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A mechanism of mineral replacement: Isotope tracing in the model system KCl-KBr-H₂O

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Abstract—The solid solution-aqueous solution system KCl-KBr-H₂O is used as a model system to determine the mechanism of the replacement process of one crystalline phase by another. A single crystal of KBr was allowed to react with a saturated KCl solution enriched in ^{40}K and the resulting new product phases were analyzed for changes in both anion and K isotope composition, using SEM, EDX, microprobe analysis, mass spectrometry and X-ray diffraction. The results show that the new product, K(Cl,Br), contains elements derived from both the original fluid and solid phases, indicating that both anions and K isotopes are exchanged during the replacement reaction. The interface between the advancing reaction front and the original parent crystal is sharp on a micron scale, showing no reaction profile that could indicate a solid state diffusion mechanism. Macroscopically the new phase is turbid due to the development of porosity that is consistent with a net volume deficit replacement reaction and this porosity may act as an indication that a replacement process has taken place. Single crystal X-ray diffraction patterns show the preservation of the crystallographic orientation during the replacement process. The replacement mechanism is interpreted as a result of a coupled process of dissolution and recrystallization occurring at the fluid-crystal interface. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

Whenever minerals are no longer in equilibrium with surrounding fluids, mineral replacement reactions may occur. As aqueous fluids are ubiquitous over the surface and near-surface environments of the Earth, mineral replacement is a common process, which traditionally has been described in terms of ion exchange, diffusion, or coupled dissolution-reprecipitation reactions. The results of replacement reactions can be observed as new textures, overgrowths, volume or compositional changes, where all or some of these observations have been described as reaction rims, aureoles, metasomatism (e.g., albitization) or, if the complete replacement of one mineral by another is observed, preserving the external morphology, as pseudomorphism. The most common geologic process associated with mineral replacements is metamorphism. There are many well documented observations, such as pseudomorphism, that could indicate the existence of previous replacement reactions in rocks and minerals. The important feature of pseudomorphism is the preservation of the external shape of the parent crystal, that is, its external volume. This volume preservation would require that the rate of dissolution of the parent must equal the rate of crystallization of the product if continuity across a replacement interface is to be preserved, that is, a coupled process of simultaneous dissolution and recrystallization. Examples can be seen in the recent study by Brady et al. (2001) on lawsonite pseudomorphs from Syros, Greece. Waters and Lovegrove (2002) observed that pseudomorphs after chloritoid and cordierite conserve volume, suggesting a breakdown mechanism controlled by an interface process such as slow dissolution and crystallization, rather than by a transport step. Merino et al. (1993, 1998) have worked extensively on elucidating the mechanism of pseudomorphism. They conclude that the stress

imposed by the surrounding rock on the growing phase is the important factor in forcing the coupling between dissolution and precipitation. This process may be important in the brittle regime. There are many more examples of possible replacement reactions in rocks and minerals, such as those reviewed by Putnis (2002). In all cases where a partial replacement can be observed, a sharp compositional interface between parent and product is seen. However, the actual mechanisms involved in replacement reactions are not clearly understood because of the complexity of natural fluids and mineral solid solution systems, where the physical and chemical conditions during the replacement reaction are mostly unknown. As most rock-forming minerals are solid solutions, it is worthwhile investigating conditions under which solid solutions form or change as a function of the composition of the surrounding fluids.

By using isotopically enriched solutions, new product compositions that formed as a result of a replacement reaction can be analyzed even if parent and product contain the same elements. Previous isotope-exchange studies of replacement reactions have shown that dissolution-recrystallization is a dominant component of replacement processes. Using a combination of microprobe analysis, scanning X-ray maps and secondary ion mass spectrometry (NanoSIMS), Labotka et al. (2002) showed that the hydrothermal alteration of albite to K-feldspar proceeds by a coupled cation and oxygen exchange between the Na feldspar and a solution of KCl in water enriched in ^{18}O (HD^{18}O$_{0.5}$^{16}O$_{0.5}$). By using ^{18}O as a tracer, it was shown that this simple apparent cation exchange involved breaking all the Si-O and Al-O bonds in the original structure. Their conclusions confirmed the results of O'Neil and Taylor (1967) and O'Neil (1977), who also found a one to one correspondence between cation exchange and oxygen isotope exchange. O'Neil (1977) indicated that large scale ionic replacements cannot take place without complete reconstruction of the alumosilicate structure.

Recent work (Cole, 2000; Fiebig and Hoefs, 2002), based on

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O isotope-chemical relations, also showed that the O isotope compositions parallel variations in the cationic composition, the interpretation being that the O isotope exchange is the net result of bond breaking and dissolution of the mineral and the subsequent regrowth of the new mineral. Fiebig and Hoefs (2002) go further and state that the steep chemical gradients between secondary albite and plagioclase, as well as the absence of any isotopic and chemical gradients within the albite indicate that the isotopic and elemental exchange between fluid and plagioclase are controlled by dissolution-reprecipitation along microfractures, micropores and grain boundaries rather than by diffusion. These investigations point to the conclusion that replacement reactions can be controlled by surface-interface reactions such as dissolution-reprecipitation. Dissolution-reprecipitation in this context implies stoichiometric dissolution together with the formation of a new crystal structure.

Here we present an experimental investigation of a replacement reaction in the solid solution-aqueous solution (SS-AS) system KCl-KBr-H_2O, where one salt, KBr, is replaced by another, K(Cl,Br), with which it forms a continuous solid solution. The end member solubility products of KBr and KCl are $K_{sp} = 10^{1.129}$ and $K_{sp} = 10^{0.904}$ respectively and their molar volumes are 71.734 $Å^3$ pfu and 62.283 $Å^3$ pfu, giving a 13.2% decrease in molar volume between KBr and KCl. Both KCl and KBr are cubic (NaCl structure) and form as optically clear, colorless, cube-shaped crystals when saturated solutions are allowed to slowly evaporate. They are relatively soft (H=2.5) and cleave easily on [100]. KCl exists in nature as the mineral sylvite, commonly associated with halite deposits. This simple binary salt system was chosen for investigation for the following reasons: its crystallography and SS-AS equilibria are well known (Glynn et al., 1990; Dejewska, 1999); the reactions occur on a short time scale at room temperature; and it can be used as a simple replacement model for more complex mineral systems.

The KCl-KBr-H_2O system was first investigated (Putnis et al., 2001; Putnis and Mezger, 2002) as a simple replacement model where the initial compositions of both the fluid and solid phases were known precisely. Both end members were used as initial starting solid phases and a range of aqueous solution compositions was allowed to react with the solid substrate. The Cl-Br exchange was determined using microprobe analysis of the newly formed K(Cl,Br) solid solution phases and the system could be modelled using known thermodynamic properties and supersaturation calculations. However, this previous investigation revealed no information about the role of K in the replacement reaction. In the present study, the K in the KCl solution is characterized by its concentration and $^{39}K/^{40}K$ ratio. A solution enriched in ^{40}K was used to react with a single KBr crystal containing natural isotope abundances of K. Measurements of the K isotope ratio in the solution before and after replacement reactions, as well as the ratio in the newly developed K(Cl-Br) phase, together with quantitative information about the Cl-Br exchange, provide important constraints on the mechanism of the replacement process.

Isotope tracing of either the cations or anions involved in a reaction can provide a clear indication of the nature of the replacement process. Our results may be further applied to more complex, natural systems, where the development of secondary porosity, changes in chemistry, or the presence of a sharp reaction front may indicate that a replacement reaction took place.

2. EXPERIMENTAL PROCEDURE

2.1. Replacement Reactions

KBr crystals were grown by evaporation of supersaturated KBr solutions. Crystals were cleaved into sections approximately 3 × 3 mm and 1 mm thick, parallel to (100) immediately before the replacement experiments. Preliminary experiments were made to observe the rates of reaction, to ascertain optimum reaction times needed to see a well defined reaction interface within the crystal. A saturated solution (33.3 mg/100 μL) was prepared from KCl (MERCK 99.5%). 50 μL KCl solutions were placed on the surfaces of four similarly cleaved KBr crystals (these solution volumes covered the entire surfaces of the crystals) and allowed to react for 5, 15 30 and 60 min. After the respective reaction times, the solutions were removed by pipette. To remove any remaining solution and thereby to stop the reaction progress and to avoid precipitation by evaporation, the crystals were placed on an absorbent surface and pressurized air was gently blown over the surface. After initial microscopic observations, the 15 min was found to be an optimum time for the experiment to see and characterize the reaction interface and so experiment times of 10 and 15 min were chosen for the following experiments.

A second saturated solution, enriched in ^{40}K ($^{39}K/^{40}K$ = 12.26, $^{41}K/^{40}K$ = 5.97 with a certified isotopic composition: ^{39}K = 63.77%; ^{40}K = 5.2%; ^{41}K = 31.03%, obtained from Campro Scientific (T-4003 lot2) was prepared. The KBr parent crystal has the natural isotope composition: ^{39}K = 93.25%; ^{40}K = 0.01%; ^{41}K = 6.73%, giving ratios of $^{39}K/^{40}K$ = 9325, $^{41}K/^{40}K$ = 673 (De Bièvre and Taylor, 1993). 50 μL of the isotopically enriched KCl solutions were then placed on the surfaces of two similarly cleaved KBr crystals and allowed to react for 15 min (experiment 1) and 10 min (experiment 2), respectively, after which the solutions were removed by pipette and later measured for their $^{39}K/^{40}K$ ratio. All experiments were carried out at room temperature (22 °C). A further similar experiment was observed under a reflected light microscope, but in this case, the KBr crystal was placed in a drop of saturated KCl solution, so that the solution did not cover the top of the crystal. This enabled direct observation of the moving interface. To show any differences between these experiments and simple dissolution in water, the same experiment was carried out using a similar KBr crystal and 50 μL deionized water.

2.2. Analytical Techniques

To analyze the partially replaced crystal and to expose the depth of the reaction front, the crystals were cleaved normal to the surface. Samples, of approximately 500 μg each, were taken from the replaced section using a fine mounted needle under a binocular microscope from 5 positions between the original crystal surface and the reaction front (Fig. 1). These samples were analyzed for their $^{39}K/^{40}K$ ratio using a VG Sector 54 mass spectrometer. For analysis the sample was loaded on a Re triple-filament array. The ratios were corrected
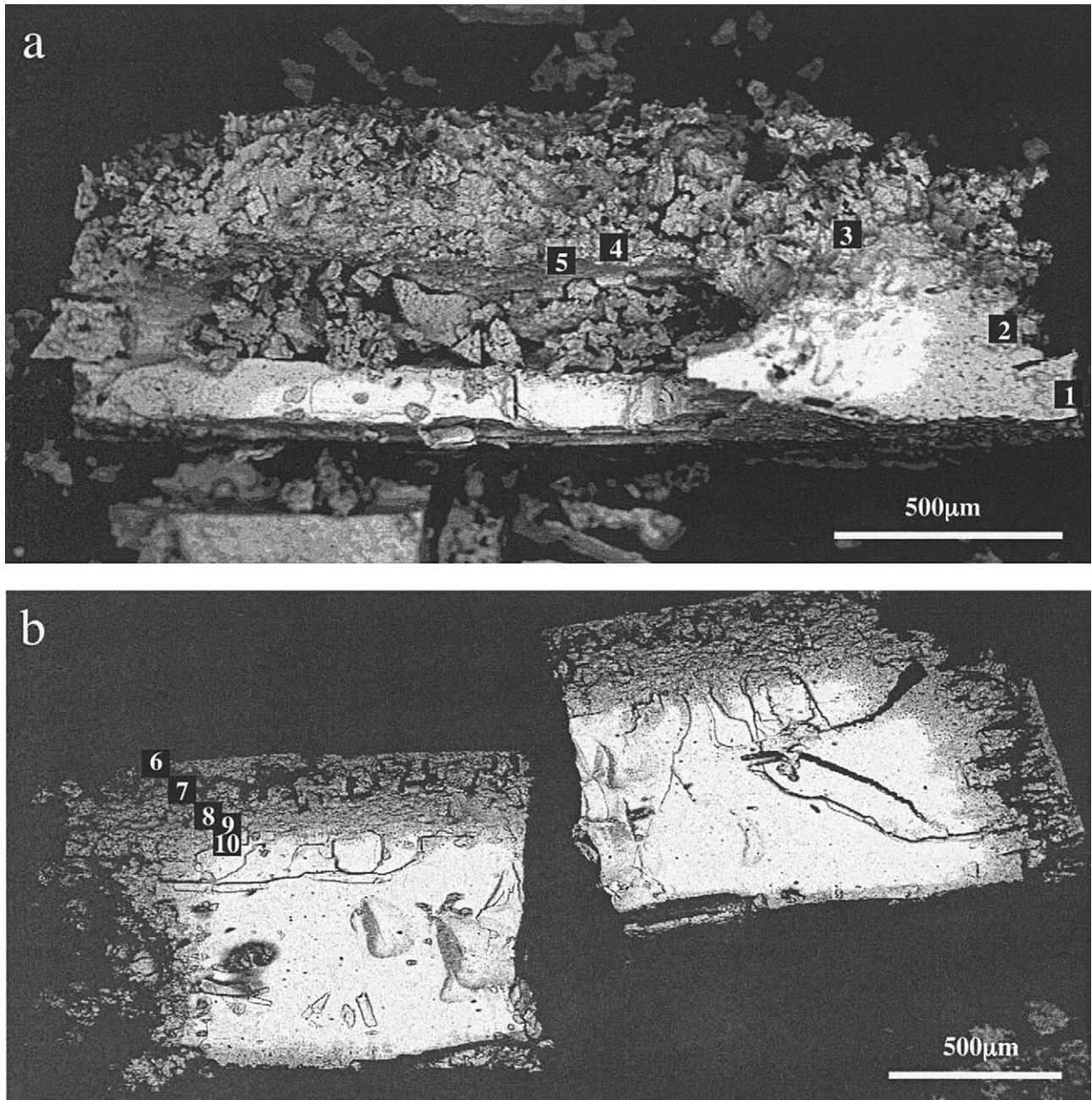
Fig. 1. Backscattered SEM images of vertical sections through replaced crystals showing positions where the samples for analysis were taken. (a) Experiment 1 (15 min), 1–5. (b) Experiment 2 (10 min), 6–10.

for mass spectrometric mass fractionation using a correction factor determined by multiple analyses of natural K.

For secondary (SEM) and back scattered electron (BSE) observations the samples were mounted onto aluminium stubs and secured with Leit-C tabs and subsequently carbon coated. The samples were imaged with a SEM (JEOL JSM 6300F) at 20 kV and using analySIS (Soft Imaging System) software. Energy Dispersive X-ray (EDX) analyses were made with a 10 min collection time, using an Oxford Instrument OX 2000 INCA system. Chemical composition of the replaced phases

was obtained by Electron Microprobe analysis (JEOL 8600 MXA).

A single KBr crystal was mounted on a fibre and a Laue X-ray diffraction pattern collected. This crystal was then dipped in a saturated KCl solution for a few minutes, then mounted again on the diffractometer and a second XRD pattern collected. After reaction with KCl, the crystal was composed of the newly replaced K(Cl,Br) phase, together with the remaining unreacted KBr parent crystal (confirmed by powder X-ray diffraction). To determine the relative crystallographic orienta-
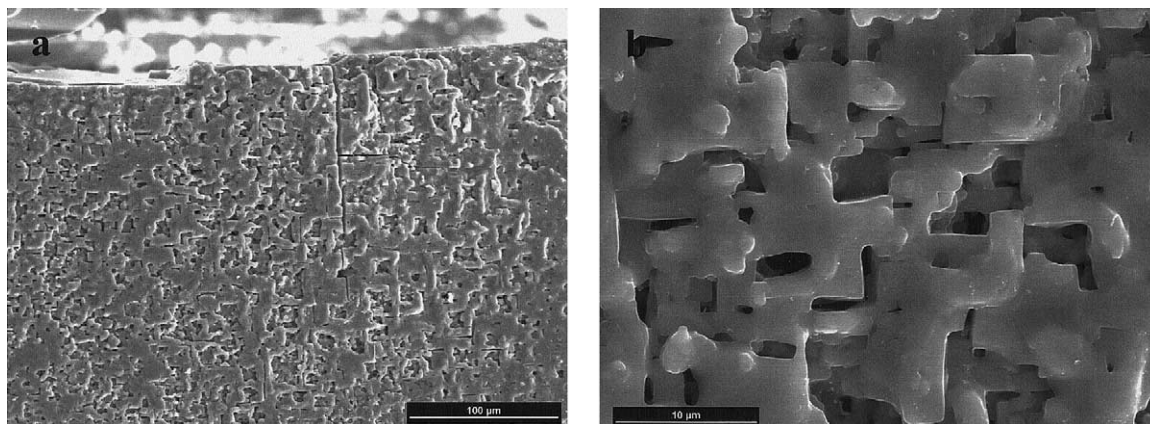
Fig. 2. SEM image of the porous surface of a crystal after replacement (experiment 2), showing the orientation of pores parallel to cleavage directions. (a) Surface of replaced crystal. (b) Magnification of (a) from a central area.

tion and coherence between the replacement and parent phase, the XRD patterns were compared.

X-ray powder diffraction data was also collected (Philips X'pert PW 3040, using monochromatic Cu Kα1 radiation) on a pure KBr parent crystal, a crystal that had reacted with a saturated KCl solution for 10 min, i.e., a mixture of KBr + K(Cl,Br), and from a crystal that had reacted with a saturated KCl solution for an hour, i.e., K(Cl,Br). Lattice parameters were determined from each pattern and molar volumes calculated. Chemical compositions of the product phases were determined from the linear relationship between molar volumes and molar fractions of the K(Cl_xBr_{1-x}) solid solution (Dejewska, 1999).

3. RESULTS

3.1. Macroscopic Observations

The original KBr crystals were optically-clear cleaved sections, which on reaction with the saturated KCl solutions, including the ^{40}K enriched KCl solution, immediately turned white and developed a friable reaction rim during the course of the experiment. The replacement reaction begins at the surface of the KBr parent crystal, confirmed by observing the reaction progress in reflected light using a binocular microscope. When a KBr crystal was placed in a KCl solution, which did not cover the crystal, an interface moving toward the center of the crystal was seen as the affected areas of the crystal changed from transparent to opaque white. The external dimensions of the original crystal were preserved throughout the replacement process. However, when the experiment was repeated using deionized water, the crystal of KBr started to dissolve immediately, remaining optically clear until it had dissolved completely in 20 s.

3.2. Scanning Electron Microscopy and Chemical Analysis

SEM images of partially replaced KBr crystals show the formation of a highly porous replaced material. On the surface, the pores are oriented parallel to cleavage directions (Fig. 2). In cross sections cleaved normal to this surface, this network of

pores extends downward (Fig. 3) to the replacement interface. Some elongated channels or cracks are also visible, although it is possible that these are a result of the cleaving process directly along the line of interconnecting pores. BSE images (Fig. 4) show that the replacement front (dark area) has a sharp, wavy interface with the original parent crystal (light area). The replaced rim shows homogeneous BSE contrast and no evidence of unreacted KBr.

From measurements of the depth of this replacement (using analySIS), information about the reaction kinetics can be derived. The reaction interface moved through the parent crystals, resulting in average rates of interface migration of 0.46 μm/s and 0.42 μm/s for reaction times of 10 min and 15 min respectively. The reaction rates decreased with time to approach an apparent equilibrium after 60 min, when all the parent crystal is replaced (Fig. 5). This is expected as the solution composition approaches an equilibrium with the solid composition for the given volume of solution and solid available for reaction

EDX analyses, elemental dot maps and line profiles (Fig. 6) across the replaced sections show the formation of a K(Cl,Br) solid solution. The Kα intensity profiles of Cl and Br through the replaced crystal are highly variable, corresponding to porosity in the replaced phase, and in the parent phase are probably due to tiny particles of the product phase on the surface, resulting from the cleavage process. The Cl profile shows a decrease toward the replacement interface, which would correspond to the continuing replacement process of the fluid evolving in composition continuously as the process proceeds. This is discussed further below. The position of the interface, measured from BSE images, occurs exactly at the same position as the ^{40}K exchange (380 μm for experiment 1 and 275 μm for experiment 2), indicating that the anions, Cl and Br, are exchanging concomitantly with the cations, K.

Microprobe data for K(Cl,Br) replacement phase was only semiquantitative because of the rough cleaved surface, but gives a maximum KCl molar fraction of 0.5 after 60 min and 0.25 after 15 min and decreases slightly 20–30 μm toward the reaction interface. The chemical composition determined from the lattice parameters (from the X-ray powder diffraction data)
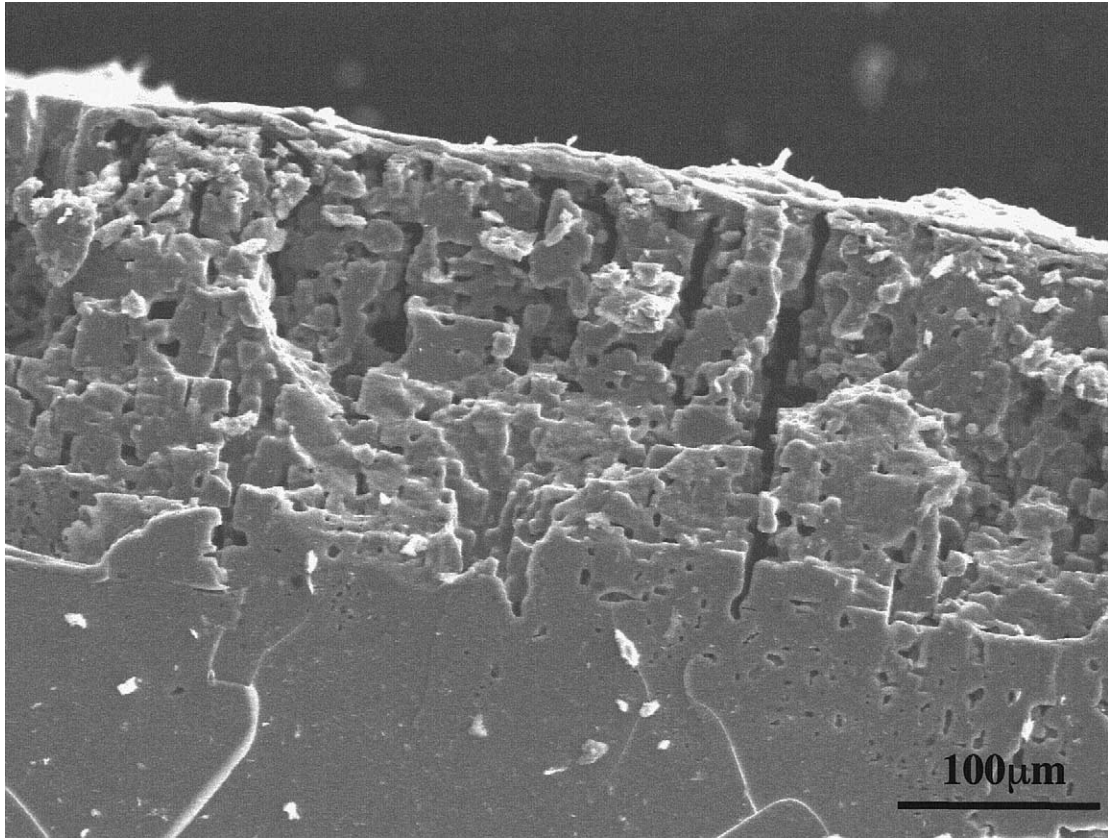
Fig. 3. SEM image of a cross section normal to the surface through a replaced crystal (experiment 2) showing the network of pores extending downward through the crystal to the replacement interface.

of the replacing phase resulted in a KCl molar fraction of 0.53 after 60 min and 0.24 after 15 min reaction times.

3.3. X-ray Diffraction

Single crystal XRD (Laue) patterns show that the crystallographic orientation of the original KBr crystal was maintained in the porous product K(Cl,Br) solid solution throughout the replacement process. This implies that one single crystal of KBr was replaced by a new K(Cl,Br) single crystal, crystallographically continuous across a very sharp (on a micron scale) reaction interface. Both the original KBr and the replaced K(Cl,Br) phase show no significant differences (Fig. 7), each having clear single crystal diffraction patterns, even though the new phase is highly porous and friable.

X-ray powder diffraction patterns (Fig. 8) of the original KBr and the new K(Cl,Br) product phases after 10 min and 60 min reaction times show the progressive change in lattice parameters with composition and time. The pattern for pure KCl is given for reference. The product phase shows significant line broadening which may be due to a variation in composition across the replaced zone, the high porosity of the product or a combination of both. From the X-ray powder data the overall molar volume decrease in the K(Cl,Br) product phase relative to the KBr parent is 3.9% after 10 min and 7.5% after 60 min. This is insufficient to account for the high degree of porosity.

3.4. Isotope Analyses

Results of measured ^{39}K/^{40}K isotope ratios are presented in Table 1 and a profile across the replaced crystal is shown in Figure 9). Isotope fractionation due to kinetic processes is negligible for these experiments, because K occurs only in the +1 valence and is relatively heavy. The ^{39}K/^{40}K in the original parent crystal is 9325. The KCl solution used in our experiments had ^{39}K/^{40}K = 12.293. The significant increase in ^{39}K/^{40}K across the replacement is consistent with the concept of a new replacement phase continuously evolving in composition together with the changing solution composition. The isotope variations shown in Figure 9 indicate that the replaced phase has incorporated K from both the parent crystal and the ^{40}K enriched KCl solution. This is also evident from the change in the measured ^{39}K/^{40}K in the solution from an initial value of 12.293 to a final value of 19.27 for experiment 1 and 19.26 for experiment 2.

3.5. Determination of the Origin of the K in the new K(Cl,Br) Phase

From the measured ^{39}K/^{40}K ratios across the replaced crystal, it is possible to calculate the amount of K that entered the newly formed K(Cl,Br) crystal from the original KCl solution and the KBr solid.

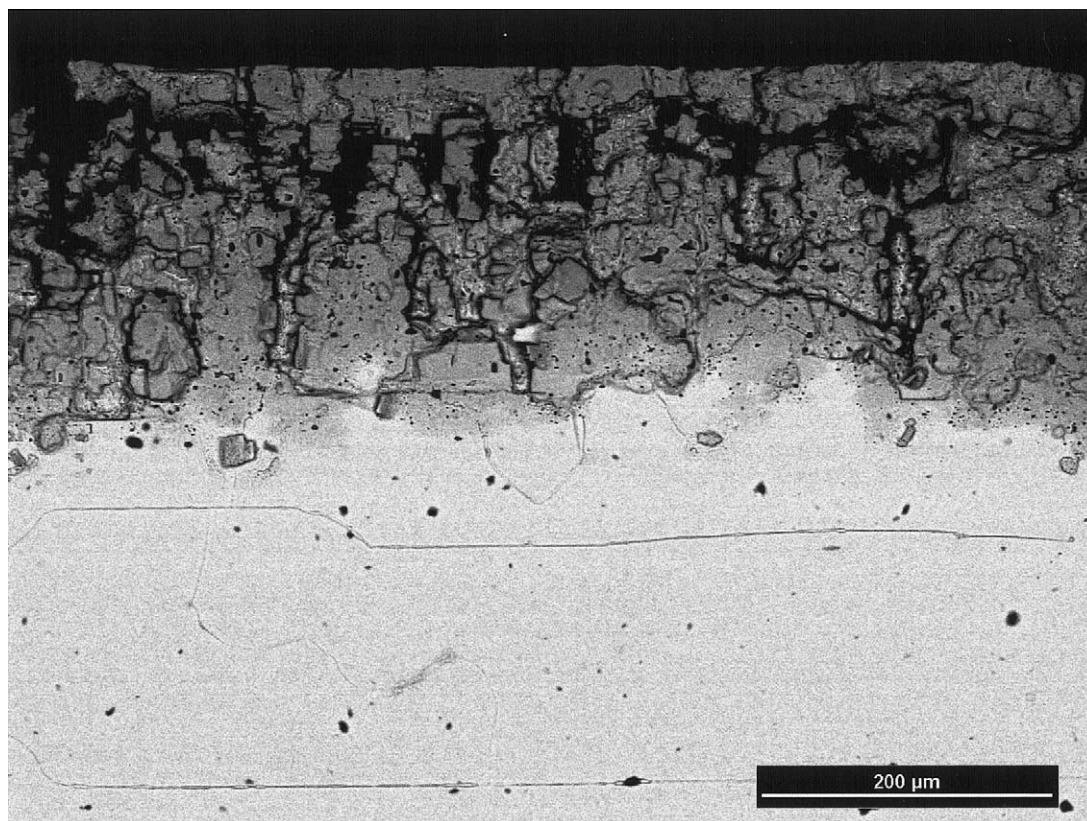If in the replacement product, K(Cl,Br), a fraction x of the K

Fig. 4. Backscattered SEM image showing the sharp replacement interface (experiment 2); the lighter center is the original KBr crystal and the darker rim is the new replacement K(Cl, Br) phase.

is derived from the parent KBr crystal and a fraction $(1 - x)$ from the ^{40}K enriched KCl solution, then:

$$(1 - x)\frac{^{40}K_{solution}}{(^{39}K + {}^{40}K)_{solution}} + x\frac{^{40}K_{KBr}}{(^{39}K + {}^{40}K)_{KBr}}$$

$$= \frac{^{40}K_{product}}{(^{39}K + {}^{40}K)_{product}} \quad (1)$$

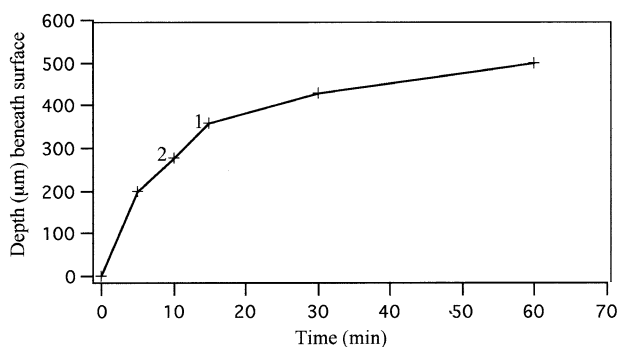Given that the measured initial solution ^{39}K/^{40}K is 12.293 and

Fig. 5. Plot shows the interface position measured from the crystal surface against time, i.e., rates of the interface migration, indicating a decrease with time approaching an equilibrium for the given solid and solution volumes. Experiment 1 (15 min) 4.2 μm/s and experiment 2 (10 min) 4.6 μm/s

the KBr solid ^{39}K/^{40}K is 9325, and if, (as in experiment 1) the final ^{39}K/^{40}K is measured to be 35.49, the value of x from the above equation gives the result that the new product phase, close to the reaction interface, has 63.4% K from the original KBr parent and 36.6% from the ^{40}K enriched KCl solution.

4. DISCUSSION

The analytical results and direct observations are consistent with a replacement mechanism of coupled dissolution-reprecipitation. The replacement reaction begins at the original crystal surface and a reaction interface moves through the original crystal. For such a replacement reaction there are two main parameters to consider: changes in composition and changes in texture.

4.1. Changes in Composition

From our results it is clear that the reaction of a KBr crystal with a saturated KCl solution to form the solid solution, K(Cl,Br), cannot be simply described as an anion exchange reaction. K isotope analyses of the present study show conclusively that K in the lattice was exchanged with K from the solution concomitantly with the anion Cl-Br exchange. Starting at the surface of the crystal, as the initial interface, a reaction front is produced that then proceeds to move through the crystal. At this interface a simultaneous dissolution-recrystallization process takes place. The implication is that the rate of
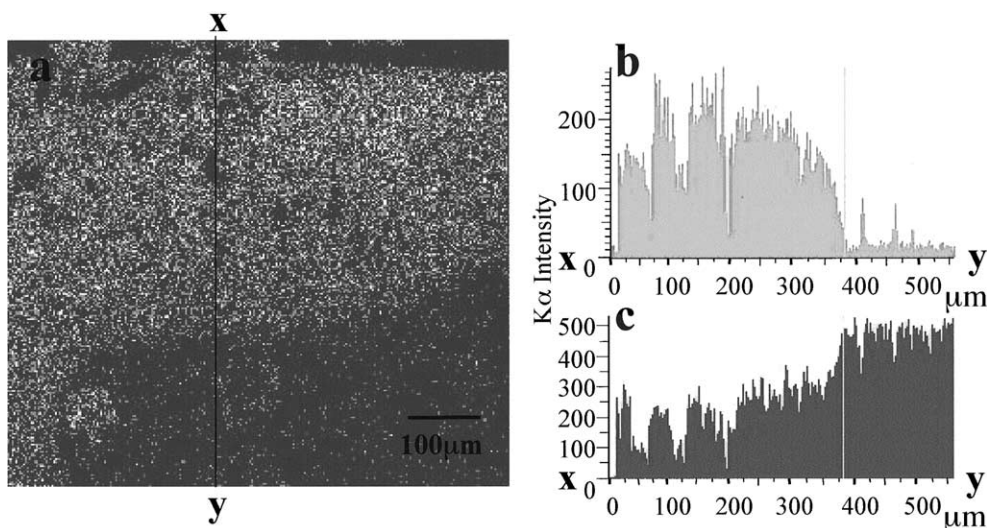
Fig. 6. a) EDX dot map of Cl distribution in the partially replaced crystal. b) Kα intensity profile of Cl through the replacement crystal. Profile corresponds to the vertical line, x-y, shown in a) c) Kα intensity profile of Br, also corresponding to x-y. The highly variable intensity profiles in the replaced phase are due to porosity, and in the parent phase are due to tiny particles of the product on the surface, resulting from the cleavage process.

dissolution of the parent phase is equal to the rate of crystallization of the product phase. To understand the compositional evolution in such a SS-AS system requires knowledge of the thermodynamic properties of all the phases involved.

To define the replacement process, the relationship between the aqueous and solid phases at equilibrium is represented on a Lippmann phase diagram (Lippmann, 1980). The Lippmann diagram for the KCl-KBr-H_2O system was calculated by Glynn et al. (1990), constructed from the experimental data of Durham et al. (1953). This diagram consists of two curves, solidus and solutus, which express the total solubility product, $\Sigma\Pi = [K^+]([Br^-] + [Cl^-])$, as a function of the solid and liquid composition, respectively. $\Sigma\Pi$ is represented on the ordinate and the activity fraction of the aqueous phase, together with the mole fraction of the solid phase are represented on a double scale on the abscissa. Horizontal tie lines connect solid and aqueous compositions at equilibrium. The two expressions

for the total solubility product, as a function of the solid and fluid composition are:

$$\Sigma\Pi_{eq} = K_{KCl}X_{KCl}\gamma_{KCl} + K_{KBr}X_{KBr}\gamma_{KBr} \quad \text{(solidus)} \quad (2)$$

$$\Sigma\Pi_{eq} = \frac{1}{\dfrac{X_{Cl,aq}}{X_{KCl}\gamma_{KCl}} + \dfrac{X_{Br,aq}}{X_{KBr}\gamma_{KBr}}} \quad \text{(solutus)} \quad (3)$$

where K_{KCl} and K_{KBr} are the solubility products of the solid solution end members; X_{KCl} and X_{KBr} are the molar fractions in the solid; γ_{KCl} and γ_{KBr} are the solid phase activity coefficient and $X_{Cl,aq}$ and $X_{Br,aq}$ the activity fraction of the ions in solution. Further discussions of solid solution solubilities and thermodynamic equilibrium states are given by Glynn (2000). Since in a solid solution the solubility product varies with the composition, the saturation in a SS-AS system must be expressed as
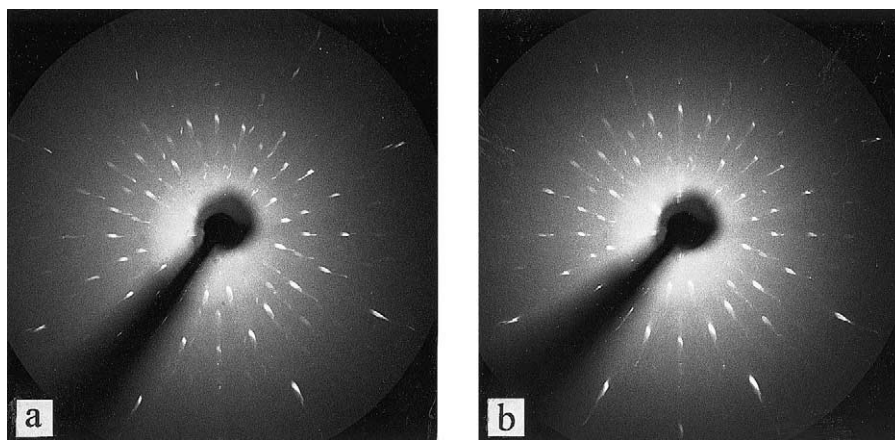

Fig. 7. Single crystal XRD (Laue) patterns show that the crystallographic orientation of the original KBr crystal (a) was maintained in the porous product K(Cl, Br) solid solution (b) throughout the replacement process.
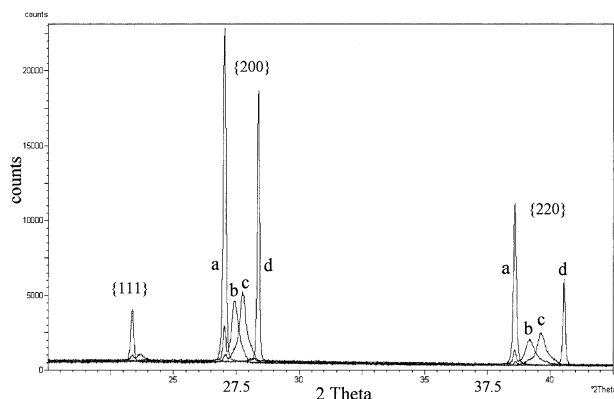
Fig. 8. X-ray powder patterns of the original KBr (peak a) and the new K(Cl, Br) product phases after 10 min and 60 min reaction times (peaks b and c respectively) show the progressive change in lattice parameters with composition and time. The pattern for pure KCl (peak d) is given for reference. The product phases show significant line broadening which may be due to a variation in composition across the replaced zone, the high porosity of the product or a combination of both.

Fig. 9. Graph shows the change in $^{39}K/^{40}K$ isotope ratios across the replaced crystal in experiment 1 (15 min). The sudden increase in $^{39}K/^{40}K$ at the reaction interface is due to the very low (0.01%) abundance of natural ^{40}K. The replaced section of the crystal clearly shows the presence of ^{40}K from the enriched solution.

a function of the composition of the solid. This means that an aqueous solution with a given composition will be differently saturated or undersaturated with respect to each composition of the solid.

In our experiments a crystal of KBr in contact with a saturated KCl solution begins to dissolve at the surface. The aqueous solution at the crystal-fluid interface becomes enriched in Br and its composition moves along the solutus in the Lippmann diagram shown in Figure 10. The addition of Br to the fluid saturates it with respect to a K(Br,Cl) solid solution at the interface and simultaneously a new phase recrystallizes, momentarily in equilibrium with the solution composition. Although a certain degree of supersaturation must be achieved to nucleate this solid solution, the high solubility of these phases as well as the fact that the nucleation is epitaxial at the surface of the preexisting KBr substrate, means that near-equilibrium conditions will be maintained throughout the process. Therefore, there is a continuous reequilibration between the fluid and the precipitating phase as the coupled dissolution-reprecipitation process proceeds.

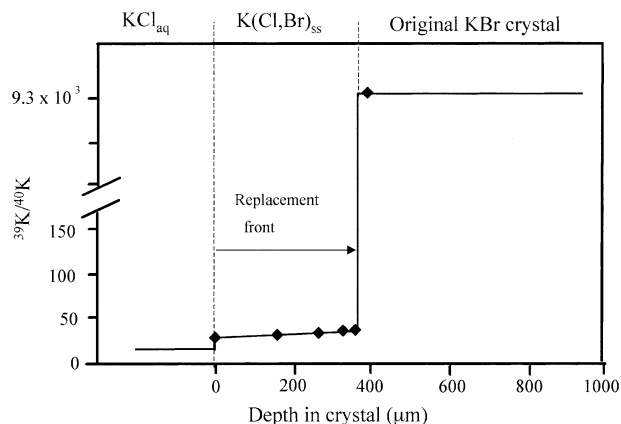The compositional evolution of the product phase moves in the direction of the arrow along the solidus curve on the

Lippmann diagram (Fig. 10). It can be seen that the solid composition must be initially Br rich at the interface and then moves along the solidus curve to become more Cl rich until an equilibrium is reached. This can only be when all of the parent crystal is replaced. The final compositions of the aqueous solution and product solid solution will depend on the solid-fluid ratio. In the experiments described here, the evolution of the composition of the product phase can be seen from the X-ray powder diffraction patterns (Fig. 8). Because the first replacement at the surface is a solid solution close in composition to the parent, it is likely that this first K(Br,Cl) replacement constrains the crystallographic uniformity across the interface, i.e., an epitaxial replacement. With the advancing interface, the previously formed new phase has to reequilibrate with respect to the changing solution composition. This means that the cell parameters of the new phase differ further from the first formed phase and consequently further from the parent phase, as can be seen in the X-ray powder diffraction lines. The continuous reequilibration between solid and liquid during the dissolution-reprecipitation process may also explain the line widths of the X-ray powder patterns as due to the compositional zoning resulting from the continuous mass transport between the reaction interface and the aqueous solution.

When a mineral is in contact with a fluid supersaturated with

Table 1. Results of the measured $^{39}K/^{40}K$ isotope ratios. Errors are within run uncertainty obtained for 20 ratio measurements.

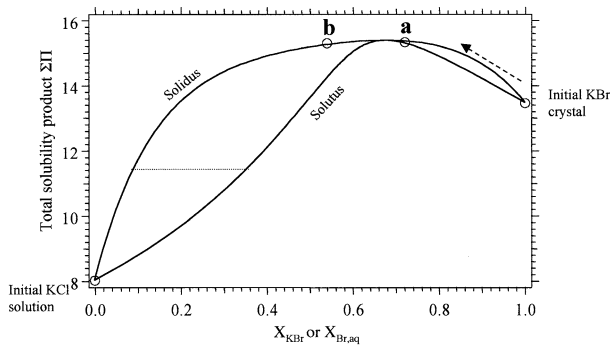| Experiment 1 (15 min)			Experiment 2 (10 min)		
Sample	$^{39}K/^{40}K$		Sample	$^{39}K/^{40}K$	
Spike	12.293 (2)		Spike	12.293 (2)	
R1 solution remaining after exp. 1	19.27 (3)	Distance in μm	R2 solution after exp. 2	19.26 (17)	Distance in μm
1	24.25 (3)	0	6	23.07 (2)	0
2	32.05 (5)	164	7	31.53 (3)	88
3	35.78 (6)	267	8	35.32 (4)	185
4	33.66 (4)	340	9	42.08 (2)	220
5	35.49 (5)	380	10	42.02 (2)	275

Fig. 10. Lippmann diagram (simplified) for the SS-AS system KCl-KBr-H$_2$O. Horizontal tie lines connect solid and aqueous compositions at equilibrium. The arrow indicates the direction of the K(Br, Cl) replacement evolution from the original KBr crystal. Positions a and b represent the respective positions of the new solid composition after 10 min and 60 min reaction time at 22°C. After 60 min the original KBr crystal was totally replaced and so this point, b, represents an equilibrium position for the replacement reaction given the relative amounts of solid and solution initially present.

respect to elements at the other compositional end of their solid solution, it is replaced by a new phase of mixed composition, momentarily in equilibrium with the fluid, which then evolves in composition for as long as the reaction proceeds.

4.2. Changes in Texture

The associated development of porosity enhanced both the reaction rate and efficiency of the process by providing possible pathways for chemical transport. A replacement reaction is often characterized by the development of porosity in the newly formed phase, that is, a resulting volume deficit. In turn, replacement reactions are promoted by the porosity of the newly formed phase which allows for the supply of the supersaturated fluid phase to reach the reaction interface. The original external dimensions of the parent crystal are preserved, so the porosity indicates that some KBr has been lost to the solution, which is also consistent with the observations from the present experiments that indicate a change in K-isotope composition of the fluid during the course of the reaction. The molar volume of the new K(Cl,Br) phase is 3.9% lower than the molar volume of the parent, KBr phase. Because this is not sufficient to account for the amount of porosity produced, we must consider the contribution from solubility differences of the SS-AS end members. In the case of the KCl-KBr-H$_2$O SS-AS system, KBr is more soluble than KCl, resulting in more KBr being lost to the solution. Therefore in any replacement, it is necessary to know the solubility of the solid phases as a function of the fluid composition, temperature and pressure, as well as the molar volume changes. Solubility diagrams (also called concentration or Schreinemaker diagrams) have been used to describe experimental solubility data for simple salt systems (Korzhinskii, 1970; Glikin and Sinai, 1991, 1993; Glikin, 1995, 1996) and from these diagrams it is possible to determine quantitatively the relative amounts of the different phases. To model the overall volume change, the two important parameters were discussed by Pollok et al. (2002). Firstly, the relative solubilities of the solid components involved in a replacement reaction

and secondly, the relative molar volume changes. Pollok et al. (2002) calculated volume changes in the KCl-KBr-H$_2$O system quantitatively and found that solubility differences between the primary crystal and the replacement phase mainly influence the sign and extent of the relative volume change, that is, whether the formation and degree of porosity as a result of a volume deficit is likely to occur. Molar volume changes also play a part but to a lesser extent, as confirmed in our experiments, where the molar volume change is relatively small. It has been shown that if solubility differences favor a volume deficit, even though the new phase has a higher molar volume, a resulting porosity can still occur. This is the case for the replacement of leucite (KAlSi$_2$O$_6$) by analcime (NaAlSi$_2$O$_6$ · H$_2$O), (Putnis, 1994), where the replacing phase, analcime, has a higher molar volume (~10%) than the parent, i.e., leucite, but the reaction always proceeds to form a highly porous analcime replacement.

If one considered the rate of migration of the interface in terms of a diffusion model where the distance migrated $x = (Dt)^{1/2}$, the value of the diffusion coefficient D obtained from our data is of the order of 10^{-6} cm^{2}s^{-1}. This value is typical of a self-diffusion coefficient in an aqueous solution and ~10 orders of magnitude larger than typical solid state diffusion rates in alkali halides. This supports the conclusion that transport in the fluid phase controls the reaction rate and that the coupled dissolution-reprecipitation mechanism proposed here is the dominant process controlling the replacement reaction.

5. CONCLUSIONS

Careful considerations of the parameters of solubility, molar volumes, chemical changes and textural observations give good indications as to whether a replacement reaction has taken place. Analysis of isotope exchanges further and more precisely constrains the replacement mechanism. The implications of our findings can be applied to more complex natural systems, but the reaction features observed in the KCl-KBr-H$_2$O system share many characteristics of natural replacement reactions:

1. The development of a replacement rim that differs compositionally from the parent crystal-mineral. Such rims or coronal reaction textures are commonly observed macroscopically in the phenocrysts of igneous rocks (e.g., Ca feldspar rich rims surrounding K rich feldspars in Rapakivi granites, such as discussed by Wark, 1992) and in metamorphic minerals where partial pseudomorphs are common. Current work, such as reported by Hellmann et al. (2002, 2003), to characterize the sharpness of the interface, will help to further understand the replacement mechanism. Hellmann et al. (2002, 2003) have reported on the "leaching" of feldspars. From high resolution TEM and chemical analyses of acid treated labradorite, they found that the interface was sharp, structurally and chemically on a unit cell scale, suggesting a dissolution-recrystallization mechanism. Such "leaching" has previously been considered as a diffusion process.

2. Secondary minerals often have a high porosity. The development of a porous texture, is often seen macroscopically as turbidity in the replaced zone. Dissolution pathways, provided by porosity, enhance the exchange of cations and anions at rates greater than expected from interdiffusion. Lee and Parsons (1997) have reported on the albitization of alkali feldspars

where the replacive albite is characteristically rich in micropores.

3. The preservation of crystallographic orientation, results from a topotactic replacement. This indicates the reaction must occur at the replacement interface as a simultaneous dissolution-recrystallization process to transfer crystallographic information across the interface. When albite $NaAlSi_3O_8$ is reacted with KCl solutions to form sanidine, $KAlSi_3O_8$, O'Neil (1977) noted the fine scale dissolution and reprecipitation in a fluid film at the interface between exchanged and unaltered feldspar.

Observation of some or all of these features may be an indication that a dissolution-recrystallization replacement reaction took place.

Implicit in the understanding of replacement reactions is the role of fluids. Fluids enable chemical constituents to be transported to the reaction site, they facilitate the concentration of elements to result in a saturated solution at or near the reaction interface and enable the more soluble elements to be removed from the replacement zone to result in the development of porosity. In turn, this porosity further facilitates the movement of the fluid through the replacement zone to the reaction interface. The broad implications of this study are that aqueous fluids play a major role in mineral replacement reactions by enabling dissolution-recrystallization processes to take place. Isotope tracers can serve to constrain this process by indicating more precisely the origin of the elements present in a replacement.

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