Dynamic feldspar alteration governed by single self-evolved fluid system

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Abstract

The evolution of hydrothermal fluids during metasomatic and/or hydrothermal processes is responsible for the formation of ore deposits and associated alteration. In systems with well-developed breccia and fractures, mineral reactions are largely driven by decompression boiling, fluid cooling or external fluid mixing, but in less permeable rocks, elements exchanges occur at fluid-mineral interfaces, resulting in a self-evolved fluid-mineral reaction system. However, the dynamic fluid evolution leading to large-scale (km) alteration remains poorly understood. We observed experimentally that the sequential sodic and potassic alterations associated with mineralization in large ore deposits, in particular Iron Oxide Copper Gold (IOCG) deposits, can occur via a single self-evolved, originally Na-only, hydrothermal fluid, driven by a positive feedback between equilibrium and kinetic factors. Albite formed first upon reaction of sanidine ((K,Na)AlSi₃O₈) with a NaCl fluid at 600°C, 2 kbar. However, with increasing reaction time, some of the initially formed albite was in-turn replaced by K-feldspar (KAlSi₃O₈). Fluorine accelerated the process, resulting in nearly complete back-replacement of albite within 1 day. These experiments demonstrate that potassic alteration can be induced by Na-rich fluids, and pervasive sequential sodic and potassic alterations do not necessarily reflect near-equilibrium, externally-driven changes in fluid alkali contents.

Introduction

Fluid-rock interactions during metasomatic and/or hydrothermal processes control crustal rheology, porosity structure, and elements redistribution within the Earth's crust¹. In mineral systems, the ore itself represents of tiny volume within an extensive (10's to 100's of km³) hydrothermal system, and many large deposits, in particular IOCG² and porphyry³, are associated with extensive (tens to hundreds of km³) alteration halos⁴⁻⁶. These halos form as a result of thermodynamic disequilibrium between rock and fluid, and many of the characteristic mineral reactions are driven by alkali (Na,K) exchange. An evolution from sodic to potassic alteration is a key feature of IOCG deposits. The current consensus is that this evolution is caused by changing chemical and/or physical conditions^{2,7} (e.g., cooling; decompression boiling; decreasing water to rock ratio), and can be well approximated as a (near-) equilibrium system⁸. However, recent progress in our understanding of the mechanisms of fluid-driven mineral reactions has highlighted the significance of kinetic factors and local equilibria in controlling the evolution of fluid-mineral systems⁹. Interfacial fluids at fluid-mineral boundaries control reaction kinetics and mineral stability, and the complex feedback between fluid flow, reaction progress, and transient, reaction-induced porosity is a key driver of crustal-scale fluid-rock interaction¹⁰⁻¹².

We hypothesize that the widespread temporal and spatial association between sodic and potassic alteration may be facilitated by an interplay of kinetic and equilibrium thermodynamic factors at the fluid-mineral interface. To test this idea, we examined the alteration of a mixed Na-K-feldspar (sanidine) in a self-evolved, originally Na-only hydrothermal fluid (NaCl or NaF) in closed system experiments at isothermal, isobaric conditions. Since feldspars make up more than 50% of Earth's crust, their complex compositions and/or textures can shed light on the crustal thermal and alteration history^{13,14}. Pioneering

experiments investigated the microstructural and chemical evolution of feldspars under hydrothermal conditions^{15–18}, and concluded that the reactions proceeded via a fluid-driven interface-coupled dissolution-precipitation mechanism, but the reactions products were broadly in-line with predictions from equilibrium thermodynamics. In contrast, we observed a remarkable sequential sodic and potassic alteration of sanidine rather than the expected albitisation. The replacement kinetics also increased dramatically in F-rich systems. Based on the characterization of the products and thermodynamic modelling of the fluid-mineral interaction, we show that sequential sodic and potassic alterations can be driven by Na-rich fluids at regional scale (i.e., not much K in the fluid is required to stabilise K-feldspar versus albite), and promoted by a self-evolution process at the micro-scale.

Experiments And Analytical Methods

We reacted sanidine, $K_{0.62(1)}Na_{0.33(1)}Ca_{0.042(6)}AlSi_3O_8$ ($n = 13$; Table S1 in Supplementary Data) in NaCl and NaF solutions. For each experiment, around 0.11 mmol sanidine and 0.15 mmol halide (NaCl or NaF) as well as 2 mmol of normal deionized water ($H_2^{16}O$) or $H_2^{18}O$ water (from Isoflex company) (Table S1) were loaded into a gold capsule (diameter: 3 mm; length: 25 mm). The sealed capsules were heated to 600 °C at 2 kbar for run durations between 1 and 5 days. These P-T conditions are within the range of alteration/mineralization process of the high-temperature evolution of porphyry Cu systems (350–700 °C¹⁹; 400–840 °C²⁰) and IOCG deposits (e.g., 500–550 °C in the Mt Isa province⁷; > 600 °C in the Gawler Craton²¹).

The products' textures and compositions were characterised using Scanning Electron Microscopy (SEM) and Electron Micro Probe Analyser (EMPA). The nature of the reaction products was verified with Powder X-ray diffraction (pXRD), but Mineral Liberation Analysis (MLA) was used to quantify phase fractions, since pXRD was not able to distinguish the newly formed K-feldspar from the original sanidine. Some experiments were conducted in ^{18}O -enriched water to monitor fluid-mineral exchanges^{15,16,22}, with ^{18}O distribution measured semi-quantitatively by nano-Secondary Ion Mass Spectrometry (nano-SIMS) and Raman spectroscopy. Analytical methods and starting material are described in detail in Supplementary Data.

Reaction Textures And Products

The main reaction products from both NaCl and NaF solutions are albite and/or K-feldspar (Fig. 1; Table S2); small amounts of biotite formed in NaCl-only solutions, and fluorite and ilmenite in NaF-bearing solutions (Fig. S1). Fluorite and biotite occur mainly along the reaction front between albite and sanidine or filling pores.

In NaCl-solutions, the overall reactions proceeded through three stages. Stage I: an albite rim replaces the outmost part of sanidine (Fig. 2A). There can be large (5–20 μm wide) gaps between the reaction rim and the pristine sanidine or a sharp interface between them (Fig. 2A). Stage II: a new K-feldspar appears (Fig. 2B), replacing the albite formed in stage I from the outside of the grain. The interface between the

new K-feldspar and albite is sharp without any micro-scale porosity. Stage III: as the reaction proceeds from rim to core, thin K-feldspar rim forms via partial replacement of the albite rim (Fig. 2C). The new K-feldspar is characterized by higher K and lower Na contents than the starting sanidine (Figs. 2GH, S2). However, only small amounts of the new K-feldspar phase form, and this quantity increases only slightly over time (0.08 vol% after 3 days, and 0.41 vol% after 5 days; Fig. 1A; Table S2). The reaction process was greatly accelerated in the F-bearing system (Figs. 2D-F): large amounts of K-feldspar formed within only 1 day as thick rims around the parent sanidine core (20 vol% of the new K-feldspar phase; Fig. S3), with only small amounts of relic albite remaining (Fig. 1B; Figs. 2D-E, I-J). Small euhedral K-feldspar grains nucleating on the surface of the sanidine seeds or growing into the solution were only observed in F-bearing solutions (Fig. 2F). In a few areas, K-feldspar directly replaces sanidine (Fig. 2F insert), in which case the albite rim is fully back-reacted. Hence, in these experiments, potassic alteration is induced without any external K-input, via dynamic evolution driven by an initial disequilibrium between mineral and Na-only fluid.

Thermodynamic Modelling

The aim of this section is to predict the system evolution under equilibrium conditions, and then use these predictions to identify potential kinetic effects that may explain the observed sequential sodic and potassic alterations. Thermodynamic calculations are challenging since our experiments involve reaction between a complex electrolyte solution with evolving composition and mineral solid-solutions with a miscibility gap (Fig. 3A). We used GEM-Selektor (details in the Supplementary Data), since the suitability of this package to effectively model this complex thermodynamic situation has been demonstrated^{23,24}. At 600 °C, the sanidine composition used in our experiments is within the miscibility gap between K-feldspar and albite, though it is close to the single-phase boundary (Fig. 3A). The Lippmann diagram in Fig. 3B depicts the aqueous ion concentrations ($X(\text{Na}^+, \text{aq})$; green solutes line) in equilibrium with a given solid solution composition²⁵ ($X(\text{Ab})$; red solidus line). In the presence of a Na^+ -rich fluid ($X(\text{Na}^+, \text{aq}) > 0.85$), the equilibrated solid is an albite-rich feldspar (Fig. 3B). At a $X(\text{Na}^+, \text{aq})$ of 0.85, a peritectic point is reached where the aqueous phase co-exists with two solid solutions: albite with $X(\text{Ab}) = 0.88$, and K-feldspar with $X(\text{Ab}) = 0.35$ (Fig. 3C). When $X(\text{Na}^+, \text{aq})$ decreases slightly below 0.85, the Na content of the equilibrated solid solution decreases dramatically, forming a K-feldspar with $X(\text{Ab}) \leq 0.35$ (Fig. 3B). Hence, these calculations show that K-rich ($X(\text{Ab})$ of 0.13 to 0.22) feldspars can coexist with Na-rich aqueous solutions ($X(\text{Na}^+, \text{aq})$ of 0.72 to 0.83; Fig. 3B): K-rich fluids are not required to drive potassic alteration.

Progressive replacement of sanidine has been modelled by aliquot titration of sanidine in a fixed amount of solution at experimental conditions (2 kbar, 600 °C). Three different equilibrium scenarios were considered in terms of solution used, i.e., pure H_2O , and NaCl and NaF solutions (Figs. 3D-F). In pure H_2O (Fig. 3D), dissolution of sanidine quickly results in equilibration of the solution with a feldspar of composition close to that of the titrated sanidine. In the NaCl solution (Fig. 3E), albite is predicted to form first, resulting in decreased Na^+ and increased K^+ in solution. When the sanidine/water molar ratio is

around 0.25, two different products (Na-poor K-feldspar and a Na-rich albite) formed at the peritectic point. The NaF solution showed a similar evolution, but the equilibrium peritectic point was reached at lower sanidine/water ratio (Fig. 3F).

Hence, the equilibrium simulations show that unless sanidine dissolves congruently and buffers fluid composition (Fig. 3D), sanidine should be replaced by two feldspars at the peritectic point (Figs. 3E-F), with a final fluid composition with $X(\text{Na}^+, \text{aq}) = 0.85$. These predictions tally with previous experiments¹⁸, whereby an $\text{Ab}_{60}\text{Or}_{40}$ feldspar was replaced by coarse-grained, coexisting albite and K-feldspar upon reaction with $\text{H}_2\text{O}/\text{HCl}$ solutions (Fig. 3G).

However, our experiments display different textures and final product compositions than those predicted by equilibrium thermodynamic modelling (Figs. 2, 3H). The most significant difference is that there is no evidence for *co*-precipitation of two feldspars in our experiments: albite first replaces sanidine, and then this newly formed albite – and some sanidine – are replaced by K-rich feldspar along a separate, independent reaction front (Fig. 3H). This indicates that mineral formation in this system is governed by interfacial fluids at the reaction fronts with compositions different from the bulk solution.

Reaction Mechanism

The formation of biotite, fluorite and ilmenite coexisting with albite tallies with the complete dissolution of sanidine releasing the minor amounts of incorporated Ca, Ti, and Fe. The sharp boundaries between sanidine and albite/K-feldspar and the pseudomorphic replacement are characteristic of the ICDR reaction mechanism⁹. This ICDR mechanism was further confirmed by experiments conducted using isotopically tagged (^{18}O) water, showing sharp interfaces with large contrasts in $^{18}\text{O}/^{16}\text{O}$ isotopic composition between parent sanidine ($^{18}\text{O}/^{16}\text{O} < 0.003$) and albite/K-feldspar (Figs. 4, S4-S6). This indicates that Si–O and Al–O chemical bonds were broken during the replacement in both Cl- and F-bearing solutions and that oxygen exchanged widely with the solution²², in line with the ICDR mechanism. An increase in ^{16}O in the framework of K-feldspar was further observed with increasing reaction time: K-feldspar formed within 1 day from NaF solution had $^{18}\text{O}/^{16}\text{O}$ ratios around 2, compared to 1.4 after 5 days (Figs. 4, Fig. S4). This suggests that K-feldspar undergoes continuous *dynamic recrystallization*, which is recorded by uptake of increasing amounts of ^{16}O from dissolved sanidine over time. Such a dynamic recrystallization implies that the original composition (elemental and isotopic) and texture (including porosity) of the newly formed feldspars can evolve rapidly (hours) in contact with a fluid.

Fluorine increased the rate of back-reaction, but the reaction mechanisms were similar regardless of Cl and F availability: sanidine dissolution, initial albitization, followed by back-replacement by K-feldspar. Initial sanidine dissolution results in the formation of a solution surface layer with elevated K^+/Na^+ ratio relative to the bulk solution; however, albite formed first, in accordance with the initial bulk fluid composition.

As the reaction rim expands, chemical exchanges between the reaction front and the bulk solution occur either through (transient) reaction-induced porosity¹⁰, or in the absence of a connected porosity network as in our experiments, along the reaction interface^{15,16}. As the albite rim becomes thicker, the removal of K^+ from the interface and the supply of Na^+ from bulk fluid to form albite are expected to slow down, resulting in the local enrichment of K^+ . However, albite with little change in composition continues to precipitate, and K-feldspar never nucleates at the reaction front between albite and sanidine. Instead, K-feldspar starts replacing albite from the outside of the grains, forming a second, decoupled reaction interface (Fig. 2) in contrast to the co-precipitation of albite and K-feldspar from thermodynamic modelling. The newly formed K-feldspar is inhomogeneous and characterised by a lower $Na/(Na + K)$ ratio (0.13 ~ 0.31 with average 0.22) than pristine sanidine (~ 0.35) (Fig. S2). This wide composition range of K-feldspar implies a continuously evolving interfacial fluid which may become variably enriched in K^+ throughout the reaction. Altogether, these observations suggest a strong link between nucleation and feldspar composition: once albite nucleates with a particular composition, it continues to grow, irrespective of interface fluid composition. Then a similar process happens with nucleation of a K-rich feldspar, leading to near complete replacement (back reaction) of the earlier formed albite. Hence, the back-reaction responsible of K-feldspar formation is the result of kinetic processes that prevent the equilibrium co-precipitation of two feldspars under the conditions of our experiments.

Pervasive Successive Feldspar Replacement In Nature

Many ore-forming systems, including some porphyry^{4,19} and most IOCG deposits²⁸ are associated with large-scale sodic alteration overprinted by potassic alteration³¹. Understanding the dynamic evolution of hydrothermal fluids in these alteration halos is the focus of a large body of research aiming at defining the sources of precious and base metals, as well as identifying geochemical and mineralogical indicators for guiding mineral exploration^{26–27}. In general, successive alteration styles are explained as reflecting either (i) changing fluid compositions over time, (ii) temperature changes in externally-derived convective systems^{26,29}; (iii) Na-addition via interaction with evaporite-bearing wall rocks³⁰; or (iv) magmatic unmixing of $H_2O-CO_2-NaCl \pm CaCl_2-KCl$ fluids caused by decreases in temperature and/or pressure³¹. However, our experimental and thermodynamic results show that this alteration sequence can also be achieved through a single self-evolved NaCl-rich hydrothermal fluid at constant temperature and pressure.

In the K-feldspar alteration envelope of the Butte porphyry system, $X(Na^+,aq)$ ranges from 0.77 to 0.85 for hydrothermal fluid at 400–840 °C²⁰. These fluid compositions are typical for magmatic fluids, that are originally rich in $NaCl$ ³². Thermodynamic modelling indicates that these fluids lie near the composition of a fluid equilibrated with albite and K-feldspar ($X(Na^+,aq) \sim 0.85$ @ 600°C; Fig. 3), and could initiate proximal albitisation or potassic alteration, depending of local conditions. Albitisation reactions result in a decreasing $X(Na^+,aq)$, and a small decrease would result in the formation of K-feldspar. However, equilibrium thermodynamic modelling suggests that potassic alteration in such a steady state system would be limited, and would feature co-existence of albite and K-feldspar, contrary to field observations of

early albite and late potassic alteration. Our experiments reveal that kinetic factors acting at the reaction interface may be important in forming potassium alteration zones surrounding and/or above the sodic alteration zone in such systems. The energetic barriers that need to be overcome to change from K-feldspar nucleation and growth to albite nucleation effectively result in the formation of K-feldspar even past the point where the fluid at the reaction front becomes supersaturated with respect to albite due to increasing Na/K ratios caused by K-feldspar precipitation. This maintains a high level of disequilibrium at the reaction front, which in turn contributes to pervasive mineral replacement.

In conclusion, sequential sodic and potassic alterations may be controlled by a self-evolved originally Na-enriched hydrothermal system, instead of externally driven chemical or physical changes. In nature, this internally-driven process most likely works in tandem with external drivers (e.g., the addition of external fluids, decrease of temperature and/or pressure, fluid unmixing). Plümper et al.¹⁰ recently highlighted the importance of the coupling between nano-scale reaction mechanism, that forms a transient reaction-induced porosity, and macro-scale fluid flow for explaining pervasive crustal, fluid-present reactions (e.g., metamorphism; dolomitisation). Our results show that another type of coupling between an internally driven kinetic process at the nano- to micro-scale, and externally driven factors (predictable using equilibrium thermodynamics) at the macro-scale, may contribute to explaining the widespread occurrence of albitisation as well as the common occurrence of potassic alteration overprinting this sodic alteration. In this case, the nano-scale factor is related to nucleation and growth at the fluid-mineral interface, and is controlled not only by external physical parameters such as pressure and temperature, but also by fluid composition, in our case the nature of halide (Cl versus F). These dynamic processes remain difficult to assess on a theoretical basis, and experiments remain critical in defining the mechanisms and kinetics of fluid-induced mineral reaction in the crust.

Declarations

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Figures

Figure 1

Fraction of reactant and reaction products as function of time in pure NaCl (A) and NaF solutions (B).

Figure 2

Reaction products and textures as a function of reaction time in NaCl- and NaF-solutions. (A-F) BSE images; NaCl solution for 1 (A), 3 (B) and 5 days (C), and NaF solution for 1 (D, E) and 5 days (F). (G-J) EMPA chemical maps of grains shown in (C) [G, H] and (D) [I, J].

Figure 3

Thermodynamic modelling of the stability of Na-K-feldspars and the evolution of solids and solution composition during hydrothermal reaction at 600 °C, 2 kbar. Starting compositions of fluids and minerals are listed in Table DR2. In all diagrams, X(Ab) is the percentage of albite end-member, and $X(\text{Na}^+) = a(\text{Na}^+)/[a(\text{Na}^+) + a(\text{K}^+)]$, where a is the activity coefficient of the associated ion. (A) Miscibility gap. (B) Lippmann diagram, and (C) its Na-rich portion; the thick and thin lines are the stable and metastable segments, respectively. Modelled mineral and fluid compositions during titration in (D) pure water; (E) NaCl; and (F) NaF solutions. (G) shows the equilibrium replacement of sanidine by co-existing albite and

K-feldspar¹⁸, a texture consistent with the predictions of models (D-E); and (H) is the sequential sodic and potassic replacement texture observed in this work.

Figure 4

Nano-SIMS analysis of reactions products formed in ^{18}O -enriched solutions within 1 day (A-C) and 5 days (E-F). (A, B, E, F) BSE images showing the reaction products; (C, G) oxygen isotopes maps; (D, H) $^{18}\text{O}/^{16}\text{O}$ line profiles of locations shown in (C, G). Note the brighter field in left side of C is due to charging issues, which result in higher counts of ions detected (Fig. DR5).

Supplementary Files

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