The hydrothermal alkaline alteration of potassium feldspar: A nanometer-scale investigation of the orthoclase interface

Roland Hellmann, Yuanyuan Zhai, Eric Robin, Nathaniel Findling, Sathish Mayanna, Richard Wirth, Anja Schreiber, Martiane Cabié, Qingdong Zeng, Shanke Liu, et al.

Roland Hellmann, Yuanyuan Zhai, Eric Robin, Nathaniel Findling, Sathish Mayanna, et al.. The hydrothermal alkaline alteration of potassium feldspar: A nanometer-scale investigation of the orthoclase interface. Chemical Geology, 2021, 569, pp.120133. 10.1016/j.chemgeo.2021.120133 . hal-03389010

HAL Id: hal-03389010
https://hal.science/hal-03389010v1

Submitted on 22 Oct 2021

The hydrothermal alkaline alteration of potassium feldspar: a nanometer-scale investigation of the orthoclase interface

Roland Hellmann*[a], Yuanyuan Zhai[b,c,d,1], Eric Robin[e], Nathaniel Findling[a], Sathish Mayanna[f,2], Richard Wirth[f], Anja Schreiber[f], Martiane Cabié[g], Qingdong Zeng[b,c,d], Shanke Liu[b,c], Jianming Liu[b,c,d,3].

[a]Université Grenoble Alpes and CNRS, ISTerre, F-38058 Grenoble Cedex 9, France

[b]Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

[c]Innovation Academy for Earth Science, Chinese Academy of Sciences, Beijing 100029, China

[d]College of Earth Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

[e]Université Grenoble Alpes, IRIG, MEM, CEA, Grenoble, France

[f]Helmholtz Centre Potsdam, GFZ Deutsches GeoForschungsZentrum, Interface Geochemistry Sektion 3.5, Telegrafenberg, D-14473 Potsdam, Germany

[g]Aix Marseille Université, CNRS, Centrale Marseille, FSCM (FR1739), CP2M, F-13397 Marseille, France

[1] current address: Shenzhen Xinhua Middle School, Shenzhen 518109, China

[2] current address: Carl Zeiss Microscopy GmbH, D-73447 Oberkochen, Germany

[3] retired

Key words: orthoclase feldspar alkaline hydrothermal alteration, coupled interfacial dissolution-reprecipitation (CIDR), analytical transmission electron microscopy (TEM), energy filtered TEM (EFTEM), TEM-EDXS, electron energy loss spectroscopy (EELS), orthoclase-fluid interface, secondary cement phases, CASH and CSH, K fertilizer

*to whom correspondence may be addressed.
Email: roland.hellmann@univ-grenoble-alpes.fr

ABSTRACT

Potassium feldspars ($KAlSi_3O_8$) are ubiquitous minerals in the Earth's upper crust. This family of minerals has been the subject of numerous experimental and theoretical investigations concerning their dissolution kinetics and the mechanisms controlling chemical alteration at acid and neutral pH, and at temperatures ranging from ambient to hydrothermal conditions. On the other hand, considerably less research on the dissolution behavior of K-feldspars has been carried out at alkaline conditions, in particular at pH > 9 and elevated temperatures. Filling in this gap in knowledge is the major motivation for this study. More specifically, we wanted to document and understand how the K-feldspar interface structurally and chemically evolves during alteration in order to determine the mechanism of dissolution. In this study we examined interfaces of orthoclase samples that were altered in separate experiments in a $Ca(OH)_2$-H_2O solution ($pH_{25°C}$ 12.4) at 190 °C for 24 hours. We used a combination of focused ion beam (FIB) milling and advanced analytical transmission electron microscopy (TEM) techniques to investigate the structure and chemistry of the near surface region of post-reaction grains, with particular attention being given to the fluid-solid interface. Even though each grain diminishes in volume due to dissolution, high-resolution TEM imaging indicates that the feldspar structure itself remains completely intact and crystalline, as evidenced by lattice fringes that abruptly terminate at the grain edge. Nanometer-scale chemical composition measurements and mapping by TEM-EDXS (energy dispersive X-ray spectroscopy) and EFTEM (energy filtered TEM) show that the chemistry of the parent feldspar also remains unchanged at the interface. In particular, there is no evidence for the incursion of Ca from the fluid solvent into the structure, either by interdiffusion or by a replacement process. Taken together, the TEM observations point to a sharp chemical reaction front characterized by the congruent (i.e. stoichiometric) release of all elements from the feldspar structure.

Nanometer-scale measurements by high resolution analytical TEM also reveal that a surface alteration layer (SAL) of amorphous material forms in situ at the expense of the feldspar structure. The interface demarcates a spatially coincident and nm-sharp chemical and structural discontinuity between the parent feldspar and the amorphous phase. The amorphous SAL has a variable thickness, from under 10 nm up to ~200 nm. This is likely one of the first observed occurrences of a significant surface amorphous layer on feldspar due to alteration in an alkaline solvent. The lack of a gap between the two phases points to an interfacial dissolution-reprecipitation process that continuously operates during hydrothermal alteration, and mostly likely right from the onset of contact with the fluid. After the initial formation of the amorphous layer, a 1-2 μm-thick porous amalgam of secondary crystalline phases comprised of calcite, tobermorite, and hydrogrossular, as well as other minor phases, precipitated over

the SAL. These authigenic crystalline minerals formed during the experiment (hydrothermal alteration, followed by fluid loss due to evaporation) by a classical thermodynamically-controlled precipitation process as the reactor bulk fluid became increasingly concentrated.

We propose that a coupled interfacial dissolution-reprecipitation (CIDR) mechanism best explains the chemical and structural properties of the interface and the formation of an amorphous surface layer. In fact, many recent studies postulate that a CIDR process controls feldspar dissolution and the formation of SALs at acid and circumneutral pH over a wide range of temperatures. Combining these previous results with our new observations supports the idea that a unique and unifying mechanism likely controls chemical alteration of feldspars in all aqueous fluids.

1 INTRODUCTION

1.1. Research goals

The feldspar-water system is arguably one of the most important in the earth sciences, in particular with respect to chemical weathering associated with water-rock interactions. This is primarily due to the preponderance of feldspar minerals in the upper continental crust and at earth's surface (Klein and Philpotts, 2017). Feldspars are chemically robust framework silicates and thus dissolve very slowly, with the kinetics of dissolution depending strongly on pH and temperature. While the aqueous alteration of feldspars has been extensively investigated experimentally and theoretically, the overwhelming majority of studies have focused on alteration at conditions encompassing acid, circumneutral, and weak alkaline pH conditions (i.e., pH 1-9), and at temperatures less than 100 °C. There are several reviews of feldspar dissolution rates as a function of pH at ambient conditions, e.g., Blum and Stillings, 1995; Bandstra et al., 2008; at elevated temperatures up to hydrothermal conditions, see, e.g., Hellmann, 1994; Yuan et al., 2019; and references therein. The review of feldspar alteration by Yuan et al. (2019) is a good starting point for a synopsis of both new and not-so-recent work concerning both dissolution rates and mechanisms of feldspar alteration reactions in aqueous fluids.

In this study we examine post-reaction solid-fluid interfaces of alkali feldspars in order to elucidate the mechanism of chemical alteration in alkaline aqueous fluids with a very high pH. As discussed in more detail in section 1.3, it is at these conditions where there is a real need for more experimental data, which in turn explains one of the motivations for our research. Moreover, we wanted to document and understand how the crystal structure evolves both structurally and chemically when in contact with a very basic pH solution at elevated temperature. Many studies have reported the formation of surface altered layers (SALs) on feldspars undergoing chemical alteration at acid, circumneutral, and mild alkaline conditions (e.g., Hellmann et al. 2003, 2012; and references therein), We note, however, that literature data on feldspar hydrolysis at basic pH conditions (> pH 9) are not numerous, this in particular being true for temperatures above 100 °C. For this reason we posed the question whether this interfacial process, in other words SAL formation, also operates when an alkali feldspar is exposed to an aggressive basic pH solution at elevated temperature. In response to this question, the present research is among the first that has focused on a detailed structural and chemical examination of feldspar interfaces after basic pH alteration using high-resolution analytical TEM techniques.

The overarching goal of our study was to focus on nanometer-scale TEM measurements to characterize structural and chemical changes to the interfacial region that encompasses the near surface of the primary feldspar and abutting authigenic secondary phases. We were in particular interested in two elements, K and Ca. The behavior of K is fundamental, as it is a good tracer element for following the overall hydrothermal alteration process, starting with its release during dissolution of the parent feldspar, and then understanding its distribution with respect to the precipitation of secondary authigenic phases (see e.g., Zhai et al., 2021). On the other hand, determining the mobility and distribution of Ca is primordial since $Ca(OH)_2$ makes up the solvent, and thus it is important to measure its distribution at high spatial resolution in order to determine whether or not it penetrates into the orthoclase structure. In addition, important framework elements, such as Si, Al, and O, were also measured by TEM. Taken together, our TEM data provided us with the means to propose an operative mechanism at the nanometer-scale for K-feldspar alteration at basic pH.

Even though the present research is uniquely devoted to orthoclase feldspar, it is worth reiterating that there are 3 common alkali feldspar polymorphs that share the same nominal formula, $KAlSi_3O_8$. However, their atomic structures are not identical. Sanidine is the polymorph that forms at the highest temperature and fastest cooling rates, whereas orthoclase and microcline crystallize at lower temperatures and are characterized by much slower cooling rates. The temperature and rate of crystallization affects the degree of Al/Si ordering on the tetrahedral sites, with sanidine displaying the highest disorder, and microcline the lowest. Both sanidine and orthoclase crystallize in the monoclinic system (H-M, class 2/m), while microcline crystallizes in the triclinic system (class $\bar{1}$). Classical studies, such as by Brown and Parsons, 1989, have addressed important processes that include ordering rates and phase transformations of the various K-feldspar polymorphs. These phenomena are intimately related to the creation of internal microstructures, which in turn can affect global dissolution behavior. While important for controlling the overall kinetics of K-feldspar dissolution, quantifying the effects of crystallographic structures at the micrometer to sub-micrometer-scale, as well as the degree of Al/Si ordering, was not an objective of this study (for the effects of ordering on dissolution, see, e.g., Yang et al., 2013, 2014a,b). In addition, a detailed mineralogical-crystallographic characterization of the hydrothermal secondary products was also not carried out here. Nonetheless, another study on hydrothermally altered microcline and sanidine focuses on the distribution and concentrations of released K in secondary authigenic phases (Zhai et al., 2021).

1.2. Brief review of surface alteration processes

One of the key aspects for elucidating the mechanism of dissolution of any primary crystalline or glassy phase is a detailed understanding of surface altered layers that typically form in situ on a retreating (dissolving) surface. This involves using high-resolution analytical techniques in order to measure their chemistry and structure, as well as the respective interfacial gradients with the parent phase (e.g., see Hellmann et al., 2003, 2012, 2015). These layers are amorphous and generally have a chemical composition distinct from the parent mineral (or glass). Many recent studies on feldspars altered at acid to circumneutral pH conditions, in both the laboratory and in the field, have documented their presence using TEM techniques (e.g., Hellmann et al., 2003, 2012; Lee et al., 2007, 2008; references therein). In fact, nearly all polycationic silicate minerals have the potential to develop a SAL when in contact with an aqueous fluid (Hellmann et al., 2012, Ruiz-Agudo et al., 2012). Related to SAL formation is an equivalent process termed mineral-mineral replacement, but in this case a secondary mineral replaces the primary mineral (see reviews in Putnis, 2009, 2014).

Traditional thinking regarding both SAL formation and mineral-mineral replacement posits that they are controlled by an interdiffusion process between preferentially leached cations in the parent solid and certain charge-compensating cations (including H_3O^+) in the bulk fluid (see reviews in Hellmann et al., 2012; Yuan et al., 2019). However, based on the application of relatively new and advanced analytical techniques to altered samples prepared in cross-section by ultramicrotomy (e.g., Thomassin et al., 1995; Buck et al., 2000; Hellmann et al., 2003) and focused ion beam milling-FIB (e.g. Wirth, 2004; Hellmann et al., 2012), the theory of preferential cation leaching controlled by interdiffusion has become increasingly doubtful. In fact, research over the past two decades promotes an alternative theory that is gaining widespread acceptance. It is based on a coupled interfacial process that links dissolution of the parent mineral with the synchronous interfacial reprecipitation of a secondary phase, which can be either amorphous (SAL) or crystalline. In the latter case, this is governed by a pseudomorphic replacement process (Putnis, 2002, 2009, 2014; King et al., 2011). Some minerals, in particular feldspars, can develop an amorphous SAL (Hellmann, et al., 2003, 2012), or alternatively, show replacement by a feldspar of another composition (O'Neil and Taylor, 1967; Labotka et al., 2004; Hövelmann et al., 2010). Both the nature of the primary mineral and the physicochemical conditions of the fluid determine in large part which process occurs (see details in Hellmann et al., 2012- Fig. 4). It is important that SALs and mineral-mineral replacement are not confused with the classical precipitation of secondary phases onto a mineral surface from a chemically oversaturated bulk fluid. These points are discussed in more detail further on.

1.3 Previous Work

It has commonly been assumed that feldspars, and silicate minerals in general, dissolve 'more-or-less' congruently at ambient temperatures and at neutral to basic pH conditions, without the formation of SALs. In regard to feldspars, this is based on aqueous chemistry measurements showing that non-stoichiometric dissolution is most pronounced at acid pH conditions, and significantly less at circumneutral and basic pH (Chou and Wollast, 1985; Holdren and Speyer, 1985; at elevated temperatures, see e.g., Hellmann et al., 1989; Hellmann, 1999a,b). With the application of relatively new solid-state analysis techniques in the geosciences, the formation of SALs on feldspars and other silicates received much attention in the 1990's and the decade thereafter. The pioneering studies by Petit and Dran applied several types of surface sensitive multi-eV ion beam methods, such as resonant nuclear reaction analysis (RNRA), to obtain H and cation depth profiles of chemically altered feldspars and other silicate minerals and glasses (Petit et al., 1989, 1990a,b; Dran et al., 1988; Hellmann et al., 1997). Casey and co-workers applied elastic recoil detection (ERD) and Rutherford backscattering spectroscopy (RBS) to determine H and cation depth profiles on labradorite feldspar surfaces after reaction at ambient or near-ambient temperatures over a wide range of solvent pH (Casey et al. 1988, Casey et al., 1989a,b; Arnold et al., 2002).

Other surface-sensitive techniques, such as X-ray photoelectron spectroscopy (XPS) (Hellmann et al., 1990; Chen et al., 2000) and secondary ion mass spectrometry (SIMS) (Schweda et al., 1997; Nesbitt and Muir, 1988; Nugent et al., 1998) were also used to study cation depletion in reacted feldspars as a function of pH and temperature. Other lesser known techniques, such as high-resolution in-situ X-ray reflectivity (XR) and ex-situ X-ray reflection interface microscopy (XRIM), were used by Fenter and colleagues to probe near-surface orthoclase chemistry after reaction at 25 and 50 °C in solutions at acid, neutral, and very basic pH (Fenter et al., 2000, 2010; Teng et al., 2001).

When considered together, data from most of the above-cited studies indicate that changes in the near surface of feldspars do occur during chemical alteration, both in terms of chemistry and the formation of an amorphous SAL. With the exception of alteration at acid pH conditions, these SALS are restricted to thicknesses of several molecular layers, which corresponds to the top most layers of the former feldspar structure. Moreover, some of the above studies concluded that feldspars dissolve more or less congruently at ≤ 50 °C at neutral to basic pH conditions, and that dissolution only proceeds at the immediate surface, layer by layer. While SALs are undoubtedly thin at these pHs and low temperatures, the top-down surface analytical techniques with large beam foot prints that were used in the 1990's and early 2000's were also limited in sensitivity and/or spatial resolution. For this reason, the study of reacted mineral interfaces prepared in cross section by ultramicrotomy (Thomassin et al., 1995; Hellmann et al., 2003) or by FIB (e.g., Wirth, 2004) with Å-resolved TEM techniques has proven to be a breakthrough and an enormous advantage for better characterizing altered surfaces and understanding how they form, see e.g., Buck et al., 2000; Hellmann et al., 2003.

Up to the end of the 1990s only a handful of studies had been dedicated to alkaline hydrothermal alteration of feldspars, in particular the detailed exploration of SALs and their mechanism of formation. One pioneering study used XPS and angle-resolved XPS (ARXPS) to measure the near-surface chemistry of albite ($NaAlSi_3O_8$) that had been subjected to hydrothermal alteration at 225 °C in a $pH_{(25°C)}$ 10.1 solution (Hellmann et al., 1990). This study showed, via non-stoichiometric near-surface Al/Si, Na/Si, and O/Si ratios, that SALs with thicknesses of many tens of nm form at these conditions. The possibility of relatively thick SALs developing during alteration at basic pH and hydrothermal conditions was further supported by results from an experimental study by Hellmann (1995), based on alkaline dissolution of albite feldspars at $pH_{(25°C)}$ 10.0 and 12.0 at hydrothermal conditions (100, 200, and 300 °C). Even though only aqueous solution compositions were measured, a generalized and significant non-stoichiometry was reported. These results are tantalizing, in that they provide indirect evidence for the formation of non-negligible SALs at elevated T and pH conditions. Even though these experiments used pure albite feldspar ($NaAlSi_3O_8$), the aqueous results underline a key point, namely that Na, Al, and Si, and by analogy K, Al, and Si in a K-feldspar, can be considered to be mobile during hydrothermal alteration at basic pH conditions.

A study of the Jurassic Navajo Sandstone by Zhu et al. (2006) revealed that SALs can also form under natural conditions. TEM images show the presence of a naturally occurring 10 nm-thick amorphous SAL that formed in situ on an alkali feldspar. The composition was not measured, but the authors postulate that it is K-deficient and Si-enriched. Even though the formation fluid was found to be mildly alkaline during borehole sampling, it is not known how the pH (and temperature) varied over geological time. Quite importantly, this example shows that SALs are not ephemeral features of dissolution, but can be stable over geologically long periods of time.

Over the past decade, there has been a resurgence of interest in the study of the chemical alteration of K-feldspars. The objective of many recent studies has been to use very aggressive basic pH fluids to chemically breakdown K-feldspars at hydrothermal conditions. The resulting secondary authigenic phases that are produced during chemical alteration are enriched in K. This hydrothermal product can be used directly as a K-fertilizer on soils, and is increasingly considered to be a commercially viable substitute for traditional K-rich soluble salts, such as sylvite (KCl). Such soluble salts are nearly all sourced in northern hemisphere countries (e.g., Belarus, Russia, Canada, Germany), making their long-distance transport to developing countries in the southern hemisphere financially prohibitive. The extraction of K-fertilizer from K-feldspars has a more than century-long history behind it, as described in Ciceri et al. (2015). Despite this, little is known on the exact mechanism controlling this process. It is interesting to note that over the past two decades several Chinese laboratories are spearheading this type of research (see review in, e.g., Ma et al, 2015). In these Chinese studies (and others), the generalized use of alkaline pH solutions to extract K is largely based on the economics of producing CaO from limestone, from which $Ca(OH)_2$ is easily derived; there are also 'green chemistry' considerations that come into play (Ma et al., 2015; Ciceri et al., 2017a).

Recent studies focused on the alkaline hydrothermal extraction of K from K-feldspars have for the most part been centered on identifying and describing the secondary crystalline phases that are produced. Moreover, although none has studied in detail the mechanism that controls the chemical breakdown of the K-feldspar structure, a few have proposed scenarios on how this occurs. A study by Su et al. (2015) reacted K-feldspar with aqueous KOH + NaOH solutions (8 M) at 240 and 280 °C, where the mole fractions of KOH and NaOH were varied. These authors postulated congruent dissolution of the feldspar via an OH^- mediated reaction:

$$\mathrm{KAlSi_3O_8} + 2\mathrm{H_2O} + 6\mathrm{OH^-} \rightarrow \mathrm{Al(OH)_4^-} + 3\mathrm{H_2SiO_4^{2-}} + \mathrm{K^+} \qquad (1)$$

The aqueous dissolution products on the right side of eqn. 1 consequently precipitate to form the feldspathoidal mineral kalsilite, $KAlSiO_4$. When the above reaction is carried out with NaOH solvent, sodium ions, in turn, reacting with $Al(OH)_4^-$ and $H_2SiO_4^{2-}$, lead to the precipitation of the feldspathoid hydroxycancrinite, $Na_8Al_6Si_6O_{24}(OH)_2 \cdot 2H_2O$. These crystalline phases formed as a dense amalgam of crystals, which presumably precipitated directly from an oversaturated bulk fluid (see Fig. 2, Su et al., 2015). The stoichiometric dissolution reaction detailed by Su et al. (2015) corresponds to the findings of Gautier et al. (1994), who observed that Al and Si were released congruently from a K-rich feldspar at 150°C and pH 9.0. Another study, by Liu et al. (2015), hydrolyzed K-feldspar (microcline) in NaOH, KOH, and $Ca(OH)_2$ solutions at hydrothermal temperatures up to 220 °C. They proposed a mineral-mineral replacement process controlled by dissolution-precipitation, leading to the formation of hydrated Ca-Al-silicate phases. At 220 °C they described the overall reaction as:

$2KAlSi_3O_8 + 6.3525Ca(OH)_2 + 0.195H_2O \rightarrow Ca_3Al_2(SiO_4)_{1.53}(OH)_{5.88} + 1.49Ca_{2.25}(Si_3O_{7.5}(OH)_{1.5})\cdot H_2O + 2KOH$
(2)

The above reaction, which proceeds via a transitional compound (not shown), results in the precipitation of hydrogarnet and CSH phases (calcium-silicate-hydroxide). Even though the authors describe this as a mineral-mineral replacement reaction, they did not present evidence for pseudomorphic replacement of the feldspar, which is one of the defining characteristics of a true mineral-mineral replacement reaction (see review in Putnis 2009, see also, e.g., Harlov et al. 2002; Putnis and Mezger 2004; Putnis et al. 2005; Kasioptas et al. 2008). Thus, it would be more accurate to describe the overall reaction (Eq. 2) in terms of congruent dissolution of the K-feldspar, followed by precipitation of secondary silicate phases from a chemically saturated bulk solution. Other similar studies also support this type of process (Skorina and Allanore 2015; Su et al. 2015; Liu et al. 2018, 2019).

A study by Ciceri et al. (2017a) used ultrapotassic syenite, an intrusive igneous rock with a very high K-feldspar content, and poor in quartz. This material was subjected to 5 hours of alteration at 200 °C in a $Ca(OH)_2$ solution. Based on chemical mapping and point analyses by electron probe microanalysis (EPMA) of the reacted powder (thin section-mounted), Ciceri et al. (2017a) propose that the original K-feldspar framework undergoes structural and chemical changes, and envision an OH^- mediated dissolution of the feldspar framework, accompanied by Ca-K exchange. They state that "no single grain of K-feldspar preserved its original composition", and go on to describe an amorphous phase composed in part by "severely altered K-feldspar". This terminology is rather ambiguous, in particular as to whether such a phase, from a strict mineralogical-crystallographic point of view, can still be considered to be a true feldspar. The invoked Ca-K exchange, however, falls within the framework of traditional leached layer theory (Hellmann et al. 1990; Hellmann, 1999a,b, see also reviews and references in Hellmann et al. 2003, 2012, 2015). In this case, interdiffusion ultimately controls preferential loss of K^+ from the structure and concomitant replacement by Ca^{2+} from the solution. The mechanism proposed by Ciceri et al. (2017a), however, can be questioned on a theoretical basis since it involves an ultraslow process (i.e., solid-state diffusion at 200 °C) and an exchange couple (K^+ and Ca^{2+}) involving cations with significantly different ionic radii and valence. These authors also propose other possible mechanisms, including both mechanical and chemical, to explain Ca enrichment (see electronic supplementary file, Ciceri et al., 2017a). A final comment concerns their use of EPMA. Although this technique has superior detection limits compared to TEM-EDXS and EFTEM, it has a much larger beam footprint, which means that the spatial resolution is not optimally suited for determining the mechanism of dissolution.

2 Material and methods

2.1 Sample preparation and characterization

Five different orthoclase samples were collected from 2 outcrops of a late Jurassic porphyritic felsite (an igneous rock with phenocrysts of orthoclase in a feldspathic matrix; also called orthophyre in older literature) near the cities of Xinghe and Chifeng, Inner Mongolia, China. The geological ages and emplacement histories of both felsites are very similar. These rocks were specifically chosen for their high alkali feldspar content, which in turn, makes them interesting candidates for hydrothermal K-extraction studies. This is the principal reason more common alkali feldspar-bearing rock types, like granite, were not chosen for this study.

The samples were dry crushed and ground in an agate mortar. Orthoclase grains were isolated by optical microscopy and heavy liquid separation, and then sieved, with the size fraction < 74 μm being used for the alteration experiments. The specific surface area of each powder was determined by N_2-BET analysis. Representative secondary electron SEM images of grains comprising the starting materials (size fraction < 74 μm) for all 5 orthoclase samples are shown in the electronic Supplemental Material appendix: Figs. S1a-e. As revealed by the SEM images, the large grains have a blocky morphology, and show well developed cleavage planes. They do not appear to show any extensive fracturing as a result of comminution. A few of the large grains have μm-sized internal void spaces, e.g., Fig. S1b. Based solely on an evaluation of the SEM images, these feldspars do not appear to have undergone any seritization or argillization reactions. The distribution of grain sizes is very heterogeneous, which is an expected finding for the preparation techniques used. No attempt was made to remove the abundant surface fines created during mechanical diminution of the grains.

It is widely recognized that feldspar microstructures play an important role in chemical weathering behavior and laboratory-measured dissolution rates. This has been documented for natural and experimentally weathered alkali feldspars in studies by, e.g., Lee and Parsons, 1995; Lee et al., 1998; see also references therein. The effect of microstructures on laboratory K-feldspar dissolution at alkaline hydrothermal conditions has been reported by, e.g., Locati et al., 2010, and more recently in a detailed study by Ciceri et al., 2017b. Dislocations and exsolution lamellae create localized regions of higher strain, which cause these crystallographically perturbed areas to dissolve significantly faster than the unstrained mineral structure. In this study, however, a detailed microstructural analysis of the raw alkali feldspar samples was not an immediate goal, as we were not attempting to measure the kinetics of dissolution, but rather the intrinsic mechanism of dissolution at the nanometer scale in interfacial areas that were not affected by dislocations or exsolution lamellae.

Powder X-ray diffraction (XRD) confirmed that these 5 samples are orthoclase; the individual diffraction patterns are shown in Fig. S2. In addition, XRD and Rietveld structure refinement were used to determine semi-quantitative differences in Al/Si ordering. Diffraction patterns were collected using a Pananalytical X'Pert Pro diffractometer using CuKα radiation at 40 kV and 40 mA, with a 0.0167° step size over a 2θ range of 10-90°. Rietveld structure refinements of the XRD patterns reveal that differences in structural ordering (i.e., determined in terms of Al occupancy of t_1 tetrahedral site) between the samples can be considered to be minor- an example of a Rietveld refinement of unaltered orthoclase sample CHG-2- is shown in Fig. S3.

The mean chemical compositions and nominal chemical formulae of all 5 unaltered samples, determined by X-ray fluorescence, are given in Table 1. A standard sample preparation protocol was followed, and analyses were carried out using a Shimadzu 1500 XRF spectrometer. The compositional analyses are based on 8 O atoms per formula unit, and the sum of the total cation charges (15.98-16.02) equals the total anion charge based on O.

2.2 Hydrothermal alteration

The 5 orthoclase samples (Table 1) were reacted in separate experiments. This allowed us to measure the physical, structural and chemical changes that characterize typical post-reaction feldspar-fluid interfaces at the nm-scale on grains from each sample. We deemed that this approach might be scientifically more interesting, as compared to running 5 replicates using just a single orthoclase sample. The experimental protocol that we used here has been adapted from standard methods that have been reported in other studies focused on the hydrothermal extraction of K from alkali feldspars in an alkaline medium (Su et al, 2015; Liu et al., 2015; Ciceri et al., 2017a). The use of $Ca(OH)_2$ in this study as a base was deliberate so as to avoid the common ion effect that would be associated with KOH, and to a lesser extent, NaOH.

At the start of each experiment 1 g of orthoclase grains was mixed with 1 g of fresh CaO reagent, after which 10 ml of ultrapure water were added. Given the hydrophilic nature of CaO, it is assumed that an unknown amount of the oxide reacted with atmospheric humidity to yield $Ca(OH)_2$ during the setup of each experiment. The $pH_{(25\ °C)}$ of the starting solution before the orthoclase was added was 12.3-12.5. The admixture was stirred for 5 minutes before being sealed in a 100 mL stainless steel autoclave with a teflon liner. No degassing of the solution was carried out- therefore a non-quantified amount of dissolved CO_2 was a component of the aqueous solution. The sealed autoclave was placed into an oven pre-heated to 190 °C and left for 24 h at this temperature. The autoclave was then cooled down to ambient temperature over a period of ~6 h, opened, and then heated again to 105 °C for 12 h in order to drive off any remaining fluid. The retrieved solid cake was then reground by mortar and pestle to a size fraction < 74 μm. The reground, altered material (hereafter 'hydrothermal product') served as the basis for further solid-state analyses. The entire hydrothermal alteration process and the associated analyses are schematically shown in Fig. 1. We note that one sample was reacted in duplicate, producing sample CSY-1C-a. The experimental protocol was identical, except that the second heating step at 105 °C was omitted since no liquid remained after the primary hydrothermal reaction step at 190 °C.

2.3 BET and XRD of reaction products

The specific surface areas of the fresh and altered powders (< 74 μm size fraction) were measured by N_2-BET analyses using a Belsorp-Max volumetric gas sorption instrument. The samples were first outgassed at 150 °C for 6 h under vacuum. The specific surface areas of powdered samples are based on the Brunauer–Emmet–Teller (BET) equation ($0.05 \leq P/P_0 \leq 0.2$) using 16.2 $Å^2$ as the cross-sectional area of N_2. The average surface area of the 4 starting materials is 3.4 m^2g^{-1}, while the altered average is 12.6 m^2g^{-1} (Table 2). Thus, the average surface area increased by half an order of magnitude due to alteration. As shown further on, the precipitation of an amalgam of very small secondary phases explains this finding; this has also been confirmed in other similar studies. For example, using a particle size distribution analysis of unreacted and reacted materials, Ciceri et al. (2017a- Fig. 6) noted a significant shift to smaller particle sizes upon alteration, reflected both in terms of particle volume % and particle number %.

Although the identification and detailed characterization of the crystalline authigenic phases produced in the experiments were not the goal of this study, their presence cannot be neglected since they occur within the interfacial region of the reacted feldspar grains, which was the main region of interest. For this reason, we measured K concentrations associated with these secondary phases, as this allowed us to qualitatively follow the fate of released K from the orthoclase. Below we describe the standard X-ray powder diffraction (XRD) techniques that were employed to identify the crystalline mineral phases present in the hydrothermal product- these are discussed further on in Section 3.1

The reacted samples were ground using a McCrone micronising mill to produce a size fraction < 1 μm. XRD analyses were run using a Bruker D5000 powder diffractometer equipped with a SolX Si (Li) solid state detector (Baltic Scientific Instruments) using CuKα radiation at 40 kV and 40 mA. Diffraction intensities were recorded at 0.026° 2θ-step intervals from 5 to 90° (5 s counting time per step) for bulk mineralogy determination. The identification of secondary mineral products by X-ray diffraction (XRD) was based on matching the measured diffraction spectra with the ICDD powder diffraction file database for phases that commonly occur when silicates are chemically altered at alkaline hydrothermal conditions.

The Rietveld refinement method was then used to quantify the phases in terms of mass % (we prefer this term vs. weight %). The generally accepted quantification limit is 1 mass %, although this can be lower (~ 0.5) for phases with non-convoluted peaks. We used the code Profex (Döbelin and Kleeberg, 2015), which is a graphical user interface for Rietveld refinement of powder XRD data using the program BGMN (Bergmann, 2005). In general, when the Rietveld refinement indicated that a selected phase was present at < 1 mass %, this phase was then purposely deleted from further refinements- this served to restrict the number of phases used for fitting.

The percentage of amorphous component in one sample (CSY-1C-a) was determined using a standard method, Rietveld quantitative amorphous content analysis (de la Torre et al., 2001). This method is based on measuring the XRD pattern of the hydrothermal product before and after the addition of a known, precise quantity of an internal crystalline standard. While many standards can be employed, we used pure corundum (Al_2O_3; Alfa Aesar, #42573 α phase). The sample-internal standard mixture, containing exactly 30.4 mass % Al_2O_3, was mixed and homogenized in the presence of ethanol using a McCrone mill. As already noted above, sample CSY-1C-a underwent the same hydrothermal alteration as CSY-1C, except that the heat treatment step at 105 °C was omitted. In general, XRD cannot distinguish between a discrete amorphous phase and nano-crystalline or poorly crystalline material. Therefore, the amorphous material quantified by XRD-Rietveld refinement in this study includes discreet amorphous phases, as well as nanocrystalline and poorly crystalline material dispersed among the secondary phases comprising the hydrothermal product.

2.4 Resin impregnation

After hydrothermal alteration the reacted orthoclase powders were embedded in a liquid C-based epoxy resin (Struers) that was allowed to harden in a mold. The dried mounts were then polished on SiC-coated disks in the presence of ultrapure water, finishing with a polish using a 5.0-µm granulometry. This methodology provided us with embedded cross sections of randomly oriented mineral grains and their alteration products. Even though brief contact with ultrapure water was unavoidable during polishing, the resin impregnated the secondary products, thereby protecting them from reaction with water. We also note that despite polishing, not all primary feldspar grains were flush with the surfaces of the mounts. Numerous grains remained slightly below the polished surfaces, which allowed secondary precipitated phases to be preserved in their native configuration on the grain surfaces.

For example, in Fig. 2b, note the presence of ‘free standing’ scalenohedral calcite crystals on top of the orthoclase grain. The lack of any visible signs of chemical corrosion, in particular with respect to soluble secondary phases like calcite, support the premise that the protocol we used was not deleterious. The remaining primary K-feldspar grains also did not display any evidence of additional dissolution (e.g. etch pits) from the polishing step. This is perhaps expected, as feldspars in general are quite robust minerals, and are not very reactive in pure water at ambient temperature. All samples were carbon sputter coated before analysis by FESEM (C-coat thickness was a few tens of nm).

2.5 FESEM

Even though the main analytical technique for this study was TEM, we also used scanning electron microscopy (SEM) to obtain images at the µm-scale. This allowed us to obtain an overall large-scale picture of the nature of the reacted feldspar grains. The secondary precipitates form a ‘reaction rim’ around each grain. Because the objective of our study was a detailed investigation of the orthoclase-fluid interface, we deemed it logical to also include these secondary precipitates in our measurements and observations at both the µm and nm scales.

The polished mounts from all 5 experiments were extensively investigated. Individual orthoclase grains and their rims of hydrothermally altered products were imaged with a high-resolution field emission scanning electron microscope (FESEM): Zeiss Ultra Plus (PISA Facility- GFZ Potsdam). The acceleration voltage was 20 kV, with a 120-µm aperture. The use of standard detectors allowed imaging of backscattered (BSE) and secondary electrons (SE). Chemical maps and spectra were measured by energy dispersive X-ray spectroscopy (EDXS). The FESEM is equipped with a Thermo Fisher Scientific UltraDry SDD EDX detector. The chemical spectra are based on standard *K*-lines for all elements of interest (Si, Al, O, K, Na, Ca, C). We examined the orthoclase samples by FESEM imagery, EDXS spot analyses (ZAF-corrected), and chemical maps (based on raw net counts with background subtraction). The ZAF-corrected elemental counts can be considered to be semi-quantitative. Analyses of carbon in particular are problematical because of the unavoidable contributions from the epoxy resin to the total C signal, and to a much lesser extent, from the carbon sputter coating. This resulted in probable overestimations of C in carbon-bearing secondary phases, in particular calcite that precipitated within the amalgam of secondary phases.

2.6 FIB

Using focused ion beam (FIB) preparation, electron transparent ultra-thin sections were extracted from selected grains embedded in polished sections. Two samples of resin-embedded altered orthoclase

(CSY-1C and CSY-3C) were investigated at the nanometer-scale by TEM. With respect to sample CSY-1C, two FIB lamellae were fabricated at different locations on the same grain that was previously observed by FESEM. For CSY-3C, one FIB lamella was produced from a grain that had also been investigated by FESEM. The FIB thin sections were prepared with a FEI Helios G4 UC Dual Beam (SEM-FIB) instrument housed at GFZ. In general, the FIB lamellae were milled from vertical cuts on polished grain surfaces. For each lamella, a large primary orthoclase grain was selected, and the milling location was chosen so as to include the interface between the grain and the adjacent lateral alteration rind composed of secondary precipitates.

The FIB protocol can be very briefly summarized as follows. After the deposition of a Pt strap at the chosen area on a polished grain surface, milling with a Ga beam proceeds at an accelerating voltage of 30 kV and a beam current of 47 nA, which is later on decreased to 9 nA. After the lamella is cut free from the matrix, it is transferred in situ to a Cu TEM grid, where it is welded to one of the grid posts. Once firmly attached, additional thinning takes place with a 30 kV, 41 pA Ga beam. Progressive thinning is achieved by steadily decreasing the voltage, such that in the final step, the voltage is reduced to 5 kV. The final step ensures that much of the lateral-edge amorphous material created during milling is effectively removed. The final result is an electron transparent ultrathin section with typical dimensions of 15-20 µm (length) x 5-10 µm (height) x 150-200 nm (thickness). A more detailed description of the procedure that we used can be found in Wirth (2009). Even though not available to us at the time, as a final step it is generally advisable to remove implanted Ga from FIB lamellae using an Ar ion nano-milling technique (see, e.g., Supplemental Information in Leonard and Hellmann, 2017).

2.7.1 TEM: FEI Tecnai

The vast majority of the transmission electron microscopy work was carried out on a FEI Tecnai G2 F20 X-twin FEG TEM operating at 200 kV (GFZ). This TEM is equipped with standard BF (bright field), DF (dark field) and STEM-HAADF (scanning TEM-high angle annular dark field) detectors, a post-column Gatan Tridiem energy analyzer for EFTEM (energy filtered TEM) and EELS (electron energy-loss spectroscopy), and an EDAX energy dispersive X-ray spectrometer equipped with a Si-Li detector. We did not attempt to determine complete chemical compositions at specific locations by EDXS spot analyses- this normally requires separate analysis of external standards. Instead, we scanned the electron beam within a pre-selected area (whose size was dependent on the object being analyzed), and then quantified the chemistry using three elemental atomic ratios: Al/Si, K/Si, and Ca/Si (Table 3). As a first approximation, we assumed that the ‘thin-film’ criterion holds, which means that X-ray absorbance and secondary fluorescence effects are ignored. The Cliff-Lorimer method (Cliff and

Lorimer, 1975), based on k_{AB} factors, was used to determine atom % of Al, Si, K, and Ca, allowing Al/Si, K/Si, and Ca/Si ratios to be determined. For these elements, the built-in EDAX software standardless k_{AB} factors were considered to be sufficiently accurate; however, this was not true for O. Due to Ga implantation into the lamella during the FIB fabrication process, we did not attempt to quantify Na by deconvoluting overlapping Ga *L* and Na *K* peaks in EDXS spectra.

In several instances, we recorded selected area EELS spectra of the C *K* and the Ca $L_{2,3}$ edges (in EELS spectrum mode) of prominent bands that parallel the orthoclase interface. In each case, the EELS background was fit with a standard polynomial function and subtracted from the spectrum using a standard method that is a part of the Gatan® GMS software package. In addition to EELS, we also used EFTEM to provide relatively high spatial resolution chemical maps of certain interfacial regions. EFTEM is an advanced method for obtaining chemical maps of light elements with nanometer-scale spatial resolution (Grogger et al., 2003). The detection limit is generally in the parts per thousand range. The distribution of a chosen element can be portrayed either with a 2-window (jump ratio) or a 3-window (chemical map) image. To produce a jump ratio image of a certain element, an appropriate ionization edge is chosen, and two energy-filtered images are made, one before the edge, and one after. The post ionization edge image is then divided by the pre-edge image, and the result is a jump ratio element distribution map. The 3-window map approach is based on obtaining two pre-edge images and one post edge image. The spectral background curve is then calculated, such that the area under the post-edge peak can be determined- this difference is the net core-loss signal, which is proportional to the concentration of the element.

2.7.2 TEM: FEI Themis Titan

The second TEM instrument that we used is a recent aberration-corrected FEI Themis Titan that was operated at 200 kV (Minatec, Grenoble, France). This TEM, with its four Bruker EDX detectors (30 mm^2 x 4; 0.68 radians), allows for very rapid acquisition of chemical maps with much lower beam currents compared to conventional TEM instruments (e.g., Tecnai, GFZ). We typically used beam currents of 200 pA. Because of these technical advantages, this TEM instrument was principally used to obtain high-resolution STEM and EDXS chemical maps of the interfacial regions. Measurements of certain elements, such as K and Na, on the same feldspar interfacial areas with both TEM instruments revealed the inherent advantages of the FEI Themis. It has already been reported that the measurement of accurate K and Na levels in silicates by analytical TEM is difficult due their mobility under an electron beam (van der Pluijm et al., 1988). This phenomenon is particularly prevalent in thinner areas near grain edges. Factors such as probe size and current, sample thickness, and crystallographic orientation have been shown to play important roles. In addition to these factors, the position of the detector with regard to a wedge-shaped sample (most FIB thin foils are in fact wedge-shaped in cross section) directly affects the X-ray absorption distance (Williams and Carter, 2009), which can also influence the EDXS measurements.

The EDXS chemical maps were generated by X-ray intensities measured by the 4 EDX detectors, and are based on measured elemental *K* edge intensities that have not been corrected. Thus, EDXS maps show relative concentrations for each element. On the other hand, quantitative chemical analyses of specific areas were measured with just one of the four detectors, as we selected the detector that offered the best detector-sample geometry in order to reduce as much as possible X-ray absorption effects. Moreover, specific-area chemical compositions have been corrected for X-ray absorption effects according to the iterative ζ (zeta) method described by Watanabe and Williams (Williams and Carter, 2009; Watanabe and Williams, 2006) and implemented using a specific code (Robin, 2017). This method largely surpasses the Cliff-Lorimer (i.e. *k* factor correction) method (Cliff and Lorimer, 1975) and provides a relatively accurate quantification of the chemical composition.

3. Results

3.1 X-ray powder diffraction and Rietveld refinements.

X-ray powder diffraction (XRD) of the five original hydrothermally altered orthoclase samples was used to identify the major (> 0.5 mass %) crystalline phases, followed by Rietveld refinements (Figs. S4a-e) to estimate the approximate mass percentages present. One additional sample, the replicate CSY-1C-a, was similarly analyzed (Fig. S4f). All six diffraction diagrams show a strong central peak (calcite), in conjunction with other distinct smaller peaks and numerous very weak peaks. Fitted backgrounds (Figs. S4a-e) reveal a smooth bump between 20-50° (Cu *K* 2θ), suggesting roughly similar amounts of amorphous material in all 5 samples. The replicate sample (CSY-1C-a, Fig. S4f) was analyzed specifically for its amorphous content, which was determined to be ~16 %. This compares to amorphous components of 18 % (Ciceri et al., 2017a) and 5-30 % (Liu et al., 2019) reported in other studies devoted to alkaline hydrothermal alteration of K-feldspars.

XRD confirms that the conversion of orthoclase did not go to completion in the hydrothermal runs, as the fraction of unaltered orthoclase is significant, 11-21 %. No other feldspar phases were found (> 0.5 mass %), in particular potential secondary authigenic feldspars. In all experiments, the dominant secondary phase that formed is calcite ($CaCO_3$), 35-50 %. A minor amount of the polymorph vaterite formed in only one experiment, CSY-1C-a (1.5 %). Since the orthoclase samples contain only trace amounts of Ca (Table 1), calcite is rather a byproduct of aqueous calcium cations reacting with dissolved atmospheric CO_2 in the CaO-H_2O alkaline solvent, and then precipitating during the course of the experiments.

After calcite, the next most abundant secondary phases are all silicate minerals containing variable amounts of Ca and Al oxides, and including OH and/or H_2O. Crystalline phases with these chemical components also commonly form during cement hydration experiments, which is logical, as alkaline conditions are also prevalent. We thus make use of the CASH and CSH nomenclature from the cement literature to designate in a generalized manner non-stoichiometric calcium ($\underline{C}aO$)-aluminate ($\underline{A}l_2O_3$)-silicate ($\underline{S}iO_2$) hydrate ($O\underline{H}$, H_2O) mineral phases. As described later on, the secondary products that formed are for the most part an amalgam of intergrown and superposed phases, and thus we simply refer to them together as CASH, CSH, and/or carbonate.

The sum of CASH and CSH phases make up between 43.0 and 54.3 % of the final run products, with one outlier (sample CHG-12C) at only 28.4 %. The two replicate experiments (CSY-1C and CSY-1C-a) have very similar values, 52.9 and 52.8 %. Equation 2 describes a possible macroscopic reaction for the formation of these secondary silicate phases. The two most prominent CASH minerals (18-24 %) are the cubic phases hibschite and katoite. Both are hydrated members of the (hydro)grossular garnet series (see note S1): $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$: grossular, $x = 0$; hibschite, $x = 0.2$-1.5; katoite, $x = 1.5$-3.0 (with increasing hydration OH substitutes for SiO_4 groups). The dominant CSH mineral that precipitated is tobermorite 11Å (8-31%), which crystallizes in the orthorhombic system with a fibrous or bladed habit: $Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$. Coupled substitution of $[Al^{3+} + Na^+]$ for Si^{4+} can result in an Al-substituted 11 Å tobermorite. Fitting the tobermorite peak proved to be the most challenging aspect of the Rietveld refinements, and was achieved with an adjustable mixture of micro- and nano-crystalline crystals. Using the Bragg equation we verified that the *d*-spacing was indeed 11 Å for this phase.

During the Rietveld refinements, in order to constrain our results to the major secondary phases present, we purposely excluded phases with concentrations less than 1 mass %. However, this discrimination protocol doesn't imply that these phases did not form, but simply that they precipitated very sparingly, and it was decided not to quantify them further. Thus, the crystalline phases vaterite ($CaCO_3$), bütschliite ($K_2Ca(CO_3)_2$), α-dicalcium silicate hydrate ($Ca_2SiO_3(OH)_2$), kalsilite ($KAlSiO_4$), hydroxycancrinite ($Na_8Al_6Si_6O_{24}(OH)_{1.4}(CO_3)_{0.3}{\cdot}6.35(H_2O)$), belite ($Ca_2SiO_4$), and panunzite ($(K,Na)AlSiO_4$) were excluded from our final results (excepting vaterite in CSY-1C-a). Figure S5 shows the partitioning of the hydrothermal product from the 6 alteration experiments in terms of remaining orthoclase and the major secondary crystalline phases.

In a broad sense, the secondary phases determined in our study are similar to those in other studies that have focused on alkaline hydrothermal extraction of K from alkali feldspars. It is important to note that the exact assemblage of secondary mineral and amorphous phases depends on many variables, and can be a function of different starting materials (alkali feldspar-rich rock vs. alkali feldspar), different polymorphs of alkali feldspar, differences in internal microstructures and Al/Si ordering, solvents with different chemical compositions, i.e., NaOH, KOH, $Ca(OH)_2$, and differences in temperature, run times, water/rock ratios, as well as other experimental variables. Overall, hydrogrossular and tobermorite have been reported to be generally present in other studies, but their proportions are quite variable (Liu et al., 2015, 2018, 2019; Ciceri et al., 2017a). Abundant calcite was also measured in studies by Liu et al., 2015, 2018, 2019. Phases such as α-dicalcium silicate hydrate and panunzite have been documented, but in higher proportions than in our study (Ciceri et al., 2017a; Liu et al., 2018, 2019). Moreover, some studies have found a much different assemblage of secondary minerals (e.g., Su et al., 2015), dominated by kalsilite and hydroxycancrinite, for example. One study has listed as the dominant hydrothermal product phase 'altered' K-feldspar (66.5 %, Fig. 2, Ciceri et al., 2017a), but as already discussed, the meaning of what this 'phase' actually represents is not clear.

3.2 Micrometer-scale images by FESEM and EDXS.

Numerous altered orthoclase grains from all 5 samples were examined in polished cross sections at various scales by field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDXS). Here we describe one representative sample: CSY-1C. Figure 2a is a secondary electron (SE) image of a large primary grain of orthoclase characterized by a prominent 1-2 μm-thick halo of secondary precipitated phases. This type of morphology characterizes orthoclase grains in all samples. The rind of secondary phases (Fig. 2b, location 1) contains both fine-grained material and larger bladed precipitates (probably tobermorite, with some calcite; calcite also formed individual μm-sized scalenohedral and rhombohedral crystals on the polished surface). The three globular entities above the large grain (nos. 2, 3, 4) are estimated to be an amalgam of CASH + CSH phases and calcite, with variable amounts of small orthoclase grains.

The EDXS chemical maps in Fig. 3a-f show the relative concentrations of K, Ca, Si, Al, C, and O at the same grain location (Fig. 2b). Compared to the uniformly high concentration of K in the large orthoclase grain, K is present at significantly lower levels in the alteration halo (rind, no. 1) and in the large globular entity (no. 4), but at relatively higher levels in entity 2, and particular in entity 3. Potassium at locations 1-4 is associated primarily with secondary phases, and to a lesser degree with very small orthoclase grains. The rind (area 1) is particularly enriched in Ca, but nonetheless, also contains Si, Al and O at lesser concentrations. It most likely consists of a mixture of calcite and CASH + CSH phases. Entities 2 and 3 show a relatively good correlation among K, Ca, Si and Al. In contrast, entity 4 is different: enrichment in Ca and O, low Si, and near absence in Al. Aside from a notable C presence in the resin, there are a few C hotspots present in the rind (no. 1), with lesser amounts visible in entities 3 and 4, and the periphery of entity 2 (but lacking in core). The partitioning of the total carbon signal, while heavily weighted to the resin, is of course also attributable to $CaCO_3$ (calcite) precipitates. Even though one would expect a good spatial correspondence between C and Ca, this is not always the case, e.g., in the rind (1). Binary elemental overlay maps (Figs. S6a-c) reinforce the conclusions drawn from the single element maps.

3.3 Nanometer-scale measurements of orthoclase interface by TEM.

3.3.1 Chemistry and structure of feldspar and precipitates

Figure 4a is a HAADF-STEM image of an orthoclase grain (CSY-1C) prepared in cross section by focused ion beam milling (FIB). The white arrows indicate a sharp and distinct interface between the orthoclase and the enveloping alteration halo of secondary precipitates. The precipitates display various types of morphologies, including a single large grain, granular aggregates, bladed crystals, and a probable amorphous phase characterized by a large (~400 nm) pore, abutting the orthoclase grain. The majority of the material in the alteration halo is slightly darker in tone, indicating lesser mass-density compared to the orthoclase. The 8 rectangles indicate the areas that were analyzed by EDXS (Table 3).

Areas 1 and 2 correspond to the nominal composition of orthoclase, with the expected atomic ratios; e.g., K/Si = 0.24 and 0.23 at locations 1 and 2, respectively. In other grain interior locations of this sample, similar K/Si values were recorded, resulting in an average nominal orthoclase K/Si ratio of 0.24-0.25. Curiously, at area 3, which is at the edge of the orthoclase grain, the K/Si ratio is only 0.17, which is significantly lower than the nominal value, and yet the measurement was taken fully within orthoclase. This was found to be the case with many other (but not all) EDXS measurements taken at grain edges, where in some cases, K/Si values are even lower. As detailed further on, this effect is not due to chemical alteration and leaching of K from the orthoclase, but is rather an analytical artifact. The Ca/Si ratios measured at areas 1-3 reveal that at the scale of the analyses and the analytical resolution of these particular TEM-EDXS measurements, there is no evidence for Ca entering into the orthoclase structure. Based on morphology and chemical composition, areas 6 and 8 most likely correspond to an amalgam of hydrogrossular and tobermorite phases. The phases represented by areas 4, 5, and 7 are difficult to identify, but based on chemistry and morphology, 7 may be Al-tobermorite. The large pore and low mass-density suggest that area 4 is amorphous. This area is located in what appears to be a discreet phase with low mass-density that directly abuts the orthoclase edge. Area 5 has elevated K/Si and Al/Si ratios, and a Ca/Si ratio indicating minor Ca enrichment- this phase is not identifiable, however. Notwithstanding the tenuous identification of the secondary phases, they all contain K, and in one case (area 5), a K/Si value of 0.30 is measured (i.e., compare to nominal unaltered orthoclase value of 0.22).

The HAADF-STEM image in Fig. 4b shows a cross-sectional view of a primary orthoclase grain (CSY-3C), also with a sharp boundary between orthoclase and secondary precipitates. Four areas were measured by EDXS analyses (Table 3). The chemistry of area 9 has elevated K levels, and may represent a mixture of Al-tobermorite with other phases (i.e. measured Ca/Si = 1.11). Area 10 is likely a resin-filled pore primarily composed of C and O, but K, Ca, Al, Si are measurable in the spectra, which is possibly attributable to the presence of nano-precipitates that are not visible in the image. The presence of a 60-nm thick continuous band of precipitate in close proximity to the orthoclase sets this image apart from previous examples. The EDXS spectrum reveals (area 11) a very high Ca concentration, significant C, the near absence of Si and Al, and elevated K- it is therefore most likely calcite, but in the presence of a minor phase(s) containing K. We can at this point only speculate that the elevated K concentrations might be due to the presence of K-bearing nanoparticles, or possibly even a K-rich carbonate phase, such as K_2CO_3 (formed via one possible reaction: KOH + $CO_{2\ aq}$), or even bütschliite, $K_2Ca(CO_3)_2$. The chemical analyses at area 12 correspond to the composition of unaltered orthoclase, with K/Si = 0.23. Calcium is present at the EDXS detection limit, Ca/Si = 0.0011.

A second HAADF-STEM image of the same interface (CSY-3C), but at a new location, is shown in Fig. 4c (EDXS chemistry of areas 13-16, see Table 3). The band of calcite, while not well defined, is still present, with K/Si = 0.09 (area 14). As already discussed, the measured K and Si most likely indicate the presence of minor amounts of silicate particles. Here the band is separated from the orthoclase by a precipitate (area 13) with pores having dimensions of several tens of nm (pores appear as black entities). The presence of numerous pores and the general morphology, the low mass-density, and a chemical composition inconsistent with any of the phases identified by XRD (Fig. 2), suggest that this may be an amorphous phase, perhaps similar to the one described in Fig. 4a. Areas 15 and 16 have relatively similar Al/Si and Ca/Si chemistries, and may be an amalgam of crystalline and amorphous material. Their K/Si ratios are very different, however, which at area 15 is 0.60. This elevated ratio cannot be attributed to a very low concentration of Si, given that the Si counts are the same in area 16. Whether there is any calcite in this region is not known. Figure 4c also shows the omnipresence of white-colored nm-sized precipitates. Further along the same interface, 4 more areas were characterized (areas 17-20, Table 3; TEM image in Fig. S7). Area 17, which is within another thin band of (possibly amorphous) precipitate in close proximity to the orthoclase, also has an elevated K/Si ratio = 0.19. Taken together (Figs. 4a-c, Fig. S7), these findings reveal that certain secondary phases, both crystalline and amorphous, are associated with significant levels of K.

3.3.2 Calcite in interfacial region

The intermediate resolution bright field (BF) TEM image in Fig. 5a (CSY-3C) displays another example of a continuous ~60 nm-wide linear band of calcite that runs parallel to the orthoclase interface. In BF imaging, calcite is easily distinguished by its mottled appearance. The calcite band does not touch the orthoclase, but rather occurs within an aggregate of precipitated phases characterized by bladed crystals (likely tobermorite), a large granular globule (demarcated by 3 open-ended arrows), and a fine-grained matrix between the bladed crystals. The matrix itself contains nm-sized dark grains, which probably correspond to the white grains observed in Fig. 4c. The presence of numerous bubbles (e.g., white globules, next to scale bar) throughout the precipitate most probably indicate trapped water, which would imply that the precipitation rind is significantly hydrated. The external edge of the orthoclase grain appears to end abruptly at a continuous parallel band that may be amorphous (2 white arrows, dashed tails).

To confirm the presence of calcite in the aforementioned bands (Figs. 4b,c, 5a), we recorded selected area EELS spectra of the C *K* and the Ca $L_{2,3}$ edges (in EELS spectrum mode). The deconvolved, background subtracted spectrum (Fig. 5b) of the band delimited by the solid white arrows in Fig. 5a confirms that this is calcite. The spectra show two distinct C *K*-edges, one at 289 eV and the other at 300 eV. These two edges are characteristic for calcium carbonates, and represent two different electronic transitions, the first 1s/π* (C=O) and the second 1s/σ* (C-O) (Martin et al., 1996). The peak maxima for the Ca $L_{2,3}$ peak are at 348 and 351 eV. The C and Ca spectra provide proof that the uniform and continuous bands, as evidenced in Figs. 4b,c and 5a, are crystalline Ca-carbonates. Based on the EELS spectra alone, it is not possible to distinguish between the two polymorphs calcite and vaterite, but the Rietveld refinement for this sample favor the former.

3.3.3 Does Ca enter the orthoclase structure?

To determine the chemical stability of the original orthoclase structure with respect to the Ca-rich solvent during the alteration process, we investigated whether there was evidence for Ca entering the orthoclase structure by interdiffusion, or alternatively, by the replacement of the original orthoclase with a Ca-rich secondary phase, such as anorthite, the Ca-end member plagioclase feldspar ($CaAl_2Si_2O_8$). To explore this question we used energy filtered TEM (EFTEM) imaging, a powerful and yet under-utilized TEM method in mineralogy and geochemistry. Figures 6a, b are complementary images, and both show the same well-defined interface (white arrows) between orthoclase (CSY-1C) and secondary precipitates. The first is a BF TEM image- it shows a complex amalgam of secondary precipitates, including bladed crystals, a fine-grained grey groundmass, calcite (?), nanometer-sized particles, and what appear to be extremely small globules (light grey to white, indicating possible evidence for water). The precipitates terminate abruptly at the orthoclase interface.

Figure 6b is the corresponding Ca $L_{2,3}$ EFTEM 3-window chemical map at slightly lower magnification. The widths of the 3 windows (all equal in energy) and the polynomial function used to fit the spectral background were calculated with Gatan Microscopy Suite (GMS) software. In the Ca map, white regions correspond to elevated Ca concentrations (secondary precipitates), and conversely, black regions indicate a lack of Ca, such as is the case for the Ca-devoid orthoclase structure and resin. Note that the precipitates do not have a uniform white color, which indicates variable Ca levels and/or differences in thickness. Most importantly, the chemical gradient of Ca at the orthoclase-precipitate interface is quite sharp and resembles a step-function change. Therefore, at the spatial/energy resolution of this EFTEM image, there is no evidence for the incorporation of Ca into the orthoclase structure, either by mineral-mineral replacement or by interdiffusion.

The interested reader may question why a potassium EFTEM chemical map is not shown, in particular since K is a good tracer for chemical alteration of the orthoclase structure. The omnipresence of carbon, which makes up the resin, makes this technically very difficult because the K $L_{2,3}$ and the C K ionization edges are nearly at the same energy. Deconvoluting the K and C EEL spectral signatures is technically very difficult, and thus was not attempted. The other major K absorption edges could theoretically be used, but they occur at either too high (K edge at 3607 eV) or too low energy ($M_{2,3}$ edges at 18 eV), such that in practice it would be difficult to extract a quantitative signal to calculate an image.

3.3.4 Advanced STEM-EDX: the effect of electron dose

The K/Si values measured in areas 1-3 in Fig. 4a bring up an important point, as K/Si ratios were often anonymously low at orthoclase grain edges when compared to regions a few hundreds of nm towards the interior of the grain. These elemental concentrations were measured with the Tecnai TEM using a 1 nA probe current (24.9° sample tilt). We therefore proceeded to investigate this in more detail by measuring K/Si values at another close by area on the same orthoclase grain edge with an advanced analytical TEM, the aberration corrected Titan Themis (Minatec). For these measurements we used a significantly smaller probe current of just 200 pA (0° tilt). Numerous measurements close and directly at the interface confirmed that nominal, unaltered orthoclase K/Si values were obtained. Thus, the low K/Si values described above (section 3.3.1, Fig. 4a) are clearly an analytical artifact. This example illustrates the advantages of using a 4-detector EDXS system that allows for very fast X-ray acquisition times using very low beam currents. These results also point out that orthoclase grain edges, perhaps due to a thickness effect, are more prone to alkali diffusion than grain interiors, in particular when too high beam currents are used, or if the acquisition time is too long (refer also to study by van der Pluijm et al., 1988).

Going further, to quantify the importance of the electron dose on K and Na measurements, we measured the EDXS counts of K, Na, Al, and Si on several consecutive, same-sized areas of orthoclase sample CSY-1C as a function of the total electron dose. The measurements were made towards the interior of the grain, and away from the edge. The dose is defined as the number of electrons that impinge upon 1 nm^2 of surface, and is expressed in units of $pA\cdot s\cdot nm^{-2}$. Figure 7 schematically shows the evolution of the stoichiometrically normalized elemental ratios, expressed in terms of Si/3Al, (K+Na)/Al, K/Al, and Na/K. All of the ratios are fitted to discreet linear trends over the entire range of electron doses probed. The linear and constant trend defining Si/3Al indicates that Si and Al are not affected by electron doses inferior to 0.7 $pA\cdot s\cdot nm^{-2}$. The Na/Al trend can be interpreted in terms of a very slight loss of Na with increasing dose in the ‘K, Na loss region’ of Fig. 7. On the other hand, the K/Al and (K+ Na)/Al intensities appear to be roughly constant in the low dose region (< 0.15 $pA\cdot s\cdot nm^{-2}$), but then show a marked linear decrease at higher doses. These results, somewhat surprisingly, indicate that K is much more susceptible to electron dose-induced thermal diffusion compared to Na. Overall, the relations shown in Fig. 7 indicate that TEM-EDX measurements are best done in the ‘no loss’ region corresponding to a total dose < 0.15 $pA\cdot s\cdot nm^{-2}$, in particular for measurements at thinner edge regions. Taken together, these results confirm that the anomalously low K/Si values often measured in areas close to K-feldspar grain edges are most likely due to too high electron doses (e.g., area 3, Fig. 4a).

3.3.5 Advanced STEM-HAADF-EDXS measurements of an interfacial SAL

Using the Themis TEM, we obtained a moderate-resolution STEM-HAADF image of an interfacial region on orthoclase grain CSY-1C (Fig. 8). The vertical dashed line delimits the interface between the orthoclase and a presumably amorphous surface layer (SAL). A relative thickness profile on the STEM-HAADF image, generated by iterative calculations using elemental X-ray intensities (Robin, 2017), reveals that the orthoclase edge region is thinner than the bulk material further away. There are also slight inhomogeneities in the grey tone of the orthoclase: a. the bottom half of the unaltered orthoclase region appears slightly lighter in color, b. numerous small white flecks are present on the orthoclase surface, particularly evident on the right side of Fig. 8a. These inhomogeneities are probably due to minor redeposition (sputtering) of the adjacent amorphous material (SAL) that occurred either during FIB milling, or EDXS analyses. The amorphous material is probably composed of a 'soft' gel-like material that is easily prone to electron or ion beam sputtering.

Figure 8 also shows normalized chemical profiles that were determined along the same trace used for the thickness profile. The K/Al profile is characterized by a nm-sharp, step function-like jump at the interface between the orthoclase grain edge and the abutting amorphous phase. The behavior of the K/Al ratio as it transitions from orthoclase to the amorphous phase (SAL) is due to the combined effects of a sharp increase in K concentrations and a concomitant decrease in Al. In contrast, the Na/Al ratio remains roughly constant in both phases. The profile of Si/3Al is relatively constant, with a value near 1.0 within the orthoclase. As the profile passes into the SAL, the ratio exhibits more variability, but remains close to an average of 1.0 over a distance of 0 to -30 nm. At distances < -30 nm the ratio shows a monotonic but fluctuating increase to a value of ~1.7. The fluctuations may be due to pores or other inhomogeneities in the SAL. The O/8Al profile displays virtually identical behavior to the Si/3Al profile in the orthoclase and over 0-30 nm within the SAL. However, at distances < -30 nm in the SAL, the O/8Al profile surpasses the Si/3Al profile. One interpretation for O/8Al > 1 is the presence of H_2O, indicating hydration of the SAL. The largest positive spikes in the O/8Al profile may in fact correspond to water inclusions. Even without a statistical analysis, there is a surprising correlation between many of the Si/3Al and O/8Al profile peaks in the SAL. One final note concerning the potential redeposition of amorphous material onto the orthoclase surface; there is no effect on the Na/Al, Si/3Al, and O/8Al profiles, and only a very insignificant effect on the K/Al profile within the orthoclase.

The STEM-HAADF image in Fig. 9a is derived from a cropping of Fig. 8a, thereby allowing additional details of the interface to be more clearly shown. This image clearly shows a prominent and sharp vertical interface (white arrows) that marks a sudden transition in both structure and chemistry, which is manifested by a difference in mass-density between the orthoclase (right) and an amorphous SAL (left) with lower mass-density. The even less dense large pores appear black, in particular the bottom most one. The presence of such large pores can be construed as indirect evidence for the amorphous nature of the SAL- note also their morphological resemblance to those in Fig. 4a-c. The origin of the thin vertical band that appears at the external edge region of the orthoclase is not understood, but it may be an artifact.

Figure 9b is a superposition of K, Ca, and Si EDXS maps onto the STEM-HAADF image, after a 'smooth' filter was applied. The corresponding individual elemental (Ca, K, Al, Si) EDXS maps, which have also been superposed on the same STEM-HAADF image, are shown in Fig. 9c. The individual concentrations (i.e. colors) in the latter maps are based on non-background corrected raw counts (background counts were negligible). The Al and Si maps reveal that the orthoclase-SAL chemical interface is extremely sharp at the nm-scale, due to step function-like drops in their respective concentrations in the SAL. The interface on the K map is less obvious, mainly because the concentration gradient across the boundary is much less important, in particular at the interface in the upper part of Fig. 9c. Calcium is distributed exclusively, but inhomogeneously, in the SAL. Calcium concentrations are highest further away from the orthoclase interface, with lower levels present in the 70-nm thick part of the SAL abutting the orthoclase. Note that the presence of tiny red-colored flecks on the orthoclase surface is an artifact due to redeposition, and is not representative of any penetration of Ca into the orthoclase structure (see previous discussion above).

The superposition of several elemental maps shown in Fig. 9b affords a multi-element view of the sharp orthoclase-SAL interface, as well as how Ca, K, and Si are spatially co-distributed in the SAL. As was the case in Fig. 9c, the chemical interface is spatially coincident with the mass-density interface in Fig. 9a. The vertically oriented chemical interface between the unaltered orthoclase grain (blue, right side) and the secondary precipitate (green and red, left side) is indicated by the white arrows. The orthoclase does not have a homogeneous blue color, as indicated by the presence of green patches in the lower half of the image- the possible reasons for this are discussed directly above. The transition from orthoclase to SAL (i.e., blue to green) is in particular characterized by a sharp decrease in Si and concomitant moderate increase in K. The SAL adjacent and to the left of the orthoclase interface is characterized in particular by high levels of K (vivid green color), while further away (> ~70 nm) it is enriched in Ca. Nonetheless, the distribution of red flecks within green, K-rich region indicates that Ca is distributed throughout the SAL, even where it abuts the orthoclase interface. The decrease in K concentrations roughly 70 nm distant from the interface corresponds to the predominance of the vivid red color at the far left of the image, indicating higher Ca concentrations. The limit between K-rich and Ca-rich regions in the SAL is irregular and not abrupt. Given the elevated Ca concentrations it is possible that amorphous or nanocrystalline calcium carbonate is a component of SAL. In general, the SAL also contains Si (and Al- see Fig. 9c), but at lower levels compared to the orthoclase (Si appears as dark blue-purple within the SAL). We also remark that it is likely that the SAL is water-enriched, but that quantification of H is not possible by EDXS.

The most significant finding here is the presence of this ~70-nm wide K-enriched SAL that directly contacts the orthoclase interface (note that the full thickness of the SAL is > 70 nm). To better compare the overall chemistry of these adjacent phases, quantitative EDXS measurements of K, Al, Si and O concentrations (X-ray absorption-corrected) were first made within the orthoclase (i.e. in the blue-colored area to the right of the interface, Fig. 9b)- these yielded the nominal composition of unaltered orthoclase, thereby indicating that the orthoclase retained its composition during alteration. Calcium levels were below the analytical limit, evidence that Ca substitution or replacement of the orthoclase structure did not occur. The same type of quantitative, X-ray absorption-corrected EDXS measurement of the chemical composition of the SAL was effected in the rectangular area in Fig. 8b. The results are given below and in Table 3 in atom % (atom % is preferred over weight % since atomic ratios can be immediately compared to values derived from Table 1):

C = 6.5
Na = 0.74
Ca = 5.13
K = 11.41
Si = 15.94
Al = 4.81
O = 55.45

The chemical composition of the analyzed area confirms that the amorphous phase is very rich in K, with a concentration significantly greater than that in the proximal unaltered orthoclase (i.e. XRF-derived $[\mathrm{K}_{\mathrm{orthoclase\ CSY\text{-}1}}]$ is 5.2 atom % - see Table 1). We note that the concentrations of Al and Si in the SAL are 3 and 7 atom % less, respectively, than their XRF-measured concentrations in orthoclase sample CSY-1 (Table 1). The average spectrum (not shown) corresponding to the rectangular area reveals that the C *K* peak is convoluted with the K and Ca *L* peak; thus, the error in the quantitative estimate for C (~10 %) is higher than for the other elements: Si, Al, K, Na, Ca, and O (~6 %).

3.3.6 Atomic resolution imaging of orthoclase-SAL interface

Numerous high-resolution TEM (HRTEM) images of the interfacial region (CSY-1C and CSY-3C) always show a near-atomically sharp and relatively linear structural interface. Figure 10 is a typical example of such an interface (white arrows)- the high-resolution image stems from an interface close to that in Fig. 9. In this particular area, the amorphous layer is many tens of nm thick. Here one can see lattice fringes terminating abruptly at the amorphous secondary precipitate. However, in some regions of the interface, the fringes are blurry and appear to extend beyond the interface into the amorphous phase. There are two possible reasons for this: a delocalization effect, or more probably, a highly inclined (oblique) and/or non-planar, irregular interface. It should be remembered that the interface has a considerable thickness, at least on the order of ~150 nm, which is the approximate thickness of the FIB lamella. It is to be expected that over such a distance the interface will not be perfectly planar and vertical. The non-crystallinity of the amorphous layer was verified by fast Fourier transform (FFT).

4. Discussion of dissolution mechanism

Our results show the ubiquitous presence of a continuous layer of amorphous material abutting primary orthoclase grains. This SAL is variable in thickness, ranging from under ten nm to approximately 200 nm. When imaged at moderate to high resolution, the structural interface between the orthoclase and the SAL is sharp at the 1-2 nm scale, and is spatially coincident with a very abrupt chemical boundary characterized by distinct decreases in Al and Si. The interface is also characterized by important concentrations of Ca on the SAL side, and its virtual absence on the orthoclase side. Very importantly, the SAL also contains variable and elevated concentrations of K. Our nm-scale measurements point to a first-time observed K-rich authigenic phase that forms directly and in situ at the receding interface of orthoclase during dissolution at alkaline conditions. This amorphous SAL is by far a more significant reservoir of K than hitherto measured in previous studies.

In section 3.1 we report that one sample has a moderate amorphous content of ~16 mass % (sample CSY-1C-a). Based on this measurement, we speculate that discreet amorphous phases also formed elsewhere in the hydrothermal product, in particular within the amalgam of secondary authigenic phases. We did not characterize these potential occurrences of amorphous material, as our investigation was restricted to the interfacial region of orthoclase grains. As far as we know, the only comparable analysis of an amorphous phase produced during alkaline alteration of a K-feldspar can be found in Ciceri et al. (2017a). Their study revealed the presence of amorphous grains that contain on average 3.6 wt % K.

During chemical alteration the original orthoclase grains dissolve and decrease in volume and mass, but at the nanometer to micron scale, the remaining orthoclase grain cores do not show evidence for chemical alteration, as they retain their nominal, bulk chemical composition (section 3.3.5), even at grain edges (Figs. 8, 9). In addition, all grain edges are characterized by sharp structural reaction interfaces, as evidenced by orthoclase lattice fringes terminating abruptly at the boundary with the SAL (Fig. 10). These two observations are evidence that dissolution is congruent (i.e. stoichiometric) and proceeds via a sharp reaction front that consumes the parent orthoclase structure.

One immediate question that comes to mind is why K^+, a labile cation, was not preferentially leached from the orthoclase structure during alteration, thereby leading to the formation of K-deficient leached layers? This traditional idea of leached layer formation during dissolution can be dismissed for many reasons. First, the replacement of K^+ by H^+ (or H_3O^+) from the solution can be discounted because the concentration of H^+ in the solvent is vanishingly small in a strong alkaline solution with very high pH. This would render such an exchange process improbable. Moreover, leached layer formation is controlled by interdiffusion (e.g., Hellmann et al., 2012; and references therein), and such a solid-state process is orders of magnitude too slow at the 190 °C temperature of the experiments. And finally, replacement of K^+ by H^+ would be incompatible with the orthoclase structure. Note that there is no evidence of a change in lattice fringe spacing at the orthoclase edge in Fig., 10.

A second question we can ask is why K-Ca exchange did not occur, such as postulated by Ciceri et al. (2017a). This would entail the preferential loss of K^+ from the orthoclase structure, coupled to an interdiffusion-controlled substitution by Ca^{2+} ions from the solvent, leading to the in situ formation of a Ca-rich plagioclase phase. A diffusion-controlled mineral replacement process would require evidence for anti-correlated and sigmoidal interdiffusion-coupled Ca-K profiles (see, e.g. Hellmann et al., 2012). Chemical analyses and nm-scale chemical mapping of the orthoclase interfacial region (Figs. 6, 9), however, show no evidence for the penetration of Ca into the orthoclase structure. In addition to this, an exchange process is theoretically difficult to envision due to the substantial size difference between univalent K^+ and divalent Ca^{2+}. Moreover, the formation of Ca-plagioclase reaction rind ($KAlSi_3O_8 \rightarrow CaAl_2Si_2O_8$) would also require a net addition of Al and a loss of Si to the original orthoclase structure. Again, we see no evidence for a gain of Al and loss of Si in the orthoclase structure, in particular at grain edges (Figs. 8, 9). As briefly mentioned above, a solid-state diffusive process at 190°C is simply too slow to render such a change in chemistry over the 24 h time span of these experiments. It should be remembered that solid-state diffusional processes are exceedingly slow compared to chemical reactions such as dissolution and/or precipitation below ~500 °C (see, e.g., Villa, 2016). In fact, in nature the solubility of Ca in K-feldspar at low temperatures is insignificant- only at higher temperatures can minor amounts of Ca be incorporated into K-feldspar structures. This explains why, in fact, the unaltered K-feldspars used in this study contain only trace amounts of Ca (Table 1).

The results we present strongly support a different mechanism that controls the hydrothermal alkaline alteration of K-feldspar, and stands in opposition to nearly all previous studies in this field. As elucidated in the Introduction (section 1.3), the prevailing opinion is that alteration of alkali feldspars occurs either by congruent dissolution, or by preferential leaching of K and replacement by another charge-compensating cation from solution. Our experimental results concur with the process of congruent dissolution, which in turn is accompanied by precipitation of predominantly crystalline secondary phases (calcite, hydrogrossular, tobermorite) from an oversaturated bulk solution. Where our interpretation differs from nearly all other studies (at alkaline pH conditions) is that we have measured the in situ formation of a significant amorphous phase that forms directly at the interface and at the expense of the dissolving orthoclase structure. We postulate that this amorphous SAL starts to form right at the onset of contact with the solvent fluid, and continues to form as the feldspar interface continuously recedes during dissolution. The interfacial process we are proposing represents a physically plausible process that concurs with our nm-scale observations and measurements. We refer to this process as coupled interfacial dissolution-reprecipitation, or CIDR (Hellmann et al., 2003, 2012, 2015). As discussed further on, this is a relatively new theory, and has been the subject of other chemical alteration studies concerning both silicate minerals and glasses. This same mechanism has also been applied to pseudomorphic mineral-mineral replacement reactions, where it has been referred to as interfacial-coupled dissolution-(re)precipitation, or ICDP (Putnis, 2002; Putnis et al., 2005; Geisler et al., 2005; and references therein).

Based on our finding of an abrupt and spatially coincident chemical and structural discontinuity at the interface between the edge of the orthoclase structure and the amorphous SAL, we advocate the CIDR mechanism (O'Neil and Taylor, 1967; Buck et al., 2000; Hellmann et al., 2003, 2012, 2015; Putnis, 2002, 2009). This mechanism is based on the advance of a sharp chemical reaction front into the unaltered parent phase, with stoichiometric dissolution occurring within a thin fluid film (O'Neil and Taylor, 1967) of ordered solvent molecules (Thomä et al., 2019; Parker et al., 2001; Khatib et al., 2016) at the reactive interface (Hellmann et al., 2015). Released elements that are insoluble synchronously reprecipitate at the interface, without first passing into the bulk solution, whereas soluble elements migrate to the bulk solution. The thin fluid film possesses physico-chemical and rheological properties that differ from the bulk fluid (Fenter and Sturchio, 2004; Marry et al., 2008; Knight et al., 2019), and thus reprecipitation of a secondary phase is possible even when the bulk solution is chemically under-saturated with respect to secondary phases (Hellmann et al., 2003, 2012, 2015; Ruiz-Agudo et al., 2012). The tight spatial and temporal coupling of dissolution and reprecipitation within an interfacial fluid film is one of the main characteristics that differentiates CIDR from a classical precipitation process associated with a chemically oversaturated bulk solution.

How and when the amorphous phase formed is a key to understanding the overall dissolution process in our study, and in particular, the mechanism of dissolution. The spatial ordering of the secondary phases shows that the amorphous phase was initially the first phase to form. With increasing reaction progress, secondary crystalline phases started to massively precipitate on top of the amorphous SAL as the bulk fluid became increasingly saturated with solute. The reasons for chemical oversaturation are multiple: dissolution of the orthoclase grains, a steadily decreasing fluid-solid ratio, cooling at the end of the experiment, and finally, evaporation of any remaining fluid during the final heat treatment step. All of these contributed to chemical supersaturation of the bulk solution and the classical precipitation of the secondary crystalline phases. It is interesting to note that the overall morphology of our reacted orthoclase grains, characterized by a relatively thin amorphous SAL overlain by a 1-2 μm thick rind of secondary crystalline phases, has a counterpart in a study of a naturally altered K-feldspar that has a 10 nm-thick amorphous SAL covered by a thick 3-5 μm layer of authigenic smectite (Zhu et al., 2006).

The experimental protocol did not permit us to periodically sample the solution phase, nor retrieve orthoclase grains before the end of each experiment. Nonetheless, we argue that the amorphous phase is not a classical precipitate, but rather formed in situ by CIDR, and its growth was initiated upon contact of the fluid with the orthoclase grains. Based on solubility arguments, if the amorphous phase had been a classical precipitate, it would have formed on top of the less soluble secondary crystalline phases, but the FESEM and TEM images clearly show that this was not the case. In addition, we use experimental data from a previous study (Hellmann, 1995) to further this argument. In that particular study, the release of Na, Al and Si was continuously measured during hydrothermal alteration of albite feldspar in a flow reactor at 200 °C and pH 12 KOH solution- we note that albite and orthoclase have similar structures; in addition, the alteration conditions were very close to those in the present study. While a mechanism describing how the parent solid reacts cannot be deduced solely from aqueous cation release curves, the release curves do show that right from the beginning of the experiment, the aqueous solutions show non-stoichiometry (Hellmann, 1999b), even though the solution was very undersaturated with respect to secondary crystalline phases. This data by itself can be interpreted to mean that a surface interfacial process was continuously operative in the experiment by Hellmann (1995). Going further, the Hellmann data supports our argument that an interfacial process starting right at the onset, and continuing throughout the experiment, resulted in interfacial precipitation of an amorphous SAL. Other studies in the literature concur with this idea, namely those that have measured dissolution in situ. These published experiments, at ambient and hydrothermal conditions, have measured in real time and in situ the initial reaction between silicate minerals and aqueous fluids (Hellmann, 1999a; Hellmann et al., 1992; Putnis et al., 2005; Ruiz-Agudo et al., 2012; Jordan et al., 1999; Fenter et al., 2000; Teng et al., 2001; Leonard and Hellmann, 2017). These studies all show the rapid in situ formation of a surficial gel-like phase that is an amorphous interfacial reprecipitate.

It is interesting to speculate why we did not document a pseudomorphic replacement reaction involving a Ca-rich plagioclase. Feldspar-feldspar replacement reactions in nature and experiment are widely cited (O'Neil and Taylor, 1967; Parsons and Lee, 2009; Parsons et al., 2009; Lee and Parsons, 1997; Labotka et al., 2004; Cole et al., 2004; Engvik et al., 2008; Hövelmann et al., 2010; Norberg et al., 2011; Ruiz-Agudo et al., 2014). Because CIDR is a fluid-assisted alteration process that is thought to occur in a thin interfacial fluid film, it is theoretically possible that a Ca-rich crystalline phase, such as Ca-rich plagioclase (labradorite, anorthite), could have formed at the reactive interface- as the argument of Ca^{+2} and K^{+} incompatibility due to ionic radius and charge, as well as too slow solid-state interdiffusion, would not be relevant. However, in our study, the SAL that formed was amorphous. Given that CIDR is a fluid-mediated chemical alteration mechanism, and not a solid-state process, it should be possible from a strictly theoretical point of view to form a Ca-rich plagioclase phase within the interfacial fluid, provided that the chemical components are present in the correct stoichiometric proportions and concentrations. However, there was no evidence for this having occurred. At this point we can only surmise a few reasons that possibly favored reprecipitation of an amorphous phase: *i.* a too low Ca concentration, *ii.* an extremely basic pH ($12.4_{T=25\,°C}$), *iii.* a too low temperature (190 °C) coupled to a very short time period (24 h). Perhaps over geological periods of time and at much higher temperatures, it may be possible to precipitate a Ca-rich plagioclase phase in the context of a mineral-mineral replacement reaction. Future experiments at higher *T, P* conditions, or over longer time periods, could perhaps answer this question. It is interesting to note that the reverse process, the albitization of plagioclase, has been experimentally documented at 600 °C, 2 kbars in an aqueous Na-silicate solution (Hövelmann et al., 2010).

Many frontier questions on the CIDR mechanism still remain. Since the reprecipitated layer initially forms at the interface, presumably within the extremely thin interfacial fluid film in contact with the parent mineral structure, it remains to be determined whether this fluid film of ordered solvent molecules is continuous, or not. During chemical alteration, the dissolution of the primary phase (orthoclase) is a continuous process, and it is at the ‘inner edge’ of the SAL where new material is precipitated. The chemical stability of the reprecipitated material within the thin fluid film will in large part determine its chemical composition. Although we don’t know what the pH was in the fluid film, it was undoubtedly very basic (close to the value in the bulk fluid), and at such conditions, Si and Al oxides or oxyhydroxides are very soluble. This may explain the lower levels of Al and Si that were measured in the SAL, as compared to their nominal concentrations in orthoclase. Nonetheless, the Si and Al that did precipitate in the layer (i.e., Fig. 9) would likely be in the form of $Si\text{-}O^{-}$ and $Al\text{-}O^{-}$ groups, as these groups predominate at very basic pH conditions. Released K^{+} ions may preferentially adsorb to these negatively charged sites. It nonetheless remains an open question as to why the K concentration in the SAL is so conspicuously elevated. As the amorphous layer grows in thickness over time, the first-formed and older ‘outer edge’ will be in contact with the free bulk fluid, or fluid within pores and channels of any overlying secondary crystalline precipitates that formed. Therefore, the chemical stability of the outer interface of the SAL, which controls its dissolution behavior, will be dictated by the chemical properties of the bulk fluid, and not the thin interfacial fluid film. A more detailed understanding of the composition and exact nature of the amorphous interfacial layer calls for additional research, in particular using other complementary techniques, such as X-ray adsorption or nanoRaman/FTIR. One last question that perhaps deserves further study is whether the amorphous SAL, as well as the enveloping rind of secondary authigenic minerals, eventually hinder, or at least slow down, the kinetics of the orthoclase dissolution reaction. A similar question was also posed by Zhu et al. (2006) concerning their estimation that a naturally weathering Jurassic-aged K-feldspar was dissolving 5 orders of magnitude slower than K-feldspar in far-from-equilibrium laboratory experiments at comparable pH and *T* conditions. They attributed this significant difference to the presence of a 10 nm-thick amorphous SAL, surface-adhering kaolin platelets, and a thick outer rind of authigenic smectite.

5. Conclusions

To extend our thoughts concerning the present study, an interfacial amorphous phase has been documented to form in situ at the expense of orthoclase at strong alkaline conditions. Amorphous SALs have been previously documented to form on feldspars at acid, near-neutral and weak alkaline pH conditions, with pH controlling their thickness. They are significantly thicker at acid pH than those that form at near-neutral and moderate basic pH (Hellmann et al., 2003, 2012; Lee et al., 2007). As discussed in detail in section 1.3, the majority of studies on feldspars from the 1990s and early 2000s postulated that SALs (even when very thin) form by an interdiffusion process, leading to leached layers. Despite the pioneering study of O'Neil and Taylor in 1967, it has only been over the past 20 years that natural and experimental feldspar dissolution studies at acid and near-neutral pH conditions, and in particular amorphous SAL and mineral-mineral replacement reactions, have been conceptually framed within the context of CIDR and CIDR-like mechanisms (e.g., Hellmann et al., 2003, 2012; Lee et al., 2007; Parsons and Lee, 2009; Labotka et al., 2004; Hövelmann et al., 2010; Ruiz-Agudo et al., 2014). A theoretical Monte Carlo approach also supports the CIDR mechanism for plagioclase dissolution mechanisms (Zhang and Lüttge, 2009). Perhaps the most significant contribution our new data make is filling an important knowledge gap on the mechanism of K-feldspar dissolution in strong alkaline solutions. Thus, this study can be considered to be a unifying element in terms of the dissolution process of alkali feldspars over the full range of pH conditions, and at temperatures up to an including hydrothermal conditions. Only further research will contribute to answering the question as to whether CIDR is a generic and universal mechanism of chemical alteration for all feldspars and other silicate minerals in aqueous solutions over a broad range of pH and temperature conditions.

Acknowledgements

The initial phase of this study was supported by Projects in the National Science & Technology Pillar Program during the Eleventh Five-Year Plan Period (China, No. 2006BAD10B04) and the Knowledge Innovation Project of the Chinese Academy of Sciences and the Spark Program of China (No. 2007EA173003). The aforementioned funding covered the procurement of the orthoclase samples in the field, chemical characterization by X-ray fluorescence, hydrothermal alteration in the laboratory, and leaching experiments followed by aqueous ICP analyses. The one-year stay of YZ (Nov. 2017-Nov. 2018) with the RH research group at ISTerre, Grenoble, France was financed by a State Scholarship Fund organized by the China Scholarship Council. The analytical, instrumental, and travel costs in France were supported by two ISTerre-BQR grants. B. Lanson's (ISTerre) expertise with XRD and Rietveld refinement is gratefully acknowledged, as is the valuable assistance for the BET analyses by V. Magnin (ISTerre). The geochemistry-mineralogy platform of ISTerre is partially funded by a grant from Labex OSUG@2020 (investissements d'avenir, ANR10-LABX56). We are particularly thankful for the FIB, FESEM and TEM beam time provided by Section 3.5, Interface Geochemistry (head: L. Benning), GFZ Potsdam, Germany. The financial support of the Helmholtz Recruiting Initiative (grant No. I-044-16-01) is acknowledged. We also thank J. Hughes (Univ. Vermont) for useful discussions. We thank an anonymous reviewer and the chief editor, M. Böttcher, for helpful comments that improved the manuscript.

References

Arnold, G.W., Westrich, H.R., Casey, W.H., 1992. Application of ion beam analysis (RBS and ERD) to the surface chemistry study of leached minerals. Nuclear Instruments Methods Phys. Res., B 64, 542–546.

Bandstra, J.Z., Buss, H.L., Campen, R.K., Liermann, L.J., Moore, J., Hausrath, E.M., Navarre-Sitchler, A.K., Jang, J. H., Brantley, S.L., 2008. Appendix: Compilation of mineral dissolution rates. In: Brantley, S.L., Kubicki, J.D., White, A.F. (Eds.), Kinetics of Water-Rock Interaction, Springer, New York, pp. 737–823.

Bergmann, J. (2005) Rietveld Analysis Program BGMN (http://www.bgmn.de/BGMN_manual_2005.pdf).

Blum, A.E., Stillings, L.L., 1995. Feldspar dissolution kinetics. In: White, A.F., Brantley, S.L. (Eds.), Chemical Weathering Rates of Silicate Minerals. Mineralogical Society of America, Washington, D.C., pp. 291–351.

Brown, W.L., Parsons, I., 1989, Alkali feldspars: ordering rates, phase transformations and behavior diagrams for igneous rocks. Mineral. Mag. 53, 25-42.

Buck, E.C., Smith, K.L., Blackford, M.G., 2000. The behavior of silicon and boron in the surface of corroded nuclear waste glasses: An Eftem Study. Mat. Res. Soc. Symp. Proc. 608, 727-732.

Casey, W.H., Westrich, H.R., Arnold, G.W., 1988. Surface chemistry of labradorite feldspar reacted with aqueous solutions at pH = 2, 3, and 12. Geochim. Cosmochim. Acta 52, 2795-2807.

Casey, W.H., Westrich, H.R., Arnold, G.W., Banfield, J.F., 1989a. The surface chemistry of dissolving labradorite feldspar. Geochim. Cosmochim. Acta 53, 821-832.

Casey, W.H., Westrich, H.R., Massis, T., Banfield, J.F., Arnold, G.W., 1989b. The surface of labradorite feldspar after acid hydrolysis. Chem. Geol. 78, 205-218.

Chen, Y., Brantley, S.L., Ilton, E.S., 2000. X-ray photoelectron spectroscopic measurement of the temperature dependence of leaching of cations from the albite surface. Chem. Geol. 163, 115-128.

Ciceri, D., de Oliveira, M., Allanore, A., 2017a. Potassium fertilizer via hydrothermal alteration of K-feldspar ore. Green Chem. 19, 5187–5202.

Ciceri, D., Manning, D.A.C., Allanore, A., 2015. Historical and technical developments of potassium resources. Sci. Total Environm. 502, 590–601.

Ciceri, D., Oliveira, M.d., Stokes, R.M., Skorina, T., Allanore, A., 2017b. Characterization of potassium agrominerals: Correlations between petrographic features, comminution and leaching of ultrapotassic syenites. Mins. Eng. 102, 42-57.

Cliff, G., Lorimer, G.W., 1975. The quantitative analysis of thin specimens. J. Micros. 103, 203–207.

Chou, L., Wollast, R., 1985. Steady-state kinetics and dissolution mechanisms of albite. Am. J. Sci. 285, 963-993.

Cole, D.R., Larson, P.B., Riciputi, L.R., Mora, C.I., 2004. Oxygen isotopes zoning profiles in hydrothermally altered feldspars: estimating the duration of water-rock interaction. Geology 32, 29–32.

de la Torre, A.G., Bruque, S., Aranda, M.A.G., 2001. Rietveld quantitative amorphous content analysis. J. Appl. Cryst. 34, 196–202.

Döbelin, N., Kleeberg, R., 2015. Profex: a graphical user interface for the Rietveld refinement program BGMN. J. Appl. Cryst. 48, 1573–1580.

Dran, J.-C., Della Mea, G., Paccagnella, A., Petit, J.-C., Trotignon, L., 1988. The aqueous dissolution of alkali silicate glasses: reappraisal of mechanisms by H and Na depth profiling with high energy ion beams. Phys. Chem. Glasses 29, 249-255.

Engvik, A.K., Putnis, A., Gerald, J.D.F., Austrheim, H., 2008. Albitization of granitic rocks: the mechanism of replacement of oligoclase by albite. Can. Miner. 46, 1401–1415.

Fenter, P., Sturchio, N.C., 2004. Mineral-water interfacial structures revealed by synchrotron X-ray scattering. Progress Surf. Sci. 77, 171-258.

Fenter, P., Lee, S.S., Park, C., Catalano, J.G., Zhang, Z., Sturchio, N.C., 2010. Probing interfacial reactions with X-ray reflectivity and X-ray reflection interface microscopy: Influence of NaCl on the dissolution of orthoclase at pOH 2 and 85 °C. Geochim. Cosmochim. Acta 74, 3396–3411.

Fenter, P., Teng, H., Geissbühler, P., Hanchar, J.M., Sturchio, N.C., 2000. Atomic-scale structure of the orthoclase (001)-water interface measured with high-resolution X-ray reflectivity. Geochim. Cosmochim. Acta 64, 3663–3673.

Gautier, J.-M., Oelkers, E.H., Schott, J., 1994. Experimental study of K-feldspar dissolution rates as a function of chemical affinity at 150°C and pH 9. Geochim. Cosmochim. Acta 58, 4549-4560.

Geisler, T., Pöml, P., Stephan, T., Janssen, A., Putnis, A., 2005. Experimental observation of an interface-controlled pseudomorphic replacement reaction in a natural crystalline pyrochlore. Amer. Mineral. 90, 1683-1687.

Grogger, W., Schaffer, B., Krishnan, K.M., Hofer, F., 2003. Energy-filtering TEM at high magnification: spatial resolution and detection limits. Ultramicroscopy, 96, 481–489.

Harlov, D.E., Förster, H.-J., Nijland, T.G., 2002. Fluid-induced nucleation of (Y + REE)-phosphate minerals within apatite: Nature and experiment. Part I. Chlorapatite. Amer. Miner. 87, 245–261.

Hellmann, R., 1994. The albite-water system: Part I. The kinetics of dissolution as a function of pH at 100, 200, and 300°C. Geochim. Cosmochim. Acta 58, 595–611.

Hellmann, R., 1995. The albite-water system: Part II. The time-evolution of the stoichiometry of dissolution as a function of pH at 100, 200 and 300°C. Geochim. Cosmochim. Acta 59, 1669–1697.

Hellmann, R., 1999a. The dissolution behavior of albite feldspar at elevated temperatures and pressures: the role of surface charge and speciation. Mitt. Österr. Mineral. Ges. 144, 13–44.

Hellmann, R., 1999b. Stoichiometry. In: Marshall, C.P. , Fairbridge, R.W. (Eds.), Encyclopedia of Geochemistry, Kluwer Academic Publishers, pp. 595–598.

Hellmann, R., Crerar, D.A., Zhang, R.H., 1989. Albite feldspar hydrolysis to 300 °C. Solid State Ionics 32/33, 314–329.

Hellmann, R., Drake, B., Kjoller, K., 1992. Using atomic force microscopy to study the structure, topography and dissolution of albite surfaces. In: Kharaka, Y.K., Maest, A.S. (Eds.), Water-Rock Interaction 7 Vol. I., Balkema, Rotterdam, pp. 149–152.

Hellmann, R., Dran, J.-C., Della Mea, G., 1997. The albite-water system Part III. Characterization of leached and hydrogen-enriched layers formed at 300°C using MeV ion beam techniques. Geochim. Cosmochim. Acta 61, 1575-1594.

Hellmann, R., Eggleston, C.M., Hochella, M. F., Jr., Crerar, D. A., 1990. The formation of leached layers on albite surfaces during dissolution under hydrothermal conditions. Geochim. Cosmochim. Acta 54, 1267–1281.

Hellmann, R., Penisson, J.-M., Hervig, R.L., Thomassin, J.-H., Abrioux, M.-F., 2003. An EFTEM/HRTEM high-resolution study of the near surface of labradorite feldspar altered at acid pH: evidence for interfacial dissolution-reprecipitation. Phys. Chem. Mins. 30, 192–197.

Hellmann, R., Wirth, R., Daval, D., Barnes, J.-P., Penisson, J.-M., Tisserand, D., Epicier, T., Florin, B., Hervig, R.L., 2012. Unifying natural and laboratory chemical weathering with interfacial dissolution–reprecipitation: A study based on the nanometer-scale chemistry of fluid–silicate interfaces. Chem. Geol. 294–295, 203–216.

Hellmann, R., Cotte, S., Cadel, E., Malladi, S., Karlsson, L.S., Lozano-Perez, S., Cabié, M., Seyeux, A., 2015. Nanometre-scale evidence for interfacial dissolution–reprecipitation control of silicate glass corrosion. Nature Materials 14, 307–311.

Holdren, G.R., Jr., Speyer, P.M., 1985. pH dependent changes in the rates and stoichiometry of dissolution of an alkali feldspar at room temperature. Am. J. Sci. 285, 994-1026.

Hövelmann, J., Putnis, A., Geisler, T., Schmidt, B.C., Golla-Schinder, U., 2010. The replacement of plagioclase feldspars by albite: observations from hydrothermal experiments. Contrib. Miner. Petrol. 159, 43–59.

Jordan, G., Higgins, S.R., Eggleston C.M., Swapp, S.M., Janney, D.E., Knauss, K.G., 1999. Acidic dissolution of plagioclase: In-situ observations by hydrothermal atomic force microscopy. Geochim. Cosmochim. Acta 63, 3183–3191.

Kasioptas, A., Perdikouri, C., Putnis, C.V., Putnis, A., 2008. Pseudomorphic replacement of single calcium carbonate crystals by polycrystalline apatite. Mineral. Mag. 72, 77–80.

Khatib, R., Backus, E.H., Bonn, M., Perez-Haro, M.J., Gaigeot, M.P., Sulpizi, M., 2016. Water orientation and hydrogen-bond structure at the fluorite/water interface. Sci. Reports 6, 24287.

King, H.E., Plümper, O., Geisler, T., Putnis, A., 2011. Experimental investigations into the silicification of olivine: Implications for the reaction mechanism and acid neutralization. Amer. Mineral. 96, 1503-1511.

Klein, C., Philpotts, A.R., 2017. Earth Materials: Introduction to Mineralogy and Petrology. In: Klein, C., Philpotts, A.R. (Eds.), Cambridge University Press, New York.

Knight, A.W., Kalugin, N.G., Coker, E., Ilgen, A.G., 2019. Water properties under nano-scale confinement. Sci. Reports 9, 8246.

Labotka, T.C., Cole, D.R., Fayek, M., Riciputi, L.R., Stadermann, F.J., 2004. Coupled cation and oxygen-isotope exchange between alkali feldspar and aqueous chloride solution. Amer. Mineral. 89, 1822–1825.

Lee, M.R., Parsons, I., 1997. Dislocation formation and albitization in alkali feldspars from the Shap granite. Amer. Mineral. 82, 557–570.

Lee, M.R., Hodson, M.E., Parsons, I., 1998. The role of intragranular microtextures and microstructures in chemical and mechanical weathering: direct comparisons of experimentally and naturally weathered alkali feldspars. Geochim. Cosmochim. Acta 62, 2771-2788.

Lee, M.R., Brown, D.J., Smith, C.L., Hodson, M.E., Mackenzie, M., Hellmann, R., 2007. Characterization of mineral surfaces using FIB and TEM: A case study of naturally weathered alkali feldspars. Amer. Mineral. 92, 1383–1394.

Lee, M.R., Hodson, M.E., Brown, D.J., MacKenzie, M., Smith, C.L., 2008. The composition and crystallinity of the near-surface regions of weathered alkali feldspars. Geochim. Cosmochim. Acta 72, 4962-4975.

Leonard, D.N., Hellmann, R., 2017. Exploring dynamic surface processes during silicate mineral (wollastonite) dissolution with liquid cell TEM. J. Micros. 265, 358–371.

Liu, S. K., Han, C., Liu, J. M., Li, H. (2015) Hydrothermal decomposition of potassium feldspar under alkaline conditions. RSC Advances 5, 93301–93309.

Liu, S.K., Han, C., Liu, J.M., 2018. Study of K-feldspar and lime hydrothermal reaction at 190 °C: Phase, kinetics and mechanism with reaction time. ChemistrySelect 3, 13010–13016.

Liu, S.K., Han, C., Liu, J.M., 2019. Study of K-feldspar and lime hydrothermal reaction: Phase and mechanism with reaction temperature and increasing Ca/Si ratio. Minerals 9, 46.

Locati, F., Marfil, S., Baldo, E., Maiza, P., 2010. Na_2O, K_2O, SiO_2 and Al_2O_3 release from potassic and calcic–sodic feldspars into alkaline solutions. Cement Concrete Res. 40, 1189-1196.

Ma H.W., Yang J., Su S.Q., Liu M.T., Zheng H., Wang Y.B., Qi H.B., Zhang P., Yao W.G., 2015. 20 years advances in preparation of potassium salts from potassic rocks: A review. Acta Geologica Sinica (Eng. Ed.) 89, 2058–2071.

Marry, V., Rotenberg, B., Turq, P., 2008. Structure and dynamics of water at a clay surface from molecular dynamics simulation. Phys. Chem. Chem. Phys. 10, 4802–4813.

Martin, J.M., Vacher, B., Ponsonnet, L., Dupuis, V., 1996. Chemical bond mapping of carbon by image-spectrum EELS in the second derivative mode. Ultramicroscopy 65, 229–238.

Nesbitt, H.W., Muir, I.J., 1988. SIMS depth profiles of weathered plagioclase, and processes affecting dissolved Al and Si in some acidic soil conditions. Nature 334, 336-338.

Norberg, N., Neusser, G., Wirth, R., Harlov, D., 2011. Microstructural evolution during experimental albitization of K-rich alkali feldspar. Contrib. Mineral. Petrol. 162, 531–546.

Nugent, M.A., Brantley, S.L., Pantano, C.G., Maurice, P.A., 1998. The influence of natural mineral coatings on feldspar weathering. Nature 395, 588-591.

O'Neil, J.R., Taylor, H.P.J., 1967. The oxygen isotope and cation exchange chemistry of feldspars. Amer. Mineral. 52, 1414–1437.

Parker, S.C., de Leeuw, N.H., Bourova, E., Cooke, D.J., 2001. Molecular Modeling Theory: Applications in the Geosciences. In: Cygan, R.T., Kubicki, J.D. (Eds.), Reviews in Mineralogy and Geochemistry, Geochemical Society and Mineralogical Society of America, 42, pp. 63–82.

Parsons, I., Lee, M.R., 2009. Mutual replacement reactions in alkali feldspars I: microtextures and mechanisms. Contrib. Mineral. Petrol. 157, 641–661.

Parsons, I., Magee, C.W., Allen, C.M., Shelley, J.M.G., Lee, M.R., 2009. Mutual replacement reactions in alkali feldspars II: trace element partitioning and geothermometry. Contrib. Mineral. Petrol. 157, 663–687.

Petit, J.-C., Dran, J.-C., Schott, J., Della Mea, G., 1989. New evidence on the dissolution mechanism of crystalline silicates by MeV ion beam techniques. Chem. Geol. 76, 365-369.

Petit, J.-C., Dran, J.-C., Della Mea, G., 1990a. Energetic ion beam analysis in the Earth sciences. Nature 344, 621-626.

Petit, J.-C., Della Mea, G., Dran, J.-C., Magonthier, M.-C., Mando, P.A., Paccagnella, A., 1990b. Hydrated layer formation during dissolution of complex silicate glasses and minerals. Geochim. Cosmochim. Acta 54, 1941-1955.

Putnis, A., 2002. Mineral replacement reactions: from macroscopic observations to microscopic mechanisms. Mineral. Mag. 66, 689–708.

Putnis, A., 2009. Mineral replacement reactions. In: Oelkers, E.H., Schott, J. (Eds.), Reviews in Mineralogy and Geochemistry, Mineralogical Society of America,70, pp. 87–124.

Putnis, A., 2014. Why mineral interfaces matter. Science 343, 1441-1442.

Putnis, C.V., Mezger, K., 2004. A mechanism of mineral replacement: Isotope tracing in the model system KCl-KBr-H_2O. Geochim. Cosmochim. Acta 68, 2839–2848.

Putnis, C.V., Tsukamoto, K., Nishimura, Y., 2005. Direct observations of pseudomorphism: compositional and textural evolution at a fluid-solid interface. Amer. Mineral. 90, 1909–1912.

Robin, E., 2017. Method for the determination of the mass thickness and the composition of a zone of an object using an electron beam and measurements of X-ray intensities. France patent EP 3 032 244 B1.

Ruiz-Agudo, E., Putnis, C.V., Putnis, A., 2014. Coupled dissolution and precipitation at mineral–fluid interfaces. Chem. Geol. 383, 132–146.

Ruiz-Agudo, E., Putnis, C.V., Rodriguez-Navarro, C., Putnis, A., 2012. Mechanism of leached layer formation during chemical weathering of silicate minerals. Geology 40, 947–950.

Schweda, P., Sjöberg, L., Södervall, U., 1997. Near-surface composition of acid-leached labradorite investigated by SIMS. Geochim. Cosmochim. Acta 61, 1985-1994.

Skorina, T., Allanore, A., 2015. Aqueous alteration of potassium-bearing aluminosilicate minerals: from mechanism to processing. Green Chem. 17, 2123–2136.

Su, S.Q., Ma, H.W., Chuan, X.Y., 2015. Hydrothermal decomposition of K-feldspar in KOH–NaOH–H_2O medium. Hydrometallurgy 156, 47–52.

Teng, H.H., Fenter, P., Cheng, L., Sturchio, N.C., 2001. Resolving orthoclase dissolution processes with atomic force microscopy and X-ray reflectivity. Geochim. Cosmochim. Acta 65, 3459–3474.

Thomä, S.L.J., Krauss, S.W., Eckardt, M., Chater, P., Zobel, M., 2019. Atomic insight into hydration shells around facetted nanoparticles. Nature Commun. 10, 995.

Thomassin, J.-H., Le Coustumer, P., Patrier, P., 1995. Mineralogy and ultrastructure of some alteration products of Yamamoto-86032 meteorite. Proc. NIPR Symp. Antarc. Meteorites 8, 185-193.

van der Pluijm, B.A., Lee, J.H., Peacor, D.R., 1988. Analytical electron microscopy and the problem of potassium diffusion. Clays Clay Minerals, 36.

Villa, I.M., 2016. Diffusion in mineral geochronometers: Present and absent. Chem. Geol. 420, 1-10.

Watanabe, M., Williams, D.B., 2006. The quantitative analysis of thin specimens: a review of progress from the Cliff-Lorimer to the new ζ-factor methods. J. Micros. 221, 89–109.

Williams, D. B., Carter, C.B., 2009. Transmission Electron Microscopy Part 4: Spectrometry, Springer.

Wirth, R., 2004. Focused Ion Beam (FIB): A novel technology for advanced application of micro- and nanoanalysis in geosciences and applied mineralogy. Eur. J. Mineral. 16, 863-876.

Wirth, R., 2009. Focused Ion Beam (FIB) combined with SEM and TEM: Advanced analytical tools for studies of chemical composition, microstructure and crystal structure in geomaterials on a nanometre scale. Chem. Geol. 261, 217–229.

Yang, Y., Min, Y., Jun, Y.S., 2013. A mechanistic understanding of plagioclase dissolution based on Al occupancy and T–O bond length: from geologic carbon sequestration to ambient conditions. Phys. Chem. Chem. Phys. 15 (42), 18491–18501.

Yang, Y., Min, Y., Jun, Y., 2014a. Effects of Al/Si ordering on feldspar dissolution: part II. The pH dependence of plagioclases' dissolution rates. Geochim. Cosmochim. Acta 126, 595–613.

Yang, Y., Min, Y., Lococo, J., Jun, Y., 2014b. Effects of Al/Si ordering on feldspar dissolution: part I. Crystallographic control on the stoichiometry of dissolution reaction. Geochim. Cosmochim. Acta 126, 574–594.

Yuan, B., Li, C., Liang, B., Lü, L., Yue, H., Sheng, H., Ye, L., Xie, H., 2015. Extraction of potassium from K-feldspar via the $CaCl_2$ calcination route. Chinese J. Chem. Eng. 23, 1557-1564.

Zhai, Y., Hellmann, R., Campos, A., Findling, N., Mayanna, S., Wirth, R., Schreiber, A., Cabié, M., Zeng, Q., Liu, S., Liu, J., 2021. 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. Applied Geochem.

Zhang, L., Lüttge, A., 2009. Theoretical approach to evaluating plagioclase dissolution mechanisms. Geochim. Cosmochim. Acta 73, 2832-2849.

Zhu, C., Veblen, D.R., Blum, A.E., Chipera, S.J., 2006. Naturally weathered feldspar surfaces in the Navajo Sandstone aquifer, Black Mesa, Arizona: electron microscopic characterization. Geochim. Cosmochim. Acta 70, 4600-4616.

Table 1. Chemical compositions of unaltered orthoclase samples based on XRF analyses（mass %)

Sample ID	Locality*	SiO_2	TiO_2	Al_2O_3	$Fe_2O_3^{\dagger}$	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Chemical formula
CSY-1 (#6)	Xinghe	65.96	0.02	18.39	0.22	0.01	0.05	0.22	2.96	11.48	0.01	0.52	$Na_{0.26}K_{0.67}Ca_{0.01}Al_{0.99}Si_{3.02}O_8$
CSY-2 (#3)	Xinghe	66.04	0.03	18.31	0.21	0.00	0.08	0.14	1.00	13.29	0.02	0.82	$Na_{0.09}K_{0.78}Ca_{0.01}Al_{0.99}Si_{3.04}O_8$
CSY-3 (#4)	Xinghe	65.61	0.01	18.10	0.42	0.01	0.04	0.13	1.73	13.45	0.01	0.54	$Na_{0.15}K_{0.79}Ca_{0.01}Al_{0.98}Si_{3.02}O_8$
CHG-2 (#2)	Chifeng	66.16	0.03	18.07	0.31	0.00	0.18	0.30	2.63	11.66	0.01	0.78	$Na_{0.23}K_{0.68}Ca_{0.01}Al_{0.98}Si_{3.03}O_8$
CHG-12 (#11)	Chifeng	66.20	0.03	18.37	0.22	0.00	0.13	0.23	2.50	11.43	0.01	0.79	$Na_{0.22}K_{0.67}Ca_{0.01}Al_{0.99}Si_{3.03}O_8$

† total iron oxide;
LOI: loss on ignition

*all localities are in
Inner Mongolia, China

Table 2. BET (N_2) specific surface areas of orthoclase samples

Sample ID	BET unaltered (m^2/g)	BET altered (m^2/g)
CSY-1C (#6)	3.8	13.7
CSY-2C (#3)	2.1	12.4
CSY-3C (#4)	4.9	13.3
CHG-2C (#2)	2.8	11.1
CHG-12C (#11)	*	*

* insufficient sample available

Table 3. EDXS-measured elemental atomic ratios (unaltered orthoclase measured by XRF), and probable secondary phases- when identification was not possible, the phases are marked as CASH/CSH + carb (see text). Measurement locations in Figs. 4a-c, Fig. 9b, Fig. S7. np = nanoparticles

ortho #6 CSY-1C	Al/Si	K/Si	Ca/Si	probable phase, remarks
1	0.34	0.24	-	orthoclase
2	0.33	0.23	0	orthoclase
3	0.31	0.17	0.01	orthoclase
4	0.21	0.10	0.67	amorphous (?)
5	0.53	0.30	0.02	CASH
6	0.16	0.06	2.60	CASH/CSH + carb
7	0.19	0.01	0.72	CASH/CSH + carb
8	0.15	0.07	0.74	CASH/CSH + carb
Fig. 9b	0.30	0.72	0.32	amorphous SAL
unaltered	0.33	0.22	0.003	$Na_{0.26}K_{0.67}Ca_{0.01}Al_{0.99}Si_{3.02}O_8$

ortho #4 CSY-3C				
9	0.11	0.12	1.11	CASH+carb
10	-	-	-	resin
11	0.97	0.67	45.43	calcite
12	0.35	0.23	0.001	orthoclase
13	0.25	0.10	0.21	amorphous (?)
14	0.15	1.23	13.42	calcite
15	0.15	0.60	1.26	CASH/CSH + carb + np
16	0.10	0.09	1.10	CASH/CSH + carb + np
17	0.20	0.19	0.35	amorphous (?)
18	0.12	0.005	0.27	CASH/CSH + carb
19	0.18	0.06	1.07	CASH/CSH + carb
20	0.34	0.25	0.002	orthoclase
unaltered	0.32	0.26	0.003	$Na_{0.15}K_{0.79}Ca_{0.01}Al_{0.98}Si_{3.02}O_8$

Figure Captions

Fig. 1. Experimental protocol flow-chart for alkaline hydrothermal alteration process- see Materials and Methods, section 2.2 for details.

Fig. 2. Field emission scanning electron microscope (FESEM) secondary electron images of a polished section showing a primary orthoclase grain in cross section after hydrothermal alteration. a) Single grain (CSY-1C) surrounded by a rim of secondary crystalline phases. b) Close-up of rim (1) and globular entities (2-4) comprised of an amalgam of secondary phases, including amorphous material, calcite, and CASH + CSH phases.

Fig. 3. Mono-elemental chemical maps measured by FESEM-EDXS (energy dispersive X-ray spectroscopy) of the same area as in Fig. 2b. The individual elements are indicated at the inner bottom corners of each image. The white arrows demarcate the interface between orthoclase and the alteration rim of secondary products. K, Ca, Si, and Al are present at significant concentrations in most of the secondary globular entities (2-4), whereas Ca is particularly enriched in area 4, and somewhat in the rim (1)- the high [Ca] in area 4 may point to enrichment in calcite. The majority of C is associated with resin, and its occurrence in areas 1-4 corresponds in large part to the presence of calcite.

Fig. 4. Focused ion beam (FIB) ultrathin sections imaged by high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM). Rectangles indicate areas of EDXS analyses- results reported in Table 3. White arrows demarcate the orthoclase interface with secondary products. a) Cross sectional image reveals both amorphous (4) and crystalline secondary products (5-8) in close contact with an orthoclase grain (CSY-1C, nos. 1-3). Analysis area of rectangle 8 is only partially shown. The bladed crystals are likely to be tobermorite. b) Image showing orthoclase grain CSY-3C (12), calcite (white band, 11), other secondary crystalline phases (9), and resin (10). c) Image of same interface (CSY-3C) at different location; note the amorphous phase (13) with large pores contacting the orthoclase interface, the white band is likely a calcite layer (14). The small white particles (lower half of image, including analyzed areas 15, 16) are presumed to be nano-sized precipitates.

Fig. 5. a) Bright field (BF) TEM image of orthoclase grain (CSY-3C) and its interface (dashed white arrows) with secondary precipitates. Note the bladed crystals (tobermorite), the globular entity (bounded by 3 white arrows), and a band of calcite (opposing white arrows). The precipitate region is hydrated, as evidenced by the white globules (e.g., over scale bar) that are likely to be water-rich inclusions. Note

also the abundant small black nano-size grains throughout the precipitate (these appear white in Fig. 4c). b) Deconvolved spectrum, obtained by selected area electron energy loss spectroscopy (EELS), serves to identify the calcite band, based on distinct C *K* (289 eV and 300 eV) and Ca $L_{2,3}$ (348 and 351 eV) edge structures.

Fig. 6. a) BF TEM image of orthoclase grain (CSY-1C) showing well-defined structural and mass-density interface (white arrows) between crystalline orthoclase and secondary precipitates. b) Ca $L_{2,3}$ energy filtered TEM (EFTEM) 3-window chemical map of the same region at slightly lower magnification. White areas are Ca-rich, and conversely, black areas are devoid of Ca, such as the orthoclase grain and resin. Note the sharp change in Ca concentration at the interface. Secondary precipitates also appear at right edge of image.

Fig. 7. EDXS-derived ratios of Na, Na + K, K, and Si, all normalized with respect to Al, as function of total electron dose, measured with a Titan Themis TEM on various adjacent areas of unaltered orthoclase. The trends indicate that K, and to a lesser extent Na, are particularly mobile under a TEM electron beam, indicating that they should be measured with a total electron dose < 1.5 pA·s·nm^{-2}. These results explain anomalously low K values measured at orthoclase grain edges (see text, also Fig. 4a- area 3).

Fig. 8. HAADF-STEM image of a post-reaction orthoclase grain edge with an abutting amorphous surface altered layer (SAL). The relative thickness profile (in white- based on iterative calculations using elemental X-ray intensities) indicates a significant change in thickness at interface between the 2 phases. This image and the accompanying EDXS chemical profiles were obtained with a total electron dose = 1.4 pA·s·nm^{-2}. The 4 elemental ratio profiles reveal quite different behaviors. The K/Al ratio shows a sudden jump right at the interface, whereas the Na/Al ratio remains constant in both phases. The Si/3Al and O/8Al profiles remain roughly constant within the orthoclase (ratios ≈ 1), but at the interface the ratios suddenly start to fluctuate- this may be due to pores or other inhomogeneities in the SAL. At distances further away from the interface (< -30 nm), both ratios show a fluctuating but monotonic increase.

Fig. 9. TEM images of the same area as in Fig. 8, but slightly enlarged and cropped. a) HAADF-STEM image showing a sharp mass-density interface (white arrows) between orthoclase (CSY-1C) and an amorphous SAL. Note the presence of the large pore in the SAL. b) Superposed HAADF-STEM image

and EDXS chemical maps of K, Ca, and Si (scale bar = 50 nm, applies to panels a) and b). The abrupt chemical discontinuity between the orthoclase and the SAL (white arrows) is coincident with the sharp mass-density change. The interface is in particular demarcated by the very sharp change in Si concentration (blue). The amorphous SAL contacting the orthoclase is particularly K-rich, while further away it is distinctly enriched in Ca. The rectangle demarcates where an average chemical composition of the precipitate was determined by EDXS- see text and Table 3). c) Individual elemental EDXS maps- note the extremely sharp, step function-like drop in Si and Al at the orthoclase (or)- SAL boundary. The Ca map indicates that this element did not penetrate the orthoclase structure.

Fig. 10. Oriented high-resolution TEM (HRTEM) image showing nm-sharp structural interface between orthoclase (note lattice fringes) and amorphous phase. Image taken on the same interface as in preceding figure (orthoclase CSY-1C).