. Blue pixels in the precipitate rim most likely represent tiny, broken-off fragments of sanidine. Ubiquitous green pixels on the large blue grain point to incipient surface precipitation of a Ca-rich phase on the surface. The rim is composed of 3 distinct chemical phases (yellow, green, orange pixels); the resin (red) appears to be intimately mixed with the precipitates. The dominant yellow phase is extremely C-rich, and may include a Ca-carbonate component. Green pixels represent a phase that also has elevated K concentrations; this element appears to be heterogeneously distributed in the rim. By comparing the phase map with the K map in Fig. 7c, one can note that the former map reveals with greater detail the spatial variation in K (i.e., blue, green pixels) among the precipitates, especially with respect to the 10- μm -sized globular precipitate (vertical white arrow). The Ca, Si, and Al elemental maps (Figs. 7d-f) confirm the heterogeneous distribution and concentrations of these elements in the precipitates.

A representative SEM image, phase map, and set of elemental maps of a microcline polished grain mount are shown in Fig. 8a-h. The SE image in Fig. 8a reveals several prominent microcline grains (nos. 1-4) with well-developed rims and varying degrees of surface coverage by secondary precipitates. Secondary precipitates are also present as individual entities, and appear as the bright objects in the SE image (upper right quadrant). Aside from the typical morphologies already seen in Figs. 6 and 7, many of them are sub-spherical in shape (e.g., in vicinity of 5). The phase map in Fig. 8b reveals 4 major chemical phases present, with the fifth (gray color) being resin. Since resin is so preponderant in this image, C was excluded from the EDXS chemical analyses. The two prominent grains that are colored green (nos. 3, 4) are representative of microcline grains with a surface veneer of Ca-rich precipitate(s)- the measured K and Ca concentrations are nearly equal. The other two large grains (nos. 1, 2) are characterized by thick surface coverage by precipitates with different chemical compositions (1 is Al-rich, 2 is Ca-rich). The blue and red chemical phases predominantly make up the fine ground mass. The concentration of K in the 4 chemical phases is variable (Table 3c); note that the K/Si ratio is highest in the red phase, which is equal to the measured K/Si ratio in the two large microcline grains (i.e., green phase, nos. 3, 4). A

complementary multi-element EDXS-overlay chemical map of the same area is shown in Fig. 8c (C was excluded from the overall chemical composition, note also that the elemental percentages given in the inset are far from their true nominal values). The two large microcline grains (nos. 3, 4) stand out in terms of their bright red or yellow pixels, indicating predominance of Si and K, respectively. Some smaller grains and spherical precipitates also have high Si and K levels. Figures 8d-h are single element EDXS element maps for K, Si, Al, Ca and O. Based on the K map, and aside from grains 3 and 4, K levels appear to be elevated in just a few grains that surround grain 4. Whether these grains are authigenic, or simply unreacted remnants of microcline (or both), cannot be determined. The remainder of K is distributed at much lower concentrations in the fine groundmass.

4.5.1. FESEM-EDXS spot analyses

In order to complement and extend the information obtained by chemical phase and element mapping of regions spanning many μm^2 on the polished grain mounts, the chemistry of substantially smaller sized areas ($< 1 \mu\text{m}^2$) was measured by FESEM-EDXS spot analyses using an electron beam on the order of several tens of nm. The specific goal of these measurements was to determine semi-quantitative K concentrations associated with secondary precipitates on all 7 samples. The chemistry measured at each spot analysis is reported in atom % - all values are listed in Table S2. Spot analyses on three microcline samples, some with elevated K concentrations, are described below. A complete set of images and spot analysis locations for all 7 samples can be found in Figs. S4-S10.

Microcline sample LS-2C was the only sample that was also imaged in powder form, without resin impregnation. Figure 9a1 shows an SE image of the powder with 9 EDXS spots. Aside from spot 1, which is likely a microcline grain, the K concentrations range from 0.1 to 0.8 %. This micrograph reveals numerous spheroids with diameters in the 2-3 μm range. EDXS analyses of areas 2, 3, and 4 show that they are a Ca-Al-silicate (i.e., CASH), with associated K contents of 0.2-0.4 %. These spheroids were ubiquitous in all of the reacted samples- a typical one is imaged in Fig. 9a2. Despite this unusual morphology, the measured compositions correspond to hydrogrossular. High magnification FESEM micrographs reveal a complex morphology, as the spheroids are composed of interlocking irregular polygons, and are often covered with dense mats of fibrous tobermorite crystals (Fig. S5A). In other images, there is evidence that these spheres are actually hollow. Figure 9b is an SE image of LS-2C (area 1), but in this case a grain mount. Quite surprisingly, K concentrations associated with bladed crystals (calcite?) are very elevated: 3.7-4.8 %. These K concentrations are amongst the highest measured. Nonetheless, the exact identity of the K-rich phase(s) cannot be determined as these crystal clusters are part of a complex amalgam of precipitates.

Microcline sample SX-1C (area 4) is an unusual specimen in that spot 2 had the highest K concentration measured for all samples: 14.7 % (Fig. 9c1). Spot 2 is characterized by bladed crystals

(likely calcite) that overlay a substrate that is difficult to characterize. This spot also had high Ca and Si levels, but very low Al counts, suggesting a predominance of CSH phases, in addition to calcium carbonate. The adjacent spots 1 and 3 are also characterized by elevated K, with values of 5.6 and 2.0 %, respectively. To complement the spot analyses 1-3, Fig. 9c2 is a multi-element EDXS-overlay map that is combined with a BSE image; Fig. 9c3 is the corresponding K element map. Both maps clearly show a high density of yellow pixels (K) at the top of the image, often concentrated in areas of bladed crystals (Fig. 9c2), which is where the EDX spectrum at spot 2 was measured. Because of insufficient resolution, it is difficult to determine whether the yellow pixels (K) match the contours of individual bladed crystals (Fig. 9c2). One can pose the question whether the yellow pixels represent nm-sized K-rich particles? Taken together, the latter two maps confirm that the concentrations and spatial distribution of K are very heterogeneous among the precipitates. Another area on this sample was also analyzed at 4 spots, with the highest measured K concentration in a precipitate being 3.0 % (Fig. S6a).

4.5.2. FESEM-EDXS spot analysis correlations

In order to graphically show all of the results, as well as to explore possible correlations between K and the other major elements that make up the secondary phases, the measured concentrations of Ca, Al, Si, and C are plotted as a function of K in Fig. 10 for the entire set of microcline and sanidine EDXS spot chemical analyses (Table S2). The graphical data represent three groups of spot analyses, listed in decreasing order: a. secondary precipitates making up fine groundmass and precipitate rims, b. precipitates and crystal clusters on top of K-feldspar surfaces, c. relative precipitate-free K-feldspar surfaces. When all of the measurements are considered together, the K concentrations are extremely variable, 0 – 7.4 % (all values in atom %). The one K-rich outlier can be evidenced on the far-right side of the graph. To compare, unaltered feldspar surfaces, either with minimal surface precipitates or clean, have K concentrations on the order of 6-7 %. At first glance, the overall data set is very complex, but a few correlations can be elucidated.

There is a strong clustering of the data within a region that is delimited by elemental concentrations for Ca, Al, Si and C < 20 % and K values in the range 0-1.5 %. This dense data population defines no obvious trends. In contrast, for K values > 1.5 %, the Si-K, Al-K, and C-K couples appear to define positive linear trends with shallow slopes; in the same K range, the Ca-K couple data are more dispersed, making it difficult to define a clear trend. A few of the Ca-K data correlate with elevated K concentrations (2-6 %), and point to K associated with Ca carbonate phases (i.e., with associated elevated C concentrations), or with CASH and CSH phases (high Ca values). Some of the Ca-K data also plot on or near the abscissa- these represent sparse Ca-rich precipitates on K-feldspar surfaces. Overall, the data delimited by K > 1.5 % can be interpreted to denote a positive correlation between K and CASH, CSH,

and possibly Ca-carbonate phases. Going further, one can argue that the Ca-K and C-K couples define another population of data with a strong vertical trend, delimited by $K < 1.5 \%$, and extending to 47 % with respect to C and 32 % with respect to Ca. As a caveat, the C measurements must be evaluated with caution due to the presence of C-based resin throughout the secondary precipitates. Nonetheless, the overall vertical trend of the C-K couple seen in Fig. 10 appears to be real. To test this, the C vs K relation was graphed for just LS-2C powder (i.e. no resin present), and it too showed a clear vertical trend showing weak K concentrations associated with variable C contents (graph not shown).

4.6. STEM-EDXS, HRTEM and EFTEM

The K-feldspar interface and abutting secondary precipitates were examined on all altered samples by various high-resolution TEM techniques- here we present representative results from one microcline and one sanidine sample; see Fig. S11a-c for additional examples. All chemical analyses using STEM-EDXS to measure Al, Si, K, Ca concentrations are based on standardless Cliff-Lorimer k_{AB} factors (Cliff and Lorimer, 1975) integrated into the software. Concentrations are reported in relative atom % in Table 4: note that these relative concentrations cannot be directly compared to complete elemental compositions measured by FESEM-EDXS (as reported in Table S2). All of the TEM work is based on FIB-prepared TEM foils- a typical foil prepared from a polished grain mount is shown in the BF TEM image in Fig. 11a.

Sample LS-2C imaged in STEM mode (Fig. 11b) reveals a non-altered microcline grain surrounded by a reaction rim of secondary authigenic phases, with a sharp interface between the two (black arrows). The respective K/Si ratios at areas 1 and 2 are 0.22 and 0.24, which are close to the nominal value measured by XRF (0.26, Table 1b); calcium is below the detection limit in both areas ($Ca/Si = 0.0006$). The secondary precipitates are a dense mass of intergrown, overlapping, and diverse phases- most form a nondescript aggregate, making it difficult to recognize distinct crystal morphologies. The density of the amalgam is not uniform due to the presence of numerous pores and void spaces. Some crystalline phases are prominent, such as the large bladed crystals up to ~250 nm in length (white arrows). There is also evidence of smaller blocky grains with irregular and angular outlines that may be fragments of primary microcline grains. The measured chemistry of areas 3 and 4 shows in particular enrichment in Ca and Si, with significantly less Al, and even lesser amounts of K (2.4-2.7 %) and C. This chemistry suggests a predominance of CSH (tobermorite), with lesser amounts of CASH phases.

A higher magnification BF TEM image of the same grain is shown in Fig. 11c. The continuity of the wavy diffraction contrast in the microcline indicates that the crystalline structure was maintained during alteration. At the interface a roughly 10-nm thick semi-continuous band of material separating the microcline from the secondary precipitates is just barely visible (opposing white arrows). Among the various crystalline phases are prominent bladed crystals, one such crystal (likely tobermorite) is located

near the oblong white vesicle close to top of image. Vesicles are scattered throughout the groundmass, and range in size from 150 nm down to just a few nm. A granular texture appears to characterize almost the entire area occupied by the secondary precipitates, and can be attributed to the omnipresence of both nm-sized particles and pores. It is reasonable to speculate that these nanometer-sized grains were precipitated during the alteration process.

Figure 11d, a BF image, illustrates a sanidine grain with a linear and sharp interface (white arrows), and abutting secondary phases. The sanidine displays cryptoperthitic texture evidenced by exsolution features defined by K-rich sanidine and Na-rich albite lathes. Running parallel to the sanidine interface is a continuous band of material (medium grey) up to a few tens of nm in thickness. Authigenic precipitates, including bladed crystals (black arrows) that float in a texture-less groundmass, low mass-density globules, and large empty void spaces characterize most of this image to the left of the sanidine grain. The darker aggregate within the large void space (near middle of image) is an extraneous metal corrosion product. Chemical analyses confirm that area 1 is sanidine, albeit with a low K/Si ratio (the low K is balanced by elevated Na in the unaltered sample- see Tables 1a, b). A low K signal is evident in area 2, but more importantly, the measured Ca concentration is zero (i.e., below analytical limits). This is strong evidence that there was no K-Ca exchange, and that area 2 is still within the unaltered sanidine, as evidenced by a normal Al/Si ratio. The low level of K may be an artifact, as significant loss of K has been previously documented at feldspar grain edges, where it is prone to migration under an electron beam (van der Pluijm et al., 1988). Area 3, which straddles the interface, has an elevated K concentration, and Ca is above background levels. Area 4 is in an area that is most likely amorphous; this amorphous material probably extends at least 100 nm from the feldspar interface in this particular location. A comparison of the relative composition of sanidine (area 1) and the amorphous material in area 4 reveals that K levels are 3x higher, whereas Si decreases by 50 % and Al by 80 %, and Ca jumps from ~0 to an amount equaling that of K (Table 4). Although C was not quantified in area 4, the C K EDXS peak is very small. Thus, this material (based on area 4) can be described as a K, Ca and silica-rich amorphous phase (Table 4).

The chemistry of the interfacial region slightly below the one shown here was also probed at several locations within the secondary crystalline phases- see Fig. S11a. Another interface in a different location revealed elevated K and Ca values in the abutting authigenic phase, which is also likely to be amorphous- see Fig. S11b. A final area that was investigated is shown in Fig. S11c.

In order to better document the nature of the thin band of material shown previously, we revisit the same sanidine interface. In the BF image in Fig. 11e, located slightly above that in Fig. 11d, this band appears as a distinct amorphous layer at the interface with the sanidine structure- its thickness varies from 20 to 80 nm, and it has a lower average mass-density than the parent feldspar grain. The mutual interface between it and the sanidine structure is always sharp (white arrows) at the nm-scale. Where the

crystalline-amorphous boundary is not perfectly sharp, we attribute this to the effect of an oblique and/or irregular interface between the two phases. The banding visible in the perthitic sanidine is assumed to be due to alternating K and Na-rich lamellae (chemical composition not verified). When viewed at higher magnification, the interface is crenulated- this may be caused by preferential dissolution retreat of the Na-rich albite lamellae compared to the more resistant K-rich sanidine lamellae.

The amorphous nature of the material, and in particular the nm-sharp interface, was confirmed by high resolution TEM (HRTEM) imaging at various locations on the sanidine interface. Figure 11f was obtained along the interface shown in Fig. 11d. In this particular interfacial region the amorphous layer is many tens of nm-thick. The lattice fringes end abruptly at the interface with the amorphous material (white arrows). The crenulations reveal that each concave area (white arrows) is associated with what appears to be a minor ‘perturbation’ of the crystalline structure, which is typically due to crystallographic strain at the boundaries of K and Na-rich domains in a perthite structure (Lee and Parsons, 1995). The crenulations are likely to be an expression of differential dissolution rates. The inset shows a selected area electron diffraction (SAED) pattern that was obtained by placing a spread electron beam (to minimize irradiation damage) directly on the interface, such that it shows the signatures of both the crystalline structure (zone axis oriented) and the amorphous material in terms of diffraction spots and a diffuse ring, respectively.

Previously discussed STEM-EDXS analyses (Figs. 11b, d) on interfacial regions of feldspar grains indicate that Ca did not enter into either the sanidine or the microcline structure. To confirm this, a series of energy filtered TEM (EFTEM) chemical maps were made on several of the FIB sections. Representative Si and Ca jump ratio EFTEM elemental maps of the interfacial region of microcline sample LS-2C are shown in Figs. 11g, h. The inset in Fig. 11g is a STEM image of a portion of the interfacial region that was subsequently mapped with respect to both Si and Ca. The black arrow in the inset delimits the sharp interface between the microcline and the secondary precipitates, which are dominated by bladed crystals in this particular area.

The Si map (Fig. 11g), determined using the Si $L_{2,3}$ ionization edge, clearly demarcates the microcline interface (right-facing white arrows; note that the chemical interface is not sharp in the upper right region- see Supp. Info. 6). The microcline is characterized by an elevated and homogeneous Si concentration, whereas the Si-containing authigenic phases appear to have slightly lower Si concentrations, which are also variable. This variability in Si concentrations may simply be due to a thickness effect within the amalgam. Using the Ca $L_{2,3}$ ionization edge, a complementary Ca jump ratio map was generated of the same area, and is shown in Fig. 11h. This map also shows a clear and sharp chemical interface (right-facing white arrows), but in this case, the microcline has a black tone, indicating that Ca did not enter the microcline structure. This is evidence at the nm-scale that the chemistry of the K-feldspar structure remains unchanged, including right up to the interface at the grain edge. The black tone

characterizing the microcline is not homogeneous, as there is a slightly darker black band ~100 nm in thickness at the outer region of the grain. We are not sure about this observation, but it could simply be an artifact of the EFTEM measurement. The Ca map also shows that there are Ca-rich phases present, as well as other phases that have lesser amounts of Ca in their structure (see black arrows). It is likely that CSH and CASH phases predominate, with minor amounts of Ca-carbonate. Interpreting the grey scale (i.e., Ca content) of the precipitates is tenuous, however, as it also depends on the thickness of the amalgam. In both upper right quadrants of the Si and Ca maps (Figs. 11g, h), the opposing white arrows delimit the presence of a thin band of material that we construe to be an amorphous surface layer (same as imaged in Fig. 11d-f). If this assumption is valid, the amorphous layer has a lower Si concentration than the microcline, and has an elevated Ca level. A complementary K EFTEM map of the same interfacial area was not possible due to spectral overlap (see section 3.7).

4.7. *Implications of TEM results*

The observations provided by the BF, STEM, and HRTEM images, in combination with EFTEM chemical jump ratio maps, clearly demonstrate that the microcline and sanidine structures remain structurally and chemically intact (i.e. unaltered) during the hydrothermal alteration process, even though the volume of each K-feldspar grain diminishes due to mass loss during dissolution. This precludes the idea that so-called leached layers form by the preferential release of interstitial cations and their replacement by counter cations from the bulk solution. Leached layer theory, applied to this study, would stipulate that preferentially released K is replaced by Ca during alteration (see reviews of leached layers in Hellmann et al., 1990, 2003, 2012, 2015). We didn't find any evidence that Ca, present at high concentrations in the solvent, penetrated the feldspar structure at the fluid-solid interface. Instead, the TEM results indicate that dissolution takes place at a sharp chemical reaction front where the solvent contacts the outer edge of the feldspar structure. Taken together, the TEM results point to an authigenic amorphous phase that forms directly at the feldspar interface. The two phases are separated by a sharp interface that marks a spatially coincident and nm-sharp structural and chemical discontinuity. Despite this discontinuity, at the nm-scale there is no gap between the crystalline K-feldspar structure and the amorphous material. All of these characteristics would support the idea that the amorphous phase forms in situ at the expense of the dissolving K-feldspar. Moreover, these data point to a congruent (stoichiometric) dissolution process at a sharp dissolution front.

The position of the amorphous layer with respect to the primary feldspar grains indicates it formed first, and most likely, at the onset of contact with the solvent. At some point at higher reaction progress during the alteration process, secondary crystalline phases started to precipitate- this means that phases such as tobermorite, hydrogrossular, and calcium carbonate (calcite, vaterite) precipitated from the solution on top of the already-formed amorphous phase. The physical and chemical characteristics of the

amorphous material-potassium feldspar interface lead us to believe that the amorphous layer formed by coupled interfacial dissolution-reprecipitation (CIDR). The relevance of this mechanism, as applied to the same experimental protocol of K-feldspar alteration, is the subject of a future study, and thus will not be elaborated on further. The interested reader can refer to numerous studies dedicated to how this mechanism controls both mineral and glass dissolution, see e.g., O'Neil and Taylor, 1967; Buck et al., 2000; Labotka et al., 2004; Hellmann et al., 2003, 2012, 2015; Putnis, 2002, 2009; Putnis et al., 2005; Geisler et al., 2005; Hövelmann et al., 2010; King et al., 2011; Ruiz-Agudo et al., 2012, 2014. To the best of our knowledge, this is the first time that CIDR has been proposed as a mechanism that controls the alkaline alteration of K-feldspar.

5. Conclusions and Future Directions

The three short-term leaching tests (section 4.2) demonstrate the efficacy of the hydrothermal process that was used to transform K-feldspar to secondary authigenic phases. Short term leaching in water (test 1, Fig. 3a) reveals just how much more K is released compared to Si and Al. This particular result suggests that contact with water suffices for the rapid release of K from the authigenic phases. There are several speculative reasons that may explain why K is so labile.

Rapid release in water can imply that K is structurally incorporated into soluble phases, such as Ca-carbonates, amorphous and poorly crystalline material, or even nanoparticles. Calcite, the dominant secondary mineral phase, and vaterite are both very soluble and dissolve rapidly in water. The question then arises whether K was incorporated into the carbonate structure via coprecipitation, resulting in carbonates with variable K/Ca ratios? Liu et al. (2015) reported the presence of K_2CO_3 and $K_2Ca(CO_3)_2$ in their post-experiment crystalline products. In our case, however, these phases were of minor importance (< 1 mass %). Similar reasoning, in particular with respect to the amorphous surface altered layer (SAL) shown in Figs. 11d,e,f can be used to suggest CIDR-controlled alteration of the parent feldspar and reprecipitation of a K-rich SAL.

Alternatively, rapid release of K in water may also imply an adsorption process. It is possible that potassium (K^+) sorbs to negative surface sites in the amorphous SAL, or in the secondary crystalline phases, such as tobermorite and hydrogrossular (hibbschite and katoite). We can also consider sorption of K^+ to surface carbonate groups. While a detailed analysis of K^+ adsorption on calcite surfaces is beyond the scope of this discussion, we note that molecular dynamics (MD) simulations have revealed that the large radius of the K^+ ion (1.38 Å) prevents it from penetrating the strongly bound hydration layers that characterize the calcite surface (Hofmann et al., 2016). This can be construed as evidence that K^+ is not strongly sorbed on carbonate precipitates in our study, and this could have contributed to the high degree

of K release in water that was measured. And finally, we note that dissolution of soluble phases and release of sorbed K^+ are not mutually exclusive, since both processes may occur in tandem.

The slow leaching of K from the hydrothermal product is also an important process, in particular in terms of fertilizer performance in a soil over long time periods. Rapid leaching in a very acidic solution, i.e., tests 2 and 3 (Fig. 3b,c), can in fact be considered to be an analog process for slow dissolution of authigenic (alumino)silicate phases and concomitant K release in a near-neutral pH pore fluid. The acid leaching test results (Fig. 3b,c) imply that enhanced dissolution of secondary silicate phases, which also includes remaining K-feldspar grains, is largely responsible for elevated K release to the solution (Ca-carbonate phases, of course, also dissolve faster). This result can be interpreted in terms of K incorporation into secondary silicate phases, followed by their subsequent release- this is supported by the correlation in Fig. 5c. As an example, the presence of charge-balancing K^+ in the Al-tobermorite structure has been documented in these types of hydrothermal products (Ciceri et al., 2017a). Whether or not K can be incorporated into hydrogrossular phases is not known. Other K-bearing silicates that are typical hydrothermal alteration products, such as kalsilite (Su et al., 2015) or panunzite (Ciceri et al., 2017a), probably had no effect on the K release budget in the present study, as their concentrations were far too low in the hydrothermal product.

The EDXS measurements (FESEM and TEM, sections 4.5.1 and 4.6) provide a semi-quantitative measure of K levels in the secondary phases. These measurements show that the distribution of K is very heterogeneous both in terms of distribution and concentration. The vast majority of K levels in the precipitates, both in the interfacial region and further afield, are distinctly less than in the parent material, but nonetheless, are present at concentrations up to 2 atom % (Fig. 10), which is $\sim 1/3$ of the nominal amount in the K-feldspar. In specific locations, however, such as in the amorphous SAL or in a few precipitate amalgams, K concentrations are equivalent, or even significantly higher than in the original K-feldspar. The TEM measurements highlight a K concentration hotspot in an amorphous SAL phase that is also enriched in Ca, but with much less Si, and hardly any Al (Table 4). Because our TEM-measurements were restricted to interfacial regions, we cannot say whether any amorphous phases also formed in conjunction with secondary crystalline phases not proximal to K-feldspar grains. However, the FESEM-EDXS measurements reveal that within certain secondary precipitate amalgams very high K concentrations exist, e.g., in particular the very enriched K-outlier datum in Fig. 10. As already shown for certain areas, e.g., SX-1C area 4, Fig. 9c1; LS-2C area 1, Fig. 9b; Table S2, these K-hotspots generally seem to occur in regions characterized by clumps of bladed crystals that have a calcite morphology. However, these bladed crystals are not isolated, but are mixed with other uncharacterized phases. We note, moreover, that the majority of areas characterized by a high density of bladed crystals have significantly lower K concentrations (< 2 atom %), including areas in close proximity to where elevated K concentrations are measured (Figs. 9c1,c2,c3).

The FESEM and TEM observations clearly show that the secondary precipitates are a complex amalgam of multiple phases, comprised of both crystalline minerals and amorphous material. With few exceptions, such as the amorphous SAL, we have only been able to measure K levels in mixtures of phases rather than in individual crystals. The analytical techniques and methods that we used had intrinsic limitations, as they did not allow us to quantitatively determine which specific crystalline phases are the principal reservoirs of released K, nor, in a crystal chemistry sense, how K is associated with these phases. The nanoparticles that are ubiquitously present among the precipitates deserve more study (e.g., Fig. 9c2), as they may play a key role in the rapid release of K to fluids, even at near-neutral pH. To evaluate their potential importance to the K budget would require state-of-the-art TEM instrumentation and methods to measure their chemistry and structural properties.

To predict the molecular-scale behavior of K, ensuing studies should address how K is associated with each secondary phase, in particular whether it is structurally incorporated (via coprecipitation or substitution, i.e., as with Al-tobermorite), or simply sorbed to specific negatively charged surface sites. Moreover, subsequent research should also consider the use of advanced complementary techniques, such as X-ray absorption, nanoRaman spectroscopy, or even scanning transmission X-ray microscopy. While this list is far from exhaustive, such techniques have the potential to better elucidate the chemical environments of K at the near-atomic level.

We can now postulate very briefly what might happen at the macroscopic scale once the hydrothermal product is distributed as a fertilizer on a K-deficient soil. As already discussed, reactive phases in the hydrothermal product will release K rapidly when in contact with water. The more slowly dissolving secondary CASH and CAS phases will release K at rates a few orders of magnitude slower. Since the conversion of K-feldspar grains will never be 100% using the present protocol, the original feldspar grains present in soil treated with hydrothermal product will continue to weather and decompose so long as they remain in contact with aqueous fluids (precipitation, soil pore fluids). This will result in the continuous release of K, Al, and Si (see e.g., Sanz Scovino and Rowell, 1988), albeit at very slow rates, and most likely even slower than the dissolution of CASH and CAS phases. The amorphous SAL, which is dependent on the lifetime of each feldspar grain, can be included as a phase that will continuously release K over long time periods. All SALs can be considered to be dynamic phases- they continue to form in situ and at the expense of the parent K-feldspar so long as fluid is able to reach the feldspar interface. The release of K from a SAL occurs at its external edge where it contacts pore fluids. Dissolution reactions at the outer boundary, in fact, ensure that the SAL does not become infinitely thick over time. Additional crop and soil remediation benefits procured from the use of K-feldspar-derived hydrothermal products are described in Supp. Info. 2.

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Figure Captions

Fig. 1. Flow chart showing the principal steps of the experimental protocol: mixing of reactants, alkaline hydrothermal decomposition of the K-feldspar, drying step, solid-state characterization methods (right side) and short-term leaching tests (left side).

Fig. 2. X-ray powder diffraction and Rietveld refinements were used to determine the mineral composition of hydrothermal products. Panels *a-g* show major crystalline product phases that precipitated after alteration of the sanidine (FHS-1C) and microcline samples, expressed in terms of mass %. The bar graph in panel *h* indicates the mass % of tobermorite (CSH) and hydrogrossular (CASH) phases present in the hydrothermal products. Note: the fitted X-ray powder diffraction patterns are shown in Fig. S3.

Fig. 3. Aqueous results based on 1-hour leaching tests of hydrothermal product in acid solution (HCl) and water at ambient temperature- see Table S1 for data. (a) Comparison of aqueous concentrations after leaching in water. The relative cation concentrations ($[K] > [Si] > [Al]$) indicate that the hydrothermal product would readily release K into a near-neutral pH soil pore fluid. (b) Comparison of conversion ratios ($[\text{mass element}]_{\text{leachate}}/[\text{mass element}]_{\text{K-feldspar}}$) for all 7 samples, in both acid solution and water. The large differences between K vs. Si and Al conversion at neutral pH implies that released K is associated with phases that are water soluble and dissolve rapidly. The % conversion of K from WLST-1C in water reads 19.4 %. (c) Aqueous concentrations of K, Si, Al leached from hydrothermal product TYG-4C compared to original starting material TYG-4, after contact with either acid solution or water. The up to 2 orders of magnitude increase in cation release concentrations (especially K) after alteration points to the efficacy of the hydrothermal alteration process, and shows the promising potential of the hydrothermal product for use as a ready-to-use K-fertilizer.

Fig. 4. Correlation diagrams showing relationships between secondary and primary phases, or between carbonate and silicate secondary phases. (a) Calcite precipitation as a function of amount of reacted K-feldspar (b) Tobermorite and hydrogrossular precipitation as a function of reacted K-feldspar (c) Ca-carbonate precipitation as a function of hydrogrossular precipitation.

Fig. 5. Percentage K conversion in water as a function of composition of hydrothermal product: (a) % K vs. K-feldspar remaining in hydrothermal product (b) % K vs. Ca-carbonate (c) % K vs. tobermorite and hydrogrossular. The linear trends in panels *b* and *c* are questionable due to poor correlation coefficients- see text.

Fig. 6. FESEM and EDXS images of sanidine sample FHS-1C in polished grain mount. (a) BSE FESEM image showing primary sanidine grains (e.g., white arrow in all panels) surrounded by secondary reaction products. (b) Chemical phase map of same area: unaltered sanidine grains (salmon color), sanidine grains covered by precipitates (dark blue), and secondary authigenic precipitates (other colors). The two insets give the areal percentages of the different chemical phases present in the image. The dominant phase is resin (bordeaux red in image, bright red in insets)- see text for other phases. The ‘tuning fork’ particle (fuchsia color) above the arrowed grain is an extraneous dust particle. (c-f) Element specific chemical maps. Calcium is the only element solely associated with secondary precipitates. The scale bars read 200 μm .

Fig. 7. Sanidine grain FHS-1C and corona of secondary precipitates in polished grain mount imaged by FESEM and EDXS. This grain is the arrowed grain in Fig. 6. (a) BSE FESEM image- note dust particle touching upper right edge of grain. The vertical white arrow points to amalgam of secondary precipitates- see text. (b) Chemical phase map with two insets showing areal % of phases present- the dominant phase is resin (bordeaux red in image, bright red in insets). (c-f) Individual element maps. Note the heterogeneous distribution of elements present in the precipitate amalgam (white vertical arrow). The scale bars read 10 μm .

Fig. 8. Microcline grains and corona of secondary precipitates in polished grain mount SX-1C imaged by FESEM and EDXS. (a) SE FESEM image of several large microcline grains- the numbers refer to specific grains or areas discussed in text. Grains 1 and 2 are microcline with a significant surface veneer of precipitates, whereas grains 3 and 4 are relatively free of surface precipitates. (b) Chemical phase map with inset showing areal % of phases present- the dominant grey color is resin. (c) Multiple element EDXS-overlay map: this map best reveals the chemical heterogeneity of the precipitates. The areal % of the elements do not reflect the true % of each element present- see text. (d-h) Individual element maps. Note how K is dominant in grains 3 and 4, whereas Ca is completely missing. Scale bars read 20 μm .

Fig. 9. Representative FESEM images showing the locations of EDXS chemical analyses- the compositions are listed in Table S2; additional FESEM images from all samples are shown in Figs. S4-S10. (a1) LS-2C powder area 11 (no resin present)- note numerous spherical precipitates. (a2) Ca-Al-silicate spheroidal precipitate in LS-2C powder- additional images are shown in Fig. S5A. (b) LS-2C area 1 polished grain mount- spots 3, 4, and 5 have high K concentrations (3.7-4.2 atom %). (c1) SX-1C area 4 polished grain mount- spots 2 and 3 have elevated [K], with spot 2 having [K] = 14.7 atom % (highest recorded value in study). (c2) Multi-element map overlaid on SE FESEM image- note high concentration of yellow (K) pixels at spots 2 and 3 (arrows), while [K] is much lower at spot 1. (c3) K elemental map- note the heterogeneous distribution of K, with highest [K] in upper right region of precipitate amalgam.

Fig. 10. Graphic representation of [Ca], [Al], [Si], and [C] plotted as a function of [K] based on complete set of FESEM-EDXS spot analyses (compositions in atom %). Note clustering of data in region delimited by elemental concentrations for Ca, Al, Si and C < 20 % and K in range of 0-1.5 %. At [K] > 1.5 %, the Al-K, Si-K and C-K couples appear to show weakly correlated, sub-horizontal linear trends- see text for details. Note the outlier datum with [K] = 14.7 % (SX-1C, area 4, spot 2)- this compares to [K] = 6-7 % in unaltered K-feldspar.

Fig. 11. TEM images of reacted microcline and sanidine grains, prepared in cross section by FIB. Numbered rectangles show where STEM-EDXS analyses were made: chemical compositions (relative atom % - see text) are reported in Table 4; additional TEM images with EDXS locations are shown in Fig. S11. (a) FIB-prepared TEM foil from polished grain mount LS-2C. Note primary microcline grain, sharp interface (black arrows) with secondary precipitates, void spaces, and resin. (b) STEM image of microcline LS-2C showing sharp interface between primary grain and precipitates (black arrows). White arrows point to prominent bladed crystals within amalgam of secondary precipitates. (c) BF TEM image of LS-2C, same as (b) but enlarged: cropped image modified from Fig. 7A, Zhai et al., 2020. The opposing arrows delimit a very thin band of material that semi-continuously abuts the feldspar interface. (d) BF image of sanidine grain with thin surface altered layer abutting sharp interface with sanidine interface- note also the perthitic texture in sanidine. The small black arrows point to secondary crystalline phases; the dark clump of material in center of image is a metallic contaminant. (e) BF image reveals sharp interface (white arrows) between sanidine and amorphous precipitate. The contrast in color indicates that the mass-density of the precipitate is less than the parent sanidine. The bands in the sanidine are due to exsolution lamellae. (f) High-resolution TEM image of interface with nm-sharp interface between sanidine lattice fringes and amorphous surface altered layer (SAL). Note the lack of a gap between the two phases. The SAL is hypothesized to form in situ and at the expense of the dissolving sanidine- see text. The inset is a selected area electron diffraction diagram taken at the interface. (g) The inset is a STEM image of interfacial region on microcline sample LS-2C showing a sharp interface (black arrow) with secondary

precipitates (bladed crystals). The larger image is a Si map of same area based on the EFTEM jump ratio method- the single right-pointing white arrows indicate the interface. Lighter white areas are rich in Si, dark areas are depleted. The opposing white arrows indicate probable SAL, which has less Si compared to microcline. (h) EFTEM jump ratio map of Ca of the same interface- note how the Ca distribution delimits a sharp chemical boundary (single right-pointing white arrows) between Ca-bearing precipitates (black arrows) and sanidine. The black tone of the sanidine indicates that Ca did not penetrate crystal structure during alteration. Opposing arrows indicate probable Ca-enriched SAL.