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Mineral Replacement Reactions

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INTRODUCTION

Whenever a mineral or mineral assemblage comes into contact with a fluid with which it is out of equilibrium, reequilibration will tend to take place to reduce the free energy of the whole system (i.e., of the solid + fluid). Such fluid-solid interactions span a very wide range of possible reactions, and are responsible for most of the mineral assemblages we see in the Earth's crust. However, before discussing mineral replacement reactions, we will put them into the broader context of fluid-solid interactions by considering some examples of such reequilibration.

In the simplest case, we could consider the situation where a mineral, thermodynamically stable under some specific temperature and pressure conditions, comes into contact with pure water, such as quartz within its stability field (e.g., at $T = 100$ °C and 1 atmosphere pressure). Clearly, quartz will tend to dissolve until, at equilibrium, the aqueous silica solution, which at neutral pH is $H_4SiO_{4(aq)}$, becomes saturated with respect to quartz. The reaction for this equilibration can be written:

$$SiO_{2\,(qtz)} + H_2O \leftrightarrow H_4SiO_{4(aq)} \tag{1}$$

The equilibrium solubility constant for reaction (1) is given by

$$K_{sp}(qtz) = \frac{a(\mathrm{H_4SiO_4})_{aq}}{a(\mathrm{SiO_2})_{qtz} \cdot a(\mathrm{H_2O})} = a(\mathrm{H_4SiO_4})_{aq}$$

where $a(i)_{aq}$ stands for the activity of the parenthetical aqueous species. For the case of pure quartz and pure water where the activity is 1, $K_{sp}(qtz) \sim 1.2 \times 10^{-3}$ at 100 °C and 1 atmosphere pressure. However, if under these conditions the solid silica phase in contact with pure water was cristobalite (the high temperature polymorph of SiO_2), the resulting aqueous solution, saturated with respect to cristobalite, would be supersaturated with respect to quartz, since the less stable phase is more soluble. The value of K_{sp} for cristobalite at 100 °C and 1 atmosphere pressure is $\sim 5.1 \times 10^{-3}$. Thus the thermodynamics would indicate that quartz *should* precipitate from such a solution. On the other hand, as is well known, the kinetics of nucleation may preclude any precipitation, and the solution may remain supersaturated with respect to every silica phase more stable than cristobalite. If quartz did precipitate from a solution which had equilibrated with respect to cristobalite, this transformation from cristobalite to quartz would be an example of what has been termed a "solvent-mediated phase transformation" (Cardew and Davey 1985) whose kinetics are many orders of magnitude faster than the solid state transformation of cristobalite to quartz under similar temperature conditions. However, Cardew and Davey considered that the dissolution of the metastable phase and the nucleation and growth of the more stable phase took place *independently*. In this chapter, we will be concerned about how these two processes may be coupled.

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There are many examples of polymorphic phase transformations achieved by dissolution and reprecipitation. One of the most studied is the transformation from aragonite to calcite. Early studies (e.g., Brown et al. 1962) already confirmed that the transformation at low temperatures was up to 10 orders of magnitude faster in the presence of H_2O than in the dry system. The important implication for geosciences is that aragonite preserved in high pressure rocks (within the stability field of aragonite) which have been exhumed to pressures where calcite is the stable polymorph must have remained dry during uplift (Carlson and Rosenfeld 1981; Carlson 1983; Essene 1983). The aragonite to calcite transformation is complicated in many natural environments because of the known (but poorly understood) effect of the presence of background ions in the solution, some of which accelerate and others inhibit the transformation. However, the details of the aragonite to calcite transformation in complex aqueous solutions such as sea-water are beyond the scope of this chapter.

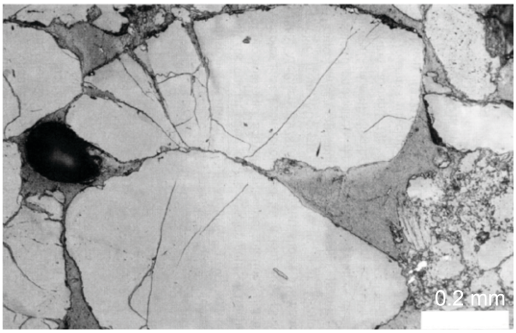


Figure 1. Indented quartz grains due to intergranular pressure solution in a sandstone. (Image: F. Renard)

Dissolution and precipitation are the principal driving mechanisms for all reequilibration reactions in the presence of a fluid phase. Relatively small free energy reductions can drive large-scale processes. For example, in a sedimentary sandstone deposit the stresses developed at quartz grain-grain contacts due to the weight of the overburden are sufficient to increase the solubility of the stressed contact relative to the unstressed mineral phase. This results in *intergranular pressure solution* (Fig. 1) which causes the dissolution of material at grain contacts, transport of material in solution and reprecipitation at sites of low stress, ultimately causing the compaction and lithification of the sediment (Rutter 1983; Gratier and Guiget 1986; Renard et al. 2000; Revil 2001; Chester et al. 2004; Lang 2004). However, even in such an apparently simple case of a dissolution–precipitation reaction, the rate controlling processes are still poorly understood. Furthermore, the pore fluid chemistry is known to strongly influence the dissolution and precipitation rates of quartz and hence the compaction rate due to pressure solution may either be increased or decreased depending on the specific ions in solution (Dove and Rimstidt 1994). The presence of other solid phases which in turn change the chemistry of the fluid by dissolution will also therefore affect the dissolution–precipitation rates. For example, the presence of a small clay fraction in the quartz can significantly enhance the pressure solution and hence the compaction rate (Renard et al. 1997).

A decrease in free energy of a solid + fluid system can also be achieved by grain coarsening. The larger surface:volume ratio of small crystals relative to large crystals translates into a higher solubility for the former, and hence the dissolution of small crystals and the precipitation onto larger crystals of the same phase is also mechanism of reducing the free energy of the system. That a reduction in interfacial free energy can drive a dissolution-precipitation reaction has been demonstrated by Nakamura and Watson (1981) who showed that dense pressed pellets of synthetic quartzite, when placed in contact with silica saturated fluid, recrystallize and coarsen by a dissolution-precipitation mechanism. Significantly, this process generates new porosity at the recrystallization front, as the fluid infiltrates the dense pellet. The porosity generation, which implies that some of the silica is transferred to the fluid phase, creates permeability in the recrystallized part of the pellet, and allows the fluid to infiltrate and remain in contact with the as yet unrecrystallized solid. Porosity generation is an important theme in this chapter.

Increasing the complexity of the fluid phase by the addition of other components dissolved in the solution, increases the complexity of the thermodynamics and the nature of the phases which can potentially precipitate. For example, if we consider the reaction between feldspar and an acidic fluid, the dissolution of the feldspar results in a fluid which becomes supersaturated with respect to kaolinite. The reaction with potassium feldspar may be written as:

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 4H_4SiO_{4(aq)} \qquad (2)$$

and the resultant solution becomes enriched in silica and potassium ions. A similar reaction can be written for the breakdown of other feldspar compositions, in which case the resultant solution would also be enriched in Na^+ and Ca^{2+}. In the presence of an applied stress, the dissolution reaction would be promoted by pressure solution, in other words the stress would drive the kaolinite-forming reaction.

If we consider reaction (2) in two sequential steps, with an acidic aqueous solution first dissolving the K-feldspar congruently to form a solution containing K, Al, and Si dissolved in some complexed form in the fluid, and then the subsequent precipitation of kaolinite when the supersaturation becomes sufficiently high for nucleation, we also need to ask how far this solution is transported from the dissolution site before kaolinite precipitates. We also might consider the role of the residual alkali and silica rich fluid in further reactions with other mineral phases. If we generalize such a dissolution–transport–precipitation scenario we can apply this to a conceptual model of how mineral-fluid reactions work in a polyphase rock. Disequilibrium between a fluid and a rock can arise by the infiltration of a fluid with composition such that it is out of equilibrium with the mineral or mineral assemblage, or by a change of temperature and/or pressure. In either case this will generally lead to a dissolution process, and the resulting fluid may become supersaturated with respect to a number of new solid phases. The application of stress in the same situation may enhance the dissolution reactions.

Such a situation has been described in the context of prograde metamorphic reaction mechanisms by Carmichael (1969) who demonstrated how in a closed system, in which the overall chemical composition of solid + fluid remains constant, a sequence of dissolution and precipitation sub-reactions can explain the textural development of a metamorphic rock on a thin-section scale. However, the sub-reactions involved in the individual steps of dissolution–transport–reaction–precipitation are metasomatic reactions i.e. with local changes in composition and redistribution of material. Thus on a small spatial scale the system is "open" while on a larger scale the system may be closed.

The linkage between deformation and induced chemical reactions in a rock has been explored by Wintsch (1985) and Wheeler (1987) and forms the basis for a unified conceptual framework in which fluid-driven dissolution-precipitation processes determine both the deformation mechanisms and the chemical reactions in the rock. Depending on the length-scale of transport of different components in the fluid, the redistribution of elements may result in very marked modification of textures during syntectonic mineral growth. Evidence for mass transfer by solution resulting in deformation is well documented in sedimentary and low grade metamorphic rocks (Passchier and Trouw 1996) and is increasingly recognized as a mechanism of deformation (dissolution and replacement creep) in higher grade mid-crustal rocks (Wintsch and Yi 2002) and high pressure metamorphic environments (Schwarz and Stöckert 1996; Stöckert et al. 1999).

In the case of kaolinite formation from granitic rocks, the development of a pure kaolinite deposit implies the long-range transport of the other elements removed from the granite. Under suitable conditions these may become concentrated and hence sufficiently supersaturated to precipitate metal-rich mineral deposits. In Cornwall, England a complex sequence of hydrothermal alteration processes eventually results in very pure kaolinite, mined as "china clay." Although most of the kaolinite-rich deposits preserve very little of the original rock texture, the formation of kaolinite *pseudomorphs* after Carlsbad-twinned feldspar is not uncommon. Figure 2 shows an example of such a pseudomorph, defined as a replacement of a parent mineral by a product phase or phase assemblage, while preserving the external shape and dimensions of the parent. Such a phenomenon is not merely a mineralogical curiosity, but raises quite fundamental issues about the nature of dissolution, transport, and precipitation during fluid-mineral interactions, including metaomatism, metamorphism, diagenesis, and chemical weathering. Clearly, in the case of pseudomorphism, the dissolution and precipitation are spatially coupled.

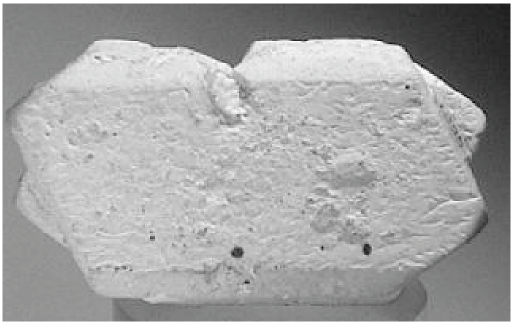


Figure 2. Pseudomorph of kaolinite after Carlsbad-twinned feldspar.

PSEUDOMORPHIC REPLACEMENT – VOLUMETRIC CONSIDERATIONS

Preservation of external shape and dimensions is a key feature of the pseudomorphic replacement of one mineral by another. There are many parent–product mineral pairs such as that shown in Figure 2 where the volume is apparently preserved. We now consider reaction (2) again, and determine the volume change involved in converting 2 moles of K-feldspar to one mole of kaolinite. Standard data bases give the molar volumes of K-feldspar and kaolinite as ~109 cm^3mol^{-1} and ~99 cm^3mol^{-1} respectively. Reaction (2) would therefore involve a volume decrease in the solids of ~50%. To preserve the external volume of the parent during a pseudomorphic replacement reaction, the reaction must be rewritten so that it is balanced on volume. The principle of balancing volumes in replacement reactions was pointed out almost 100 years ago by Lindgren (1912). To illustrate this, but approximating the molar volumes of K-feldspar and kaolinite as equal, reaction (3) is balanced so that one mole of K-feldspar is replaced by one mole of kaolinite:

$$KAlSi_3O_8 + Al^{3+} + 5H_2O \rightarrow Al_2Si_2O_5(OH)_4 + K^+ + 2H^+ + H_4SiO_{4(aq)} \qquad (3)$$

There are a number of important principles which arise from considering a reaction of this kind, as pointed out by Merino et al. (1993) and Merino and Dewers (1998). First, the replacement requires input of Al and the loss of Si. The Al in solution may come from the dissolution of a more aluminous mineral elsewhere in the rock. In replacement reactions we must consider that every element involved may be mobile and that assuming immobility of an element to balance metamorphic reactions may not be valid. A second point to consider is that the product kaolinite in the reaction may be porous and hence a volume calculation would need to take into account any porosity generated by the reaction. As we shall see however, to understand porosity generation we will need to consider other factors as well as molar volume changes.

Another common replacement reaction in rocks is the serpentinization of olivine and orthopyroxene. If we assume olivine as forsterite, Mg_2SiO_4, the orthopyroxene as enstatite $MgSiO_3$ and serpentine as lizardite, $Mg_3[Si_2O_5](OH)_4$ and take the molar volumes as ~50 cm^3mol^{-1}, ~25 cm^3mol^{-1} and ~100 cm^3mol^{-1} respectively, reactions balanced on volume could be:

$$2Mg_2SiO_4 + 2H^+ + H_2O \rightarrow Mg_3[Si_2O_5](OH)_4 + Mg^{2+} \qquad (4)$$

$$4MgSiO_3 + 2H^+ + 5H_2O \rightarrow Mg_3[Si_2O_5](OH)_4 + Mg^{2+} + 2H_4SiO_{4(aq)} \qquad (5)$$

However, textural relations between serpentinites and their parent minerals indicate that constant volume replacement may not always apply. There are observations of pseudomorphic replacement (e.g., Dungan 1979), while in other cases expansion of 50-60% has been estimated for the formation of serpentine mesh textures in olivine (Shervais et al. 2005). Figure 3 is a back-scattered SEM image of serpentinized olivine, showing a typical mesh texture. The replacement appears to preserve the volume, although it would be difficult to claim that no expansion has taken place. Without some reference points it is not always obvious whether a replacement is truly pseudomorphic. Thus although serpentinization involves a dissolution and precipitation process it is not clear under what conditions a constant volume replacement takes place and under what conditions the reaction is isochemical for some elements. For example, if we assumed that there was no significant loss of Si in the reaction, the reaction for the serpentinization of orthopyroxene could be:

$$2MgSiO_3 + Mg^{2+} + 3H_2O \rightarrow Mg_3[Si_2O_5](OH)_4 + 2H^+ \qquad (6)$$

which would imply a 50% increase in the volume. On the other hand, reaction (4) preserves both the volume and the silica composition. The release of Mg in reaction (4) is consistent with the observation in Figure 3 that the veins contain magnesite, $MgCO_3$, also indicating that the fluid contained dissolved carbonate ions.

The above examples suggest that the fluid chemistry and the stress generated by such reactions will play a role in determining whether a replacement takes place at constant volume.

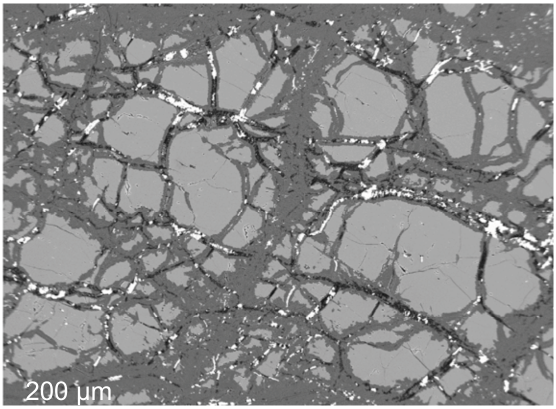


Figure 3. Back-scattered SEM image of a typical mesh texture in serpentinized olivine. The dark grey areas are serpentine, the lighter grey areas are olivine, and the black material in the veins is magnesite. The brightest phase in the veins is hematite. (Image: H. Austrheim)

STUDIES OF MINERAL REPLACEMENT REACTIONS: EXPERIMENT AND NATURE

Mineral replacement is the underlying process in the rock cycle of the Earth. The long time-scale of geological processes has frequently led to the assumption that the mechanism of mineral reequilibration is by slow reactions achieved by solid-state diffusion through crystal structures. However, the contention in this chapter is that in the presence of an aqueous fluid phase, solid state reactions compete kinetically with dissolution-precipitation reactions and that the latter will dominate over a wide range of crustal temperatures. The ubiquitous nature of mineral replacement in the crust, and the fast kinetics of dissolution-precipitation reactions means that unless reactions are incomplete and the parent and product phases can be texturally related, the mechanism of replacement and even the nature of the protolith may remain uncertain. Pseudomorphs provide a clue, but ultimately to understand the mechanism of pseudomorphism and replacement, we need to combine experimental studies with observations from nature.

The examples which follow are chosen to illustrate specific aspects of replacement processes which contribute to a better understanding of the mechanisms involved.

The replacement of calcite ($CaCO_3$) by fluorite (CaF_2)

It has long been known that carbonate fossils can be converted to fluorite by treatment in hydrofluoric acid to improve the appearance of fine anatomical details (e.g., Cookson and Singleton 1954; Grayson 1956). This somewhat surprising result was experimentally verified using cleavage rhombs of calcite immersed in hydrofluoric acid at room temperature by Glover and Sippel (1962). The principal conclusions were that (i) the replacement is pseudomorphic, (ii) the polycrystalline fluorite is composed of parallel oriented fibers which inherit their orientation from the calcite structure, (iii) the kinetics of the growth of the fluorite replacement rim is such that the thickness of the rim is linearly related to the square root of time, indicating that the rate of replacement is controlled by mass transfer through the reacted rim and (iv) the molar volume reduction results in a porous reaction rim which allows fluid infiltration to the replacement front.

The replacement of aragonite and calcite by hydroxyapatite $Ca_5(PO_4)_3(OH)$

When single crystals of aragonite or calcite are treated hydrothermally at 200 °C with an aqueous solution of diammonium phosphate, $(NH_4)_2HPO_4$, the carbonates are pseudomorphically replaced by polycrystalline hydroxyapatite, HAP (Kasioptas et al. 2008). Figure 4 shows the development of reaction rims in each case. As in the replacement by fluorite, the HAP crystals are fibrous and parallel to the reaction interface. If we write the reaction as:

$$5CaCO_3 + 3HPO_4^{2-} + H_2O \rightarrow Ca_5(PO_4)_3OH + 3CO_3^{2-} + 2H_2CO_3 \qquad (7)$$

the change in molar volume of the solid phases is −6% in the case of aragonite to HAP, and −12.7% in the case of calcite. For a pseudomorphic replacement, the molar volume change is compensated by generation of porosity in the product. This porosity allows fluid infiltration to the reaction front and also may explain the observation that the reaction is faster with calcite than with aragonite, even though aragonite is less stable than calcite at the temperature of the experiment.

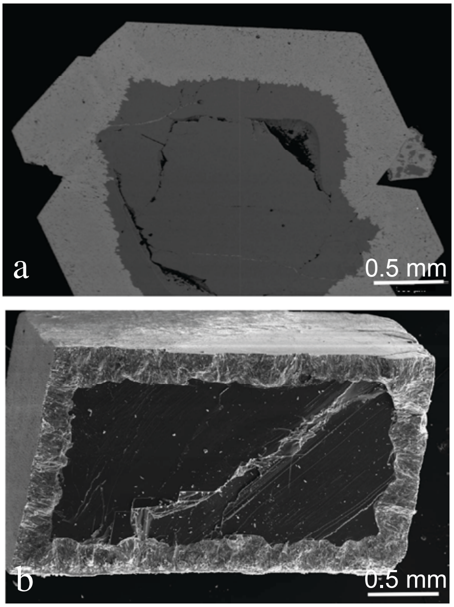


Figure 4. (a) Back-scattered SEM image of a cross-section through a partially pseudomorphed aragonite single crystal. The central darker core is aragonite, the rim is polycrystalline apatite. (b) Cleaved cross section through a partially pseudomorphed calcite crystal. The rim is polycrystalline apatite. (Image: A. Kasioptas)

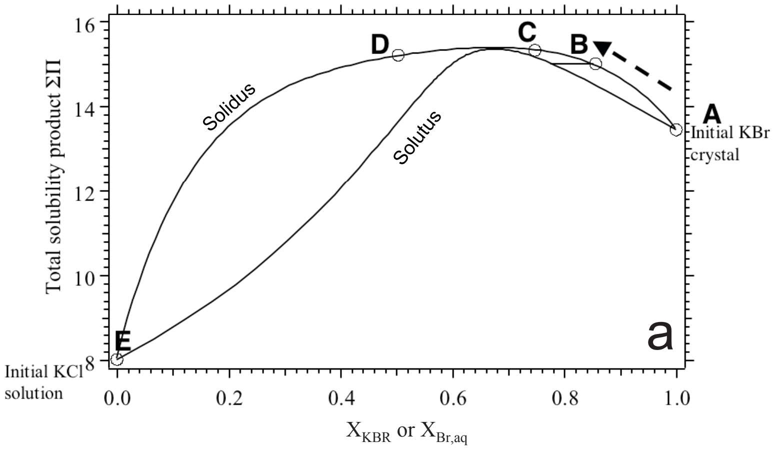
A common factor in the above examples is that the carbonates are placed in a solution with which they are out of equilibrium, and will therefore begin to dissolve, introducing Ca ions into the solution. Secondly, both calcium fluoride and hydroxyapatite are significantly less soluble than the parent carbonate phases.

One problem in analyzing such experiments is that there is generally no available data for the solubilities of the parent and product phases in the specific solvent used, nor is there kinetic data to determine the rate controlling step in the overall replacement process. Some progress has been made in this direction by a study of replacement in a simple solid solution system KBr-KCl-H_2O in which the solubilities and solid-fluid equilibria are known.

The replacement of KBr by KCl

When a single crystal of KBr is placed in a saturated KCl solution at room temperature, an immediate replacement reaction begins from the original crystal surface with dissolution of KBr and the simultaneous reprecipitation of a K(Br,Cl) solid solution (Putnis and Mezger 2004; Putnis et al. 2005). As the replacement continues the original dimensions of the crystal remain unchanged, and, with excess KCl solution available for reaction, eventually the end result is a single crystal of almost pure KCl. This remarkable and simple experiment has given us many clues about what controls the mechanism of this process. KBr-KCl forms a solid solution at room temperature and to understand the replacement process in a more quantitative way, we must refer to the equilibrium solid solution – aqueous solution phase diagram, termed a Lippmann diagram (Lippmann 1980) (Fig. 5).

At the beginning of the experiment the KBr crystal is far out of equilibrium with the KCl solution and hence will begin to dissolve. As soon as some KBr is dissolved in the KCl solution, the Lippmann diagram shows that the solution will now be in equilibrium with a new composition of the solid solution. Experiments show that the first product phase formed on the surface of the dissolving KBr crystal is a solid solution rich in KBr and that as the replacement progresses the rim becomes increasingly KCl rich (points A-E) in Figure 5a. Figure 5b shows the development of the reaction rim during the replacement. The compositional evolution of the



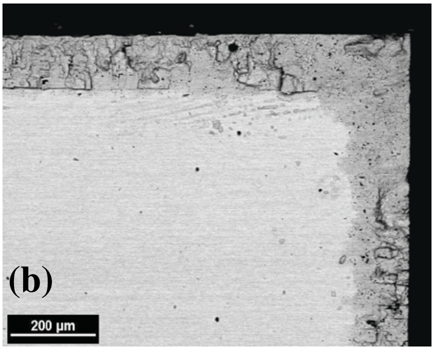


Figure 5. (a) Lippmann phase diagram for the system KBr-KCl-H_2O, with labels A-E showing the progressive change in the composition of the replaced rim shown in (b). The pale core in (b) is KBr.

reaction rim shows that it is controlled by the fluid composition at the interface with the solid. If the initial small quantity of dissolved KBr mixed with the larger volume of KCl solution, the Lippmann diagram would suggest equilibrium with a KCl-rich solid solution—i.e., the first precipitate would then be near point E—which was not found to be the case. The conclusion that the fluid composition at the interface, which also evolves with time, controls the replacement is a significant observation. Real time phase-shift interferometry (Putnis et al. 2005) also confirms that the dissolution and precipitation process is confined to a fluid boundary layer at the reaction interface, which has a different composition to the fluid in the bulk.

The kinetics of replacement is about 10 orders of magnitude faster than would be expected from a solid state ion-exchange process of Cl replacing Br. A dissolution–precipitation mechanism is further confirmed by isotope tracer experiments. When the KCl fluid is enriched in ^{40}K as a tracer, mass spectrometry confirms that the ^{40}K is incorporated in the product KCl (Putnis and Mezger 2004).

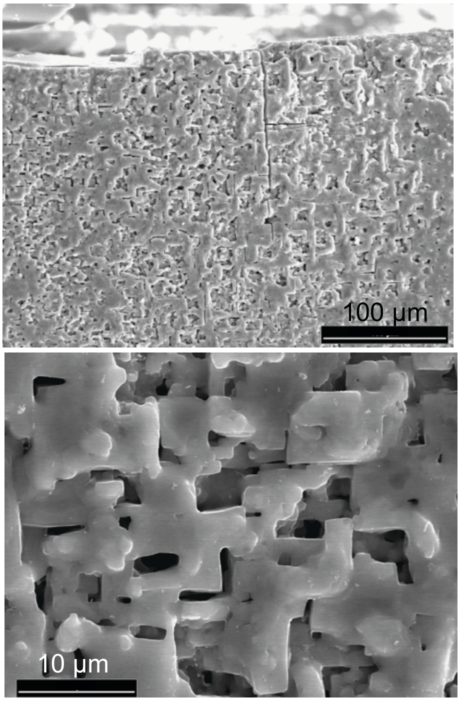


Figure 6. SEM image showing the porosity developed on the surface of a single crystal of KBr which has reacted with a saturated KCl solution. The surface composition is K(Br,Cl). [Used with permission of Elsevier from Putnis and Mezger (2004).]

A further important observation is that the product K(Br,Cl) rim is porous and permeable to the infiltrating fluid (Fig. 6), and as the compositional equilibration is achieved, textural equilibration also evolves, with the coarsening of pores and eventual loss of permeability. When the crystal composition has equilibrated with the fluid, the driving force for textural equilibration is the reduction of interfacial surface area. This is a slower process, but if the crystal remains in the fluid, eventually the rim becomes clear and pore-free. The generation of porosity allows the replacement reaction to proceed, providing pathways for mass transport. During the replacement, the porosity generated, or in other words, the volume in the reaction rim occupied by the fluid phase, is higher than would be expected from the reduction of solid molar volume in replacing KBr by K(Br,Cl). This is another important observation which indicates that the porosity generation is a function of both the change in molar volume of the solids as well as the relative solubilities of the parent and product phases in the aqueous solution. A difference in solubility means that during a replacement process, more of the parent phase may be dissolved than the product precipitated (i.e., some solid material remains in the fluid phase). Further examples of this may be found in Putnis (2002) and more experiments on replacement processes in simple salt systems are described by Glikin (2008).

The replacement of leucite $KAlSi_2O_6$ by analcime $NaAlSi_2O_6{\cdot}H_2O$

Given that both of these phases have very large structural channels (analcime is often classified as a zeolite) this pseudomorphic replacement would be considered as a typical ion exchange process where the alumino-silicate framework acts passively while the alkali ions and water molecules diffuse through the crystal structure. However, experiments by Putnis et al. (2007b), in which single crystals of leucite are reacted with a 3.5% NaCl solution at 150 °C, showed conclusively that the replacement proceeds by a dissolution-precipitation mechanism (Fig. 7a). There is no diffusion profile at the sharp reaction interface, and Raman spectroscopy shows that a tracer of ^{18}O in the aqueous solution is incorporated in the analcime aluminosilicate framework. A significant observation in this example is that although there is an increase in molar volume of 10%, porosity is generated in the analcime rim. Conventional wisdom would suggest that a volume increase should close any porosity, but in this case the porosity must be due to the fact that more leucite is dissolved than analcime precipitated, and this outweighs the effect of molar volume increase. More recent work by Xia et al. (2009a) has verified that the crystallographic orientation of the leucite is preserved after the replacement, and also that fine-scale twinning is therefore also preserved (Fig. 7b) They also noted that the rate of replacement is slowest at neutral pH and also that the porosity is dependent on the pH.

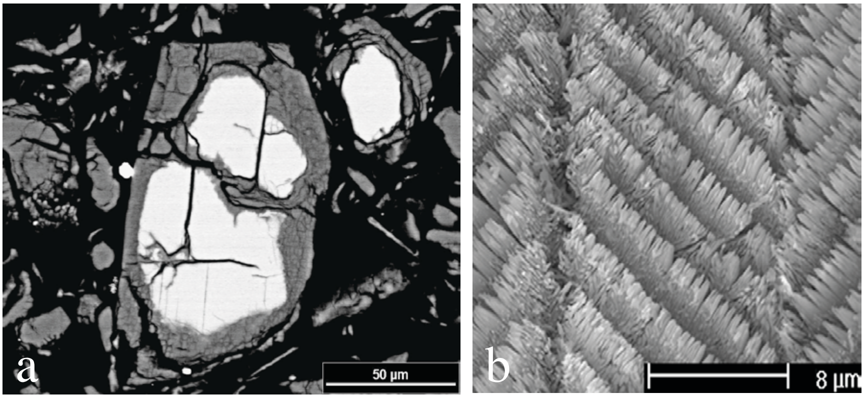


Figure 7. (a) Back-scattered SEM image of a cross section of a leucite crystal (white core), partially replaced by analcime (grey). (Image: C. V. Putnis) (b) SEM image of analcime which has replaced leucite, retaining the fine-scale twinning. (Image: F. Xia)

The replacement of pentlandite $(Fe,Ni)_9S_8$ by violarite $(Ni,Fe)_3S_4$

In a comprehensive study of the kinetics and mechanism of mineral replacement reactions, Tenailleau et al. (2006a) and Xia et al. (2009b) investigated the roles of temperature and fluid composition on the replacement of pentlandite by violarite at temperatures between 80 and 210 °C in fluids of varying pH and composition. Xia et al. (2009b) introduced the concept of the *scale of pseudomorphism* to describe the degree of spatial coupling between the dissolution and the precipitation process. When the rate controlling step (at $1 < pH < 6$) is pentlandite dissolution, nanometer scale coupling precisely preserves the morphology and internal details of the parent phase, as is seen texturally in natural pentlandite/violarite assemblages (Fig. 8). At higher pH values violarite precipitation appears to be rate limiting (and is then more “loosely coupled” to the dissolution), and the result is a less perfect pseudomorph, on a length scale of 10’s of microns rather than nanometers. The rate of replacement increases with increasing oxidants, and decreases with Ni^{2+} or Fe^{2+} addition in the fluid. Furthermore, the rate increases with temperature up to 125 °C and then decreases at higher temperatures, again emphasizing that the equilibria are controlled by fluid-solid thermodynamics. Previous publications on sulfide-sulfide replacements favoured a solid state reaction in which Fe,Ni ions were exchanged by solid state diffusion, while the sulfur close-packing remained inert. Xia et al. (2009b) show conclusively that in their experiments, and in nature, by implication from textural comparisons, that this is not the case.

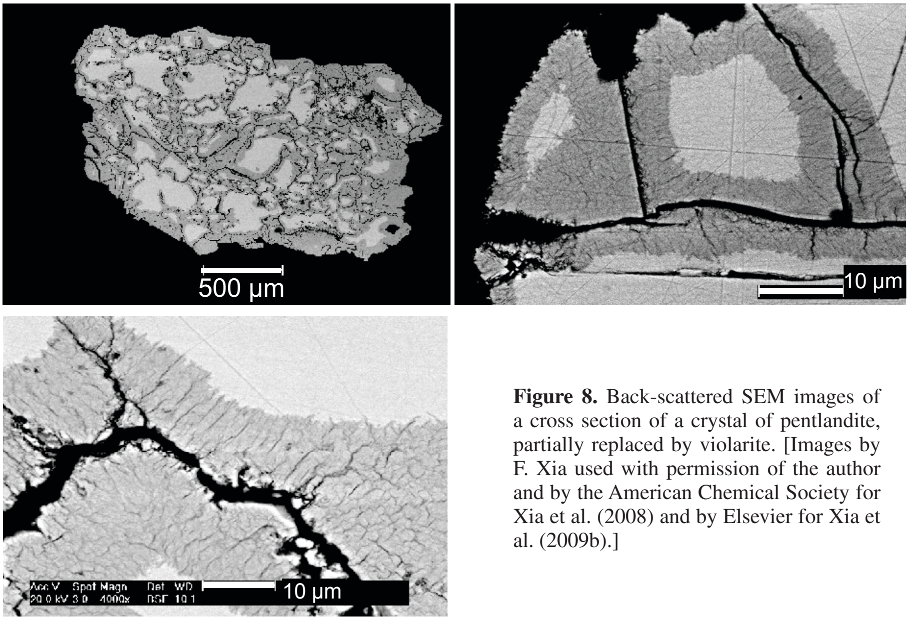


Figure 8. Back-scattered SEM images of a cross section of a crystal of pentlandite, partially replaced by violarite. [Images by F. Xia used with permission of the author and by the American Chemical Society for Xia et al. (2008) and by Elsevier for Xia et al. (2009b).]

Hydrothermal alteration of natural pyrochlore $(Ca_{1.23}Na_{0.75})Ta_{1.78}O_{6.28}F_{0.57}$

When a solid reacts with a fluid, the apparently selective removal of some components is often referred to as "leaching," a term which also carries with it the implication of a solid-state diffusion mechanism. When natural pyrochlore is treated in a solution containing 1M HCl and 1M $CaCl_2$ at 175 °C, Ca and Na are selectively removed from the pyrochlore, leaving a rim of depleted composition but with the crystal structure retained (see Fig. 9) (Geisler et al. 2005a). This may seem to support an "ion-exchange" reaction between the solid and the fluid. However, the rapid reaction rate at these moderate temperatures, the occurrence of a reaction interface that is sharp on the nanometer scale as observed by transmission electron microscopy (Geisler et al. 2005b), and the incorporation of ^{18}O from an enriched fluid into the pyrochlore structure are all inconsistent with a solid state diffusion mechanism. The data are consistent with a pseudomorphic reaction that involves the dissolution of the pyrochlore parent and the simultaneous re-precipitation of a defect pyrochlore at a moving reaction interface. Although the fluids used in the experiments are more aggressive than would be found in nature, it is remarkable that the experimental alteration features are very similar to those found in naturally altered pyrochlore samples (Geisler et al. 2004).

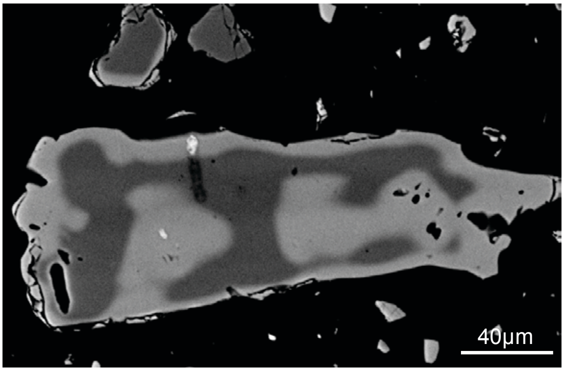


Figure 9. Back-scattered SEM images of a cross section of a crystal of pyrochlore. The darker core is the original pyrochlore composition, while the paler area is depleted in Ca and Na. (Image: T. Geisler)

The significance of pyrochlore is that ceramic materials based on pyrochlore are considered as good candidates for the immobilization of highly radioactive waste (Ewing 2005). One reason for such a choice is the low solubility of pyrochlore in aqueous fluids. However, because coupled dissolution-precipitation reactions take place at the parent-product interface, the relative solubility of the two solids is more important than their absolute solubility as only a small amount of material needs to be in solution at the interface at any one time. This same point comes up in the following example.

Reequilibration of zircon ($ZrSiO_4$) in aqueous fluids

Although ideal zircon is stable under crustal conditions, and is considered to be a very resistant mineral to alteration because of its low solubility (Tromans 2006), natural zircons formed at high temperatures can contain substituted thorium, uranium, scandium and hafnium substituting for Zr in solid solution. These solid solutions are non-ideal and are characterized by wide miscibility gaps at low temperatures. Thus the thermodynamics predicts that phases such as thorite ($ThSiO_4$), coffinite ($USiO_4$), thortveitite (Sc_2SiO_4) and hafnon ($HfSiO_4$) should exsolve at low temperatures. However, solid state exsolution textures have not been reported and are highly unlikely due to the slow diffusion of cations in zircon at crustal conditions (Cherniak and Watson 2003). However, natural zircons which have been exposed to hydrothermal fluids have regions with textures very similar to those expected from dissolution–precipitation reequilibration mechanisms. Figure 10 shows a typical example, in which the pristine zircon has a lighter back-scattered contrast and contains higher concentrations of substituted elements compared to the porous altered zircon (darker contrast) which contains inclusions of silicates such as thorite (Spandler et al. 2004; Soman et al. 2006; Geisler et al. 2007).

The interpretation of the pores and inclusions in altered zircons (Geisler et al. 2007) is that the metastable zircon solid solutions $(M,Zr)SiO_4$ have a higher solubility in a pure aqueous solution than the pure zircon end-member ($ZrSiO_4$). Therefore, even a very small amount of dissolution of a solid solution composition results in an interfacial fluid which is supersaturated with respect to a purer zircon composition, and eventually also with respect to the other end member of the solid solution ($MSiO_4$). The low temperature equilibrium expected in such a solid solution-aqueous solution (SS-AS) system (see Prieto 2009) is the coexistence of an M-poor zircon + a Zr-poor $MSiO_4$ end-member + some Zr and M ions and silicate in solution. The loss of some $(M,Zr)SiO_4$ to the solution gives rise to the porosity, which is also a necessary feature for the replacement to proceed, allowing access of the fluid to the reaction interface.

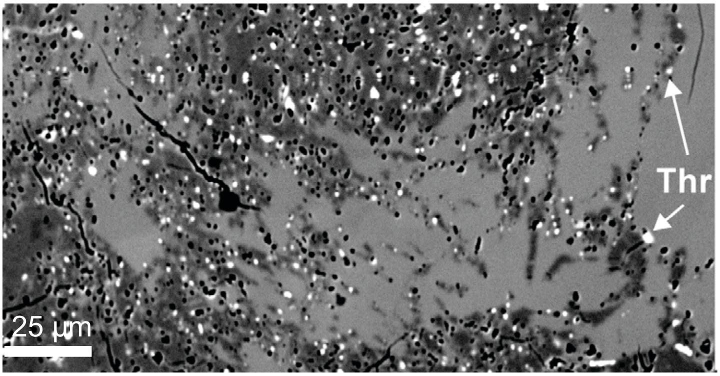


Figure 10. Back-scattered SEM images of a cross section of a zircon crystal. The pale grey area is the original Th-rich zircon, while the darker area are Th-depleted zircon, containing small bright inclusions of thorite (Thr) and pores (black). (Image: A. Soman)

This is an example of a phase separation of a solid solution driven by a fluid interaction. It could also be termed a fluid-driven "exsolution," but it would be better to restrict the term "exsolution" to a solid state process. One significant difference between solid state exsolution and a fluid-induced phase separation is that in the former, the bulk composition of the original solid solution and the total exsolved phases is unchanged, whereas in a fluid-induced phase separation components may be exchanged between the solid and the fluid, changing the bulk composition of both.

Even minor changes in chemical composition during a dissolution-reprecipitation process can have profound consequences when isotopes used in dating are involved (Martin et al. 2008). In a study of the reequilibration of magmatic zircons during metamorphism at low-temperature, high-pressure conditions, Rubatto et al. (2008) describe partial replacement textures in which zircon crystals preserve domains of primary zircon as well as domains of porous, recrystallized zircon containing inclusions of high-pressure pyroxene and epidote. The textural changes are coupled with chemical and isotopic modifications such that the primary zircon retains its U-Pb age of ~163 Ma, while the recrystallized zircon gives an age of ~46 Ma. The recrystallized zircon also loses Th which may explain the high-Th content of the epidote inclusions. The crystallographic orientation of the recrystallized zircon is inherited from the parent zircon, as expected when the dissolution and reprecipitation are closely coupled. From the compositions of the inclusions in the zircons, Rubatto et al. (2008) conclude that the recrystallization was induced by a relatively cold (<600 °C), alkaline, high pressure fluid.

Phase separation in monazite and xenotime by coupled dissolution-precipitation

Monazite [$(Ce,LREE)PO_4$] and xenotime [$(Y,HREE)PO_4$] are relatively common accessory minerals in igneous and metamorphic rocks and also often show fluid-induced reequilibration textures. Figure 11 shows a monazite sample in which the homogeneous Th-bearing monazite (Mnz1 with lighter contrast) is replaced by porous Th-depleted monazite (Mnz2 with darker contrast) + bright thorite inclusions (Seydoux-Guillaume et al. 2007). Similar textures in monazite and xenotime have been described from metasomatized pegmatites by Hetherington and Harlov (2008), who also interpret the breakdown of the solid solutions to a multiphase assemblage, and the resulting textures and compositions, by a dissolution-reprecipitation replacement process. From data on the relative solubilities of the phases involved, they estimate that the aqueous metasomatizing fluid was rich in Na^+ and K^+, and contained F^- and minor amounts of Cl^-.

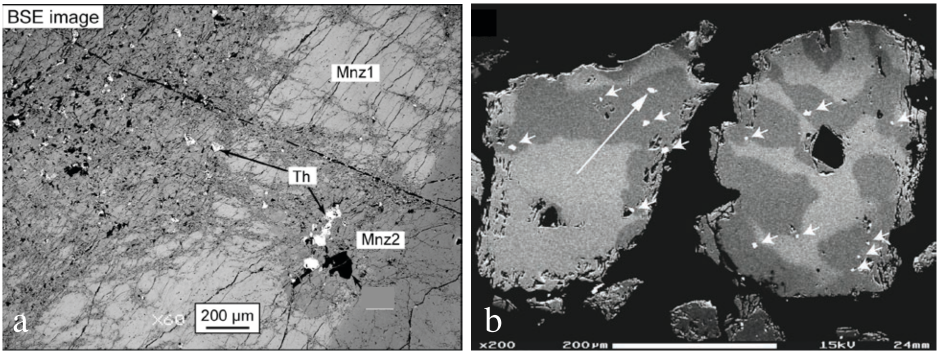


Figure 11. (a) Back-scattered SEM images of a cross section of monazite containing the parent Th-rich monazite (Mnz1) partly replaced by a Th-poor monazite (Mnz2) which contains bight inclusions of thorite (Th) (Image: A-M. Seydoux-Guillaume). (b) Experimentally metasomatized chlorapatite showing both metasomatized regions (dark) which contain monazite inclusions as well as the lighter parent monazite. (Image: D. Harlov)

Replacement processes in metasomatized apatites $Ca_5(PO_4)_3(OH,Cl,F)$

A series of papers by Harlov and co-workers (Harlov et al. 2002, 2003, 2005) demonstrate how the correspondence between natural observations and hydrothermal experiments can provide compelling evidence for the nature of aqueous fluids, and the mechanism of reactions. As in the above example, apatite minerals can contain Y + REE in solid solution, which can be released as REE-bearing phosphate phases occurring as inclusions when the apatite interacts with fluids. This is clearly seen from chemical analyses and microstructural observations of partially metasomatized apatites from the Bamble Sector, SE Norway, in which the metasomatized parts of the single crystals which are enriched in OH and F relative to the parent Cl-rich apatite, contain numerous inclusions (1-15 μm in size) of monazite and xenotime. A very similar texture can be reproduced (see Fig. 11b) by hydrothermally treating unaltered chlorapatite in a range of aqueous solutions (Harlov et al. 2002). The extent of metasomatism depended on temperature and the textures depended on the fluid composition. In pure H_2O the altered regions were porous, depleted in REE relative to the parent apatite and contained inclusions of monazite and xenotime. When a fluid containing CaF_2 was used, the metasomatized areas were enriched in F, but retained their Y + REE composition and hence had very few monazite or xenotime inclusions. Transmission electron microscopy (Engvik et al. 2009) of natural partly metasomatized chlorapatite from the Bamble Sector showed that the product OH-rich apatite is nanoporous, but shares the same crystallographic orientation with the parent apatite.

In a separate set of hydrothermal experiments using a wide range of fluid compositions at temperatures between 300 and 900 °C, Harlov et al. (2003, 2005) determined the conditions under which monazite inclusions could be induced to form from the LREE-enriched Durango fluorapatite. After reaction, only the metasomatized regions which were enriched in F and depleted in Y + REE contained monazite inclusions. Transmission electron microscopy showed that the reacted regions contained a pervasive nanoporosity, together with larger pore-spaces containing the monazite, while the crystallographic orientations of the reacted and unreacted regions were nearly identical.

The overall conclusions of these papers were that nucleation of monazite and xenotime inclusions in apatite is a function of composition of infiltrating fluid and to a much lesser extent, temperature and pressure. Even though the inclusions are often oriented they are not the product of a solid-state exsolution in fluid-absent conditions over millions of years but are metasomatically induced. This is another example of fluid-induced phase separation.

Fluoridation of bone apatite

Similar principles apply to the experimental fluoridation of bone apatite (essentially hydroxyapatite) by NaF solutions. In a study by Pasteris and Ding (2009) dentin and enamel from a modern horse-tooth were immersed in aqueous solutions with NaF concentrations from 0.1 M to 2 M, for periods up to 14 days at 19.5 °C. Dissolution of the bioapatite released Ca and P to the F-bearing solution which resulted in the nucleation and precipitation of essentially end-member fluorapatite "very near the place from which the calcium was released." The porosity and permeability in the product fluorapatite is increased due to the loss of constituents from the bioapatite to the fluid, and this permeability allows mass transport between the fluid and the reaction interface. The replacement process progresses due to the higher solubility of bioapatite relative to fluorapatite. The dissolution-precipitation mechanism, rather than a mechanism in which a diffusional front moves through the bioapatite, causing a solid state replacement of OH by F, is verified by *in situ* Raman spectroscopic analyses during the fluoridation reaction.

Replacement processes in feldspars – experiments

The initial fundamental experiments on feldspar reequilibration in alkali chloride solutions by Wyart and Sabatier (1958) and Orville (1962, 1963) were followed by O'Neil and Taylor (1967) who established the basic mechanisms which subsequent research has verified and elaborated. In experiments on the hydrothermal reaction between alkali feldspars and plagioclase and aqueous chloride solutions they found that complete oxygen isotope equilibration between the solutions and the feldspars accompanies the cation exchange which pseudomorphically transforms one feldspar composition to another. This refuted the previously accepted idea that the cation exchange was a simple solid state diffusion process in which the alumino-silicate framework remained inert. They concluded that the mechanism of cation and oxygen exchange involves a fine-scale solution and redeposition in a fluid film at the interface between exchanged and unexchanged feldspar. The oxygen isotope exchange is therefore an inevitable consequence of the replacement which is thermodynamically driven by the reequilibration of the feldspar in the aqueous fluid.

Similar experiments have been conducted using more sophisticated analytical techniques for characterizing the reaction interface in partly replaced feldspars. Labotka et al. (2004) experimentally replaced albite ($NaAlSi_3O_8$) by K-feldspar ($KAlSi_3O_8$) in an aqueous solution of KCl at 600 °C, and using a combination of electron microprobe and nano-SIMS (ion-probe) imaging showed the correspondence between Na-K and ^{18}O exchange. SIMS cannot specify whether the ^{18}O is in the feldspar structure, or in any other phases within the pore-spaces in the reaction rim, but Niedermeier et al. (2009) analyzing the products of similar hydrothermal experiments using Raman spectroscopy and imaging were able to conclusively show that the ^{18}O is in the aluminosilicate framework of the K-feldspar. Raman spectroscopy can identify the mass-dependent frequency shifts of the O-T-O vibrations in the tetrahedral rings of the feldspar structure and this can be mapped onto the Na-K chemical maps. Scanning and transmission electron microscopy (see Fig. 12) shows that the reaction interface is sharp on a nanoscale, often showing a small gap between the parent and product, as predicted 40 years earlier by O'Neil and Taylor (1967). The crystallographic orientation of the feldspar is preserved across the interface. The replaced rim of K-feldspar shows nano tube-like structures normal to the interface, which are assumed to be part of the porosity forming conduits for maintaining contact between the fluid reservoir and the reaction interface.

In the above experiments the Al:Si ratio in the feldspar remains unchanged during the replacement process, but this is not the usual case in nature. Plagioclase feldspar with compositions intermediate between albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) are replaced by albite in a wide variety of rock types and tectonic settings. This process known as "albitization" occurs at low temperatures during burial diagenesis (Perez and Boles 2005) and at higher temperatures during hydrothermal alteration of feldspar-bearing rocks (Lee and Parsons 1997; Engvik et al. 2008). On a regional scale, albitization is closely related to mineral and ore deposits (e.g., Oliver et al. 2004). Of interest therefore is the mobility of elements during albitization.

Hövelmann et al. (in press) have studied experimentally the albitization of oligoclase ($Ab_{73}An_{23}Or_4$) and labradorite ($Ab_{39}An_{60}Or_1$) in aqueous solutions of sodium silicate enriched in ^{18}O. The results confirmed that the replacement is pseudomorphic with a sharp chemical interface which progresses through the feldspar while preserving the crystallographic orientation (see Fig. 13), and that there is a direct correspondence between the replacement of the major elements and the oxygen isotopes in the feldspar structure. Transmission electron microscopy shows that the albite product is rich in defects and possibly nanopores, similar to naturally albitized plagioclase (see Engvik et al. 2009 below). The Ca from the plagioclase reacts with the fluid to form pectolite ($NaCa_2Si_3O_8OH$). Determining which elements are gained or lost to the solution requires making some assumptions. For example, balancing a replacement reaction can be achieved in a number of ways depending on which elements are mobile. For the reaction from oligoclase to albite we could make the assumption, which is usually made in metasomatic reactions, that Al is immobile. In this case we could write:

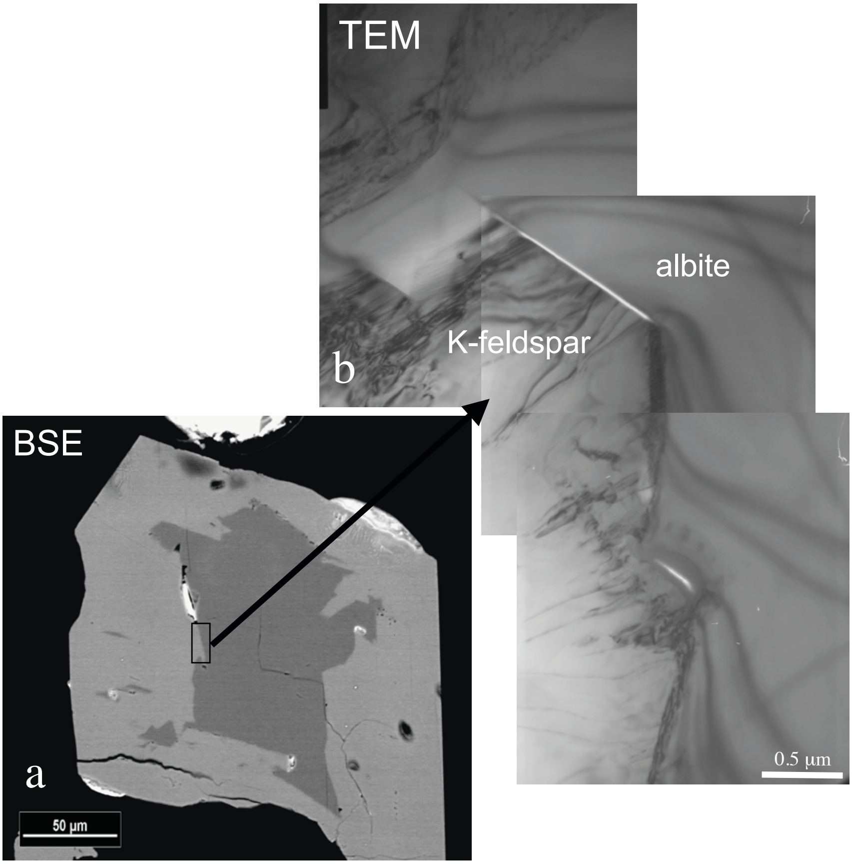


Figure 12. (a) Back-scattered SEM images of a cross section of an albite crystal (darker core) partially replaced by K-feldspar (pale grey rim). (b) TEM image of the interface between the albite parent and K-feldspar product. (Image: D. Niedermeier)

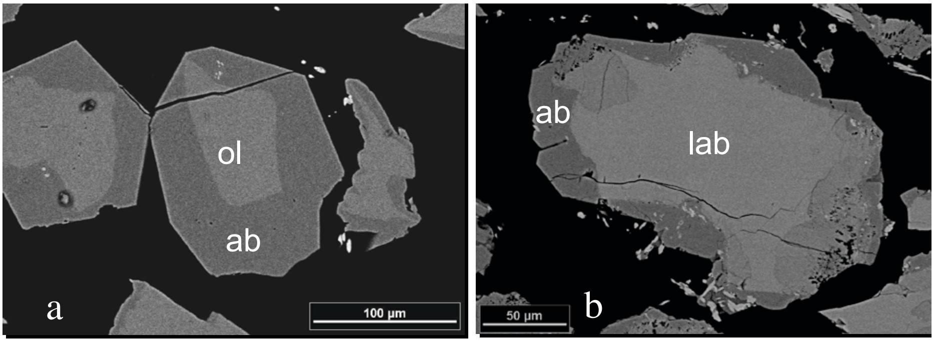


Figure 13. Back-scattered SEM images of a cross sections of (a) oligoclase crystals (ol) and (b) labradorite crystals (lab) partially replaced by albite (ab). (Image: J. Hövelmann)

$$\mathrm{Ca_{0.22}Na_{0.74}K_{0.04}Al_{1.22}Si_{2.78}O_8 + 0.59\ Na^+_{(aq)} + 0.59\ OH^- + 1.21SiO_2}$$
$$\mathrm{\rightarrow 1.22NaAlSi_3O_8 + 0.11NaCa_2Si_3O_8OH + 0.04\ K^+_{(aq)} + 0.04\ OH^- + 0.22H_2O} \qquad (8)$$

However, this would involve a large volume increase of the feldspar crystal, which is not the case, as the replacement is pseudomorphic. If the reaction is balanced on volume, then neglecting the small molar volume difference between the feldspars and the porosity due to the fact that some of the material is lost to the fluid, we could write:

$$\mathrm{Ca_{0.22}Na_{0.74}K_{0.04}Al_{1.22}Si_{2.78}O_8 + 0.59\ Na^+_{(aq)} + 0.59\ OH^- + 0.55SiO_2 + 0.22H_2O}$$
$$\mathrm{\rightarrow NaAlSi_3O_8 + 0.11NaCa_2Si_3O_8OH + 0.22NaAl(OH)^0{}_4 + 0.04\ K^+_{(aq)} + 0.04\ OH^-} \qquad (9)$$

In reaction (9) aqueous Al is assumed to be complexed by Na, but in any case, the experiments confirm that Al as well as Ca are released by the reaction. Minor and trace element analyses record considerable losses of Ti, Fe, Mg, Sr, Ba, Y, K, Rb, Pb and the LREEs from the feldspar to the fluid. In a natural setting these “charged fluids” migrate away from the sites of albitization and may precipitate mineral deposits elsewhere, even hundreds of kilometers away.

A common feature of all the experimental work on feldspar replacement reactions is that they are fast on a laboratory time-scale (days or weeks at typical hydrothermal conditions) and therefore virtually instantaneous on a geological time scale. Thus a replacement may only be recognized when the reaction front is “fossilized” due to insufficient fluid to complete the reaction.

Replacement processes in feldspars – nature

Before describing some examples of replacement reactions which involve changes in major element composition it is instructive to consider the special, but very common case in which alkali feldspars with fine-scale coherent cryptoperthite intergrowths (cryptoperthite: a nanoscale intergrowth of albite and microcline) formed by true solid-state exsolution, react with aqueous fluids. The result of this interaction with fluids has been termed “mutual replacement” in which there is a pervasive recrystallization with no significant change in bulk composition, nor change in external morphology, nor of crystallographic orientation. However, there is a profound change in the internal microstructure of the crystal resulting in a range of textures, broadly referred to as “patch perthite” or “vein perthite” (see Fig. 14). In some cases the continued coarsening retains the initial spindle shaped intergrowths reminiscent of a solid state exsolution texture (see Fig. 14b). Mutual replacement has been studied in detail by Parsons and co-workers for many years and Parsons and Lee (2009) provide an excellent review of this literature, together with new observations.

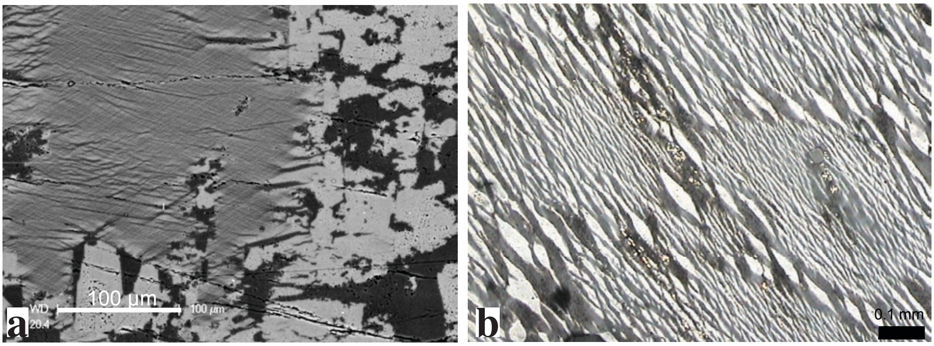


Figure 14. (a) Back-scattered SEM image of coarse patch-perthite (with black and white contrast – right) replacing the finely exsolved cryptoperthite (grey braid perthite – left). (Image: I. Parsons) (b) Optical image of a thin section of perthite showing the variable scale of phase separation due to fluid infiltration and replacement.

The thermodynamic driving force for such replacement is the reduction in the coherency strain energy generated by the exsolution. This strain energy translates into a higher solubility in an aqueous solution for cryptoperthite than for patch perthite and drives a dissolution-precipitation mechanism. In cases where there has been only partial replacement, the relationship between the strained cryptoperthite and the fluid-induced patch perthite is clearly defined. The observed development of micropores (~2% porosity reported by Parsons and Lee 2009) in the product (see Fig. 14) is a natural consequence of this mechanism since the solubility difference results in the removal of some feldspar material into the fluid phase. The development of porosity in feldspars leads to a turbidity or "milkiness" which is almost universally developed to varying extents and is evidence of pervasive fluid-rock interaction on a large scale. In contrast, feldspars which have not reacted with aqueous solutions appear dark or glassy in hand-specimen, and free of pores in electron microscope images (e.g., Fig. 15 below).

Although the bulk chemistry in this example does not significantly change, measurements of trace element compositions using LA ICPMS demonstrate that many trace elements, including REEs were lost from the cryptoperthite during the replacement (Parsons et al. 2009), further emphasizing the role of the fluid phase.

Feldspar replacement where the bulk chemistry of the feldspar is changed by interaction with alkali or alkali earth bearing fluids, are also very common, but usually not recognized unless the replacements are incomplete. In a study of a "fossil hydrothermal system" in the Rico dome, Colorado, Cole et al. (2004) describe plagioclase and K-feldspar partially replaced by albite, while retaining original grain shape and twinning. Oxygen isotope measurements show that while the plagioclase cores retain their igneous isotopic compositions, the replaced rims show low $\delta^{18}O$ values indicative of reequilibration of the feldspar with meteoric water.

In a similar study of an anorthosite rock which contains a bi-modal plagioclase assemblage of andesine ($An_{34\text{-}48}$) and bytownite-anorthite ($An_{82\text{-}98}$), the extreme heterogeneity of oxygen isotope compositions on a mm scale, and the textural relationships between the feldspars led Mora et al. (2009) to conclude that the anorthite-rich phase partially replaced the andesine during a high temperature hydrothermal alteration event. The replacement created new permeability allowing considerable volumes of meteoric-hydrothermal fluids to infiltrate the rock. In this case of "anorthitization" the fluid involved is assumed to be a Ca^{2+}-bearing aqueous solution.

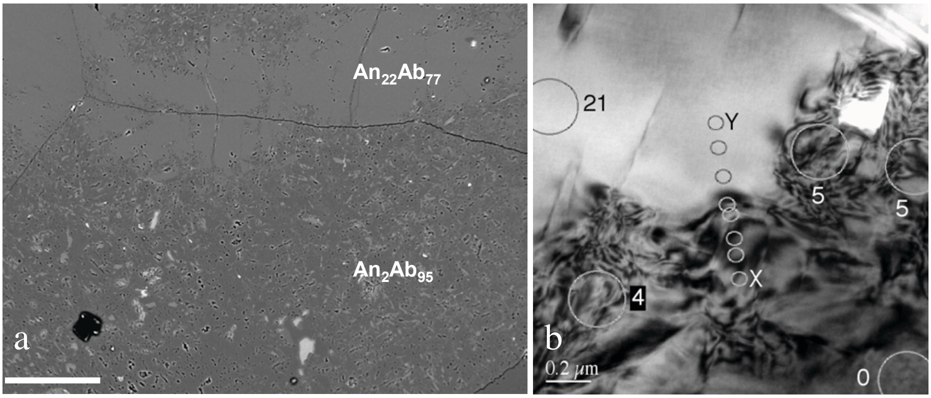


Figure 15. (a) Back-scattered SEM image of natural oligoclase (~An_{22}) partially replaced by albite (~An_2). The parent oligoclase has a smooth textured-surface, while the albite (darker grey) is full of small sericite inclusions (pale) and pores (black). (b) TEM image of an oligoclase-albite interface. The numbers refer to An-content, and the points between X and Y are positions of chemical analyses. (Engvik et al. 2008)

However to write a reaction for anorthitization of a natural rock poses the same questions as raised by reactions (8) and (9) above. A reaction which keeps the Al immobile results in a very large volume decrease due to loss of Si to the fluid. At the other extreme, if Al is present in a calcic fluid and is added to the feldspar it is possible to write a reaction in which volume is preserved. As the evidence for the compositions of fluids before and after reaction is lost in rocks, estimates of the porosity generated or the extent to which volume is preserved must be made to estimate the fluid compositions.

To illustrate the point in the simplest possible way, the anorthitization of albite could be written as:

$$2NaAlSi_3O_8 + Ca^{2+} + 8H_2O \rightarrow CaAl_2Si_2O_8 + 2Na^+ + 4H_4SiO_4 \qquad (10)$$

would involve an approximately 50% loss of volume due to the amount of silica dissolved in the fluid, but preserves the Al as "immobile." This raises problems not only whether such a large volume loss is possible in a rock, but also given the relatively low solubility of silica, whether the amount of fluid required is realistic. On the other hand, a reaction which approximately conserves volume could be written as:

$$NaAlSi_3O_8 + Ca^{2+} + Al^{3+} \rightarrow CaAl_2Si_2O_8 + Na^+ + Si^{4+} \qquad (11)$$

but involves the introduction of Al by the fluid and the loss of Si. While dissolved Al could be derived from albitization elsewhere in a hydrothermal system, the real situation is likely to lie somewhere between the extremes of reactions (10) and (11).

Regional scale albitization of granitic rocks from the Bamble Sector of SE Norway, can be recognized along reaction fronts where albitization occurs normal to fractures in essentially unaltered rock. Such reaction fronts represent the limits of fluid infiltration, and allow a detailed study of the "before" and "after" compositions and textures. In the field, these reaction fronts can be recognized by a reddening of the rock due to hematite precipitation associated with the albitization. Engvik et al. (2008) studied the replacement, on a nanometer scale, of plagioclase (oligoclase ~ $An_{21\text{-}23}$) in the unaltered rock by almost pure albite. Figure 15a shows a scanning electron micrograph of such a reaction front between oligoclase, which has a smooth and textureless contrast, and the product albite, which contains fine laths of sericite mica, occasional Fe-oxides, and numerous small pores. The replacement is pseudomorphic and there is no indication of any overall volume change i.e. the volume of oligoclase equals the volume of albite + sericite + pores. Figure 15b is a transmission electron micrograph of the reaction interface, showing both the sharpness of the interface and the complex diffraction contrast in the albite, indicative of a defect structure which includes dislocations and nano-pores as well as the larger pores seen by scanning electron microscopy. As in the other cases described above, the crystallographic orientation is preserved across the interface.

Mechanisms of isotopic exchange in calcite marble

As a final example of replacement in nature, the recent study by Bowman et al. (2009) demonstrates how high spatial resolution measurements of $^{18}O/^{16}O$ ratios using modern ion microprobes with high precision measurements on ~10 μm spot sizes, together with textural observations can clarify the mechanism of isotopic exchange. In marble from a contact aureole of the Alta Stock, Utah, two isotopically and texturally distinct types of calcite exist on a mm scale. Clear calcite grains, with homogeneous $\delta^{18}O$ values are replaced by turbid calcite with more variable and lower $\delta^{18}O$ (see Fig. 16). The turbid calcite also contains small blebs of dolomite which are interpreted as phase separation due to the interaction of clear calcite with fluid, or precipitation from the fluid during the replacement. The conclusions are that the isotopic reequilibration and Mg exchange are the result of dissolution and reprecipitation of calcite during retrograde cooling.

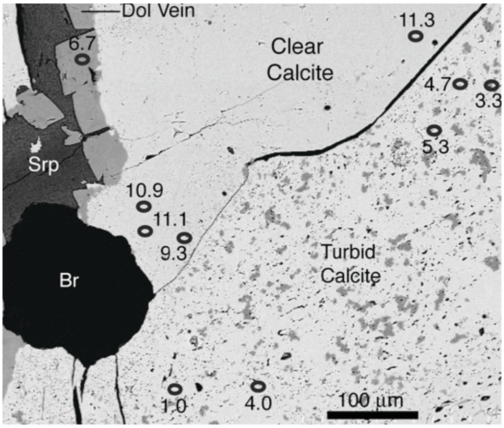


Figure 16. Back-scattered SEM image of calcite showing a parent clear calcite partially replaced by a later, turbid calcite. The numbers refer to $\delta^{18}O$ values. (Bowman et al. 2009)

Reaction induced fracturing during replacement processes

In all of the examples we have considered, we have focused on the chemical processes associated with mineral replacement. We have seen that, depending on the composition of the fluid, a reaction may be balanced to preserve the solid volume, or alternatively may involve a significant volume change. When replacement reactions involve volume changes between the parent and product, stresses are generated which may eventually cause fracturing of the mineral. On a large scale, similar processes operate during weathering, where the interplay of chemical and mechanical processes involve hydration reactions, and fracturing which allows further fluid infiltration and chemical reaction.

Experimental studies show that even when there are significant changes in the molar volume of the solid reactants, the replacement may be pseudomorphic. One example is the reaction of ilmenite ($FeTiO_3$) with acid solution, which results in a pseudomorph of the ilmenite made of polycrystalline rutile (TiO_2) (Janssen et al. 2008). In the experiments, polished cubes, prepared from a massive ilmenite sample were reacted in HCl solutions at 150 °C. Figure 17 shows a cross section through the cube after partial reaction. The dark rim is rutile, while the core is unreacted ilmenite. The most striking result is that although there is a decrease in molar volume in replacing ilmenite by rutile of ~40%, the reaction is pseudomorphic, and

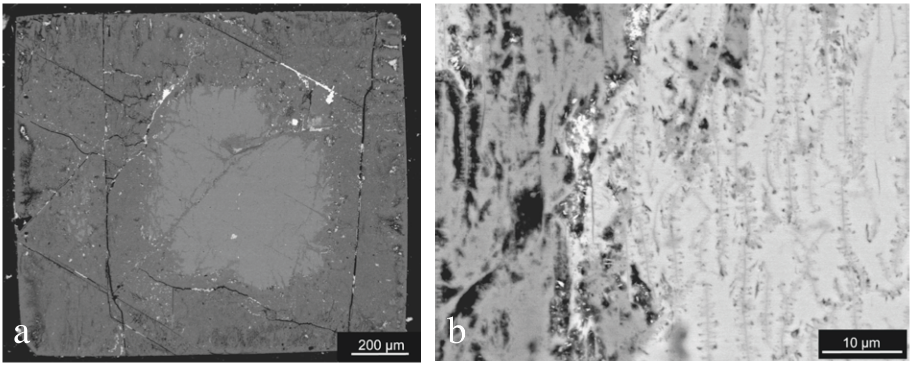


Figure 17. Back-scattered SEM images of ilmenite partially replaced by rutile. (a) Cross section of the entire sample. The lighter core is ilmenite. (b) High magnification image of the interface between rutile (dark) with black pores and ilmenite (light). Note the fine darker fracture network in the ilmenite. (Image: A. Janssen)

the difference in volume appears as a high porosity in the rutile product. Another interesting aspect of this dissolution-precipitation reaction is that the microtexture of the rutile shows three twin-related orientations, as would be expected from an epitaxial nucleation of tetragonal rutile on the surface of trigonal ilmenite. This illustrates the importance of epitaxy in controlling nucleation in a coupled dissolution-precipitation mechanism.

Ahead of the main reaction front, the ilmenite is extensively fractured throughout the whole apparently unreacted core, and the fracture pattern forms a fish-bone-like array. Within these fractures the ilmenite has been replaced by nanosized crystals of rutile. The pattern of replacement depends on the concentration of acid used. In more dilute acid the reaction is slower, but proceeds almost exclusively by the propagation of very fine fractures though the whole sample (see Fig. 18a). These fractures become sites for new lateral spreading of the reaction (see Fig. 18b), by allowing easier pathways for fluid access.

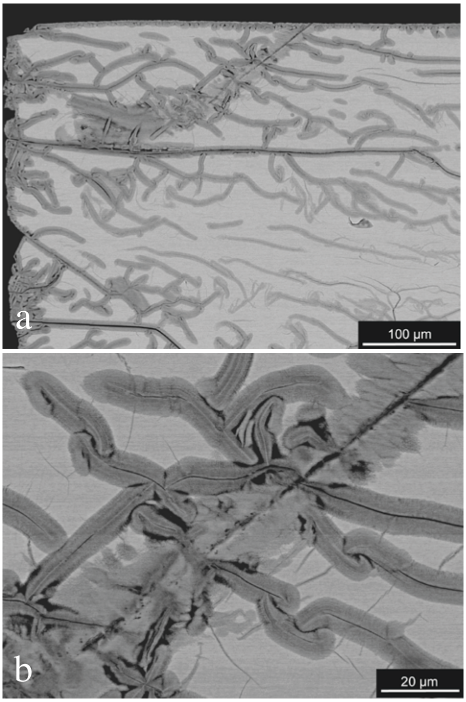


Figure 18. (a) Ilmenite, treated in dilute HCl, partially replaced by rutile along a fracture network which allows lateral spreading of the reaction. (Image: A. Janssen)

Fracturing is also a feature of pseudomorphic reactions where the molar volume of the reactants increases. One example is the replacement of leucite by analcime, described above. Despite the increase in molar volume the product phase is porous, but the strain build-up means that after a certain rim thickness of product is reached, in an unconstrained system, it tends to spall off the unreacted core. Fractures are also generated ahead of the reaction front, but not as extensively as in the ilmenite-rutile case. Another example discussed above is the serpentinization of olivine or orthopyroxene. The typical "mesh textures" of serpentinized olivine shown in Figure 3 is produced by the fracture generation associated with the replacement.

A general analysis and mechanical model of reaction induced fracturing has recently been presented by Jamtveit et al. (2009). The important result is that both porosity generation and fracturing provide pathways for fluid infiltration.

CHARACTERISTICS OF INTERFACE-COUPLED DISSOLUTION-PRECIPITATION REACTIONS

Although the above examples are not an exhaustive list, they are sufficient to identify the common characteristics of reequilibration processes in the presence of an aqueous phase. These can be summarized as follows:

(i) The dissolution and precipitation are closely spatially coupled at the interface between the parent and the product phases. This coupling preserves the external morphology of the parent.

(ii) The reaction front between parent and product is sharp with no significant diffusion profile in the parent.

(iii) The product phase develops intracrystalline porosity and permeability which allows the fluid to maintain contact with the reaction front.

(iv) In cases where there is a large increase or decrease in the solid molar volume, reaction induced fracturing produces a network of fractures ahead of the reaction front.

(v) There is an epitactic relationship between parent and product phases such that if they have the same crystal structure, this is preserved across the interface. In cases where the product phase has a different crystal structure to the parent, the product may be polycrystalline. Nevertheless in cases where the crystallographic relationships have been measured an epitactic relationship has been demonstrated.

“Porosity” as an integral microstructural feature of fluid-induced replacement

In solid state reactions, a specific transformation mechanism results in a microstructure which describes the spatial and crystallographic relationships between the parent and the product phases. This microstructure is controlled by both the thermodynamics and the kinetics of the reaction, and in a full analysis, interfaces generated by the transformation increase the free energy of the system. The microstructure reflects the competition between the thermodynamics and the kinetics of the process. It is also a *transient* feature of a reaction, and given sufficient time microstructures should coarsen to reduce the free energy. However, in solid state reactions, coarsening involves volume diffusion through the crystal, with a rate which is exponentially decreases with temperature. As the temperature falls, diffusion becomes negligible, and the microstructure becomes “frozen-in.” This can be thought of in terms of a “closure temperature” for diffusion, which limits the length scale over which diffusion can occur at a particular temperature. As the temperature is decreased, this length becomes negligible in relation to our ability to measure or observe. The preservation of microstructure is dependent on this closure, and allows us to study the transformation mechanisms.

The same concepts of microstructural development apply to interface-coupled dissolution-precipitation reactions. The addition of a fluid phase, which both contributes to and removes components from the solids, has both a thermodynamic, kinetic and microstructural significance. The fluid occupies space, and in a dissolution-precipitation reaction, the generation of “porosity” can be considered as part of the microstructure associated with the mechanism. It is that part of the microstructure occupied by the fluid phase. In experiments such as the replacement of KBr by KCl (see above) the porosity also has a crystallographic orientation, minimizing the interfacial free energy. If the porous product phase remains in contact with the fluid, it would be expected that the microstructure will continue to evolve with time. This has been experimentally observed in the KBr-KCl system, where textural equilibration follows chemical equilibration with the fluid - the porosity coarsens and eventually clears (Putnis et al. 2005). Since the mechanism of textural equilibration is also by dissolution and reprecipitation, the “closure temperature” is very much lower, in many cases down to ambient temperatures. In contrast to solid state reactions, the low closure temperatures mean that microstructures associated with dissolution-precipitation may not be preserved and evidence for the mechanisms may be lost. The preservation of the reaction interface, as seen in many of the examples above, is assumed to be the limit of fluid infiltration.

What causes the coupling between dissolution and precipitation?

It is evident from the examples above that to produce a pseudomorph the dissolution and precipitation reactions must be closely coupled in space and in time. However, the complexity of the thermodynamics of such reactions, which must take into account the overall change in the free energy of solids + fluids, the stress generated by volume changes, as well as the stress imposed by the rigid rock if the replacement takes place in a confined space, has led to different conceptual models for the origin of the coupling.

Model 1. In the examples above it is evident that the formation of the product precipitate relies on the dissolution of the parent to provide the chemical ingredients, which when combined with the fluid chemistry, produce a solution which is supersaturated with respect to the product. However, this in itself does not imply pseudomorphism and it might be expected that the most likely situation is that the dissolution and precipitation would be spatially separated. Pseudomorphism demands that the rates of dissolution and nucleation are closely coupled at the parent-product interface. Such close coupling can be achieved when the controlling mechanism is the dissolution rate, and there is a low activation energy barrier for nucleation. On the other hand, if the nucleation is the rate controlling step, implying that dissolution is fast and nucleation is slower, the coupling may not be so closely related in space and time, leading to a less exact pseudomorph or complete loss of coupling. Such a situation has been explored by Xia et al. (2009b) where the rate controlling step in the replacement of pentlandite by violarite changes as the pH changes from acidic to neutral.

The nucleation rate is controlled by factors which include the degree of epitaxy between the product phase and the parent surface. If the crystal structures of the parent and product phases are closely related, then nucleation of the product on the parent surface, maintaining the crystallographic orientation is favoured, because the interfacial energy at this new interface is reduced (see Putnis 1992, pp. 338). Thus epitaxy transfers the crystallographic information from parent to product even though the parent dissolves. The experiments by Putnis and Mezger (2004) and Putnis et al. (2005) emphasize that the fluid composition *at the interface* is the most important factor, and that during the replacement this may be different from the fluid composition in the bulk, even in a small reaction vessel. This suggests that the rate of transport of the solution species to and from the interface is an important factor which needs to be considered in formulating a quantitative description of the replacement mechanism. The composition of this boundary layer of fluid at the interface is likely to be the most important factor which controls the coupling.

Thus even a monolayer of dissolved parent phase can supersaturate this boundary layer with respect to the product. When nucleation of the product phase takes place on the surface of the dissolving parent it lies within the normal diffusion profile which would be generated in the fluid by the dissolving crystal. This defines the external shape of the original crystal as the outside surface of the new phase. Such an argument has been used by Anderson et al. (1998a,b) to describe an autocatalytic feedback between the rates of dissolution and precipitation when a product of a solid + fluid reaction nucleates on the surface of the dissolving parent phase.

A second factor which controls the nucleation rate of the product phase is the degree of supersaturation of the fluid in the boundary layer. If there is a large difference between the solubility of the product and parent, even a small amount of dissolution will result in a highly supersaturated fluid, and even in the absence of obvious crystallographic relationships between the solid phases, nucleation will be rapid. This may well be the case when calcite is replaced by apatite (Kasioptas et al. 2008) or by fluorite (Glover and Sippel 1962), both of which are many of orders of magnitude less soluble than calcite. In some cases the chemistry of the fluid may not be too critical and the interfacial fluid becomes supersaturated with respect to the product over a wide range of fluid compositions. The nucleation rate may also not be particularly sensitive to fluid composition, only to the degree of supersaturation.

Porosity in the product phase is generated whenever there is a volume deficit reaction. This volume deficit does not only refer to the change in the molar volumes of the parent and product solids, but also to their relative solubilities, which will determine how much parent is dissolved and how much is precipitated. Thus it is possible that even when the molar volume of the parent is smaller than that of the product, porosity can still be generated, as seen in the case of the leucite to analcime replacement (Putnis et al. 2007a). Another important point is that the *absolute solubilities* of the phases are not the determining factors for a dissolution-precipitation reaction to take place. Because the reactions take place at the parent-product interface, the *relative* solubility is the most important factor, as at any one time only a small amount of material needs to be in solution.

The porosity allows the mass transfer of material from the solution reservoir to the reaction interface through the solution. In the case of the replacement of KBr by KCl (Putnis and Mezger 2004) the reaction rim increases in thickness as a linear function of $(\text{time})^{1/2}$ indicating that the rate control in this case may be the diffusion of the ions through the fluid-filled interconnected pores. This was also found by Glover and Sippel (1962) for the replacement of calcite by fluorite.

The evidence from the examples above suggests that interface-coupled dissolution-precipitation is controlled (i) by the chemistry of the fluid at the reaction front and (ii) by the role of the parent mineral as a substrate for nucleation of the product. The finding that the length scale of pseudomorphism can be manipulated by changing the fluid chemistry (Xia et al. 2009b) is a powerful argument in support of this model. Further details of this model for interface-coupled dissolution-precipitation can be found in Putnis (2002), Putnis et al. (2005) and Putnis and Putnis (2007).

Model 2. Maliva and Siever (1988) proposed a model for the diagenetic replacement of one phase by another based on the argument that a replacement does not require the undersaturation of the bulk fluid with respect to the rock (the "bulk host phase") undergoing diagenesis, nor its subsequent supersaturation with respect to a new precipitating phase. From the outset, Maliva and Siever emphasize that their description of a "bulk" phase refers to free surfaces of host phase grains in contact with free pore waters, "as opposed to intergranular or intercrystalline contacts." They propose that the replacement is controlled by the force of crystallization, where this is defined as a pressure which a crystal, growing in a supersaturated solution, can exert on its surroundings. The basic idea of this model (Nahon and Merino 1997) is that when a new crystal (A) begins to grow at some point in a rigid rock, it exerts a stress on its surroundings, leading to pressure induced dissolution of adjacent mineral or rock (B). The dissolution of B *decreases* the supersaturation of the fluid relative to A and hence decreases the growth rate of A. The rates of growth of A, and dissolution of B change in opposite directions until at some point in time they become equal.

Pressure solution is the basis of the coupling between dissolution and precipitation in this model and several criteria are given as textural indicators of force of crystallization controlled replacement (Maliva and Siever 1988).

(i) Dissolution of the host phase is restricted to the interface between the parent and product.

(ii) The preservation of microstructural features of the parent phase indicating that the rates of dissolution of the parent and precipitation of the product are equal "otherwise a gap would form between them."

(iii) The presence of a euhedral product crystal faces in planar contact with the unreplaced host. The argument here is that it would not be expected that the parent phase would dissolve in such a way as to accommodate the interfacial angles of the product, without the product crystal exerting a pressure on the host.

Merino and co-workers have taken up this model to explain replacement mechanisms, specifically in weathering phenomena (Merino et al. 1993; Nahon and Merino 1997; Merino and Banerjee 2008). The mathematical formulations of the Maliva and Siever model (e.g., Dewers and Ortoleva 1989; Merino and Dewers 1998 and Fletcher and Merino 2001) involve a coupling between the growth kinetics of crystals and the mechanical response of a viscously relaxing surrounding rock or medium.

However many mineral replacements, especially those in experimental studies, do not take place in a confined space, and in surface weathering, such as in the genesis of "terra rossa" (Merino and Banerjee 2008) it is questionable whether the "rigid rock" prerequisite applies. The generation of porosity in the secondary phase is also not a feature of the Maliva and Siever model.

Nevertheless, Merino and Banerjee (2008) argue that a force of crystallization will exist at the parent-product interface, even without an externally applied stress and in surficial environments. The examples used to argue a case against Model 1 for interface-coupled dissolution-precipitation are that there are observations of parent/product mineral pairs with no chemical components in common e.g., limestone replaced by silica, or sphalerite replaced by dolomite in which the botryoidal layering structure is inherited from the parent sphalerite. Such replacements are much easier to recognize than, for example, a feldspar–feldspar replacement, and have therefore been known for many years (e.g., Lindgren 1912; Bastin et al. 1931).

The question of whether the coupling between dissolution and precipitation in fluid-induced pseudomorphic replacement is driven by solution chemistry (Model 1) or local non-hydrostatic stress and pressure solution (Model 2) is still the subject of debate (e.g., Merino and Banerjee 2008; Xia et al. 2009b). The examples given in this chapter provide compelling arguments in favour of Model 1, but these are all cases in which parent and product phases share some common chemistry such that dissolution of the parent results in an interfacial fluid in which the supersaturation is *increased* with respect to the product phase. In Model 2, pressure dissolution of the parent results in a *decrease* in the supersaturation of the fluid with respect to the precipitating phase. While it is not immediately obvious how Model 1 can be applied when there is no apparent common chemistry between the parent and product phases, the demonstrated role of fluid chemistry is easier to appreciate with Model 1 than Model 2.

The question of the role of the fluid composition on dissolution and precipitation thermodynamics and kinetics is not straightforward, as it is known that components in the fluid which do not seem to be directly related to the chemistry of the dissolving or precipitating solids can have a major effect. For example, the role of pH or the redox state in the solution are well known factors which may indirectly influence reactions. The precipitation of dolomite is enhanced by sulfate species in solution (Brady et al. 1996), and may form a link between sphalerite dissolution and oxidation and dolomite precipitation from a supersaturated solution. Background electrolytes which do not enter into the precipitating phase, but affect the hydration/dehydration of the dissolving/precipitating ions also play an important role in both dissolution and precipitation (Kowacz and Putnis 2008). However, too little is known about the role of solution chemistry to explain the kind of replacement where a whole assemblage of fine grains in a schist for example, are replaced by a single pyrite crystal.

Although the two models have different explanations for apparently similar phenomena, the effects of chemistry and induced stress are both likely to play an important role in replacement processes in rocks. When discriminating between reactions such as reactions (8) and (9), the mechanism will depend on the fluid composition, the relative free energy changes for the reactions (including the fluid thermodynamics), the molar volume changes of the solid phases, and the presence or absence of an imposed stress, as well as the kinetics of all possible (i.e. $\Delta G < 0$) reactions. In such a situation it is likely that elements of both models will need to be included in a full explanation of mineral replacement in rocks.

IMPLICATIONS OF INTERFACE-COUPLED DISSOLUTION-PRECIPITATION AS A MECHANISM FOR MINERAL REPLACEMENT

Mineral replacement reactions take place primarily by dissolution-reprecipitation processes. At high temperatures, solid state reactions which involve volume diffusion may become kinetically significant on a local scale, but the wholesale replacement of one mineral assemblage by another, in the presence of any fluid, will kinetically favour dissolution and precipitation over a solid state reaction under most crustal conditions. Similarly, deformation by dissolution-precipitation creep, rather than by solid state creep, is also likely to be the dominant mechanism at metamorphic grades up to at least amphibolite facies (Wintsch and Yi 2002).

Given that processes such as cation exchange, chemical weathering, deuteric alteration, leaching, metasomatism, diagenesis and metamorphism are all linked by common features in which one mineral or mineral assemblage is replaced by a more stable assemblage, understanding mineral replacement has implications to virtually all aspects of the rock cycle on earth. In industrial processes, understanding crystal dissolution and growth is also fundamental to modelling the rates of chemical reactions and finding new routes for the synthesis of materials. In this section we will briefly review some of these applications.

The kinetics of dissolution-precipitation and metamorphic and metasomatic reactions

One of the important conclusions from this review of replacement processes is that they are fast and that they can be driven by small reductions in free energy. In the experiments on feldspars and apatites, significant replacement takes place under hydrothermal conditions even in a few days. In other examples replacement takes at room temperature. Although the solutions used in the experiments are initially significantly out of equilibrium with the parent phase, the rapid rates suggest that in a geological context, when a fluid interacts with a solid with which it is out of equilibrium, it is inevitable that dissolution will begin to take place. The contention that the departures from equilibrium need only be small is supported by the results by Nakamura and Watson (1981) who showed that a reduction in interfacial energy was sufficient to recrystallize quartz under hydrothermal conditions. The experimental results support the analysis by Wood and Walther (1983) and Walther and Wood (1984) that in the presence of a fluid phase metamorphic reaction rates are rapid, and that dissolution-precipitation reactions should proceed at very small departures from equilibrium ("rarely more than a few degrees").

A very well-studied example of the role of fluid in a metamorphic reaction is the eclogitization of Precambrian anorthositic granulites of the Bergen Arcs, western Norway. In a classic paper, Austrheim (1987) concluded, on the basis of detailed mapping of eclogite outcrops within the granulite facies rocks, that the eclogitization is a function of deformation and fluid access, rather than being controlled by temperature, pressure and rock composition alone. Figure 19a shows a rock outcrop in which a dark vein of eclogite cross cuts the paler granulite. The vein is associated with a shear plane and fluid infiltration along which the eclogitization has occurred. The eclogitization is limited by the extent of this fluid infiltration laterally from the shear plane and in the absence of fluid, the granulite remains essentially unaltered. If we assume that the whole rock outcrop experienced the same P-T conditions, then the conclusion that the fluid triggered the eclogitization reaction is inescapable.

The effect of eclogitization can be seen at every scale, from the rock outcrop, to interfaces within individual crystals. Figure 19b shows an image of a garnet crystal from the eclogite-granulite interface. The dark part of this partially pseudomorphed crystal has the original granulite garnet composition, while the lighter regions are the eclogite composition replacement product. Electron back-scattered diffraction (EBSD) analysis confirms that the crystallographic orientation of the garnet is preserved during the replacement, but with textural reequilibration of the original sub-grain microstructure of the original granulitic garnet (Pollok

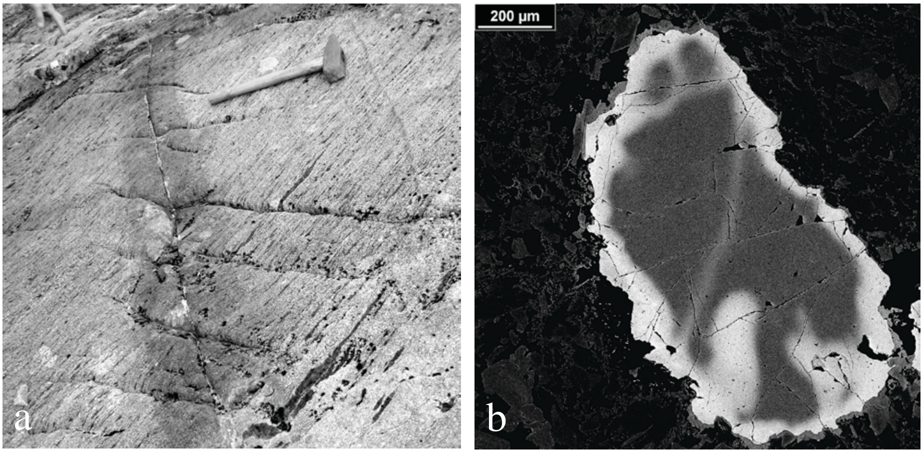


Figure 19. (a) Rock outcrop showing eclogitized rock (dark) along a fracture in the granulite. (b) A back-scattered SEM image of a single garnet crystal from the interface between granulite and eclogite. The dark parts of the partly pseudomorphed crystal have the original granulite composition, while the lighter parts of the same single crystal have a composition of eclogitic garnet. [Used with permission of Elsevier from Pollok et al. (2008).]

et al. 2008). The garnet replacement texture is interpreted as due to a coupled dissolution-precipitation mechanism.

The same principles apply to metasomatism, in which there is a significant change in the chemical composition of the rock, resulting from components added from the fluid. The distinction between metamorphism and metasomatism is a matter of degree and scale, rather than of principle. Whenever a fluid is involved in a replacement process some chemical components may be added to or subtracted from the solid phases. Even in an apparently isochemical recrystallization, trace elements may be lost to the fluid (Parsons et al. 2009), and as Carmichael (1969) has pointed out, metamorphic reactions are metasomatic if we consider a small enough sample volume.

Sub-solidus reequilibration of granitic rocks

Based on oxygen isotope studies of granites from many terrains, Taylor (1977) concluded that "gigantic meteoric-hydrothermal convective circulation systems were established in the epizonal portions of *all* batholiths, locally producing very low $\delta^{18}O$ values (particularly in feldspars) during sub-solidus exchange." The experimental work on mechanisms of cation and oxygen isotope exchange in feldspars, together with higher spatial resolution isotope data, show that the two processes are simultaneous, as would be expected from a dissolution-precipitation replacement process. It has also long been recognized that replaced feldspars are turbid due to porosity, and fluid and solid inclusions and may also be pink or red-colored (Boone 1969). More recently, Putnis et al. (2007a) showed by transmission electron microscopy that red-clouded potassium-rich feldspars from granites contain many pores up to several hundred nanometers in size, and that almost every pore contains rosettes or needles of crystalline hematite (see Fig. 20). This observation, together with the fact that the origin of the porosity is consistent with an interface-coupled dissolution-precipitation reaction, indicates that the hematite is a direct product of fluid-rock interaction. Hematite in pores is *not* consistent with solid state exsolution from a Fe-bearing feldspar. In examples where interfaces between a parent plagioclase and a product K-feldspar can be found, compositional data show that the plagioclase parent does not have enough Fe to account for the hematite by a fluid-induced phase separation mechanism, and that it was therefore introduced by the fluid.

The broader conclusions from these studies is that, as feldspars in granites are almost invariably turbid and are often red-clouded, many granites have been subject to regional alteration which have modified the feldspar compositions, and resulted in markedly discordant Rb-Sr isochron "ages" (Taylor 1977). More detailed high resolution studies by SEM and TEM of a grey granite from south-eastern Sweden, with pronounced red-staining associated with fractures (Plümper and Putnis 2009) suggest that virtually all of the feldspar in the grey *and* red parts of the rock is secondary and that the granite has a very complex sub-solidus history, such that it is not even possible to determine the nature of the original protolith. Depending on the composition of an infiltrating fluid, interaction with the rock may replace some minerals and not others, as noted by O'Neil and Taylor (1967). This leads to grain-scale isotope disequilibrium, a situation explored by Abart and Sperb (1997).

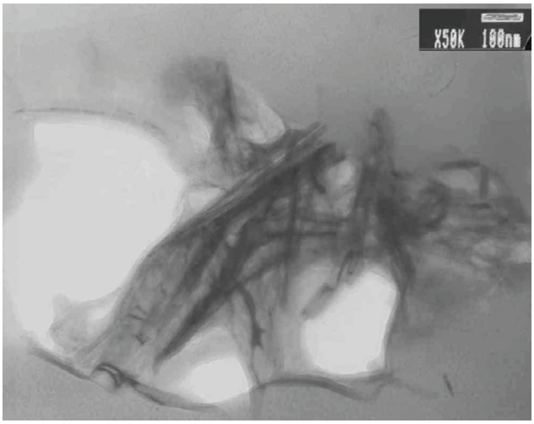


Figure 20. A single pore, containing hematite nano-platelets, in a pink feldspar from a hydrothermally altered granite. [Used with permisson of Elsevier from Putnis et al. (2007a).]

These studies suggest that the interpretation of geochemical and isotopic signatures of granites purely in terms of their magmatic origins, without considering the extent of sub-solidus reequilibration by externally derived fluids, is questionable.

Porosity and fracture generation and the mechanism of fluid transport through rocks

There is overwhelming evidence that fluids can flow through rocks. While tectonically-induced fracturing undoubtedly plays a major role in permeability development and introduction of fluid into rocks (Jamtveit and Yardley 1997), replacement reactions by dissolution-precipitation require that fluid infiltrates every part of a rock, moving *through* the minerals as they are replaced. Discussions about how fluids move through rocks are generally restricted to hydraulic fractures and grain boundaries (e.g., Kostenko et al. 2002), but porosity generation by a reactive fluid greatly increases the number of possible fluid pathways and the permeability of a rock. A replacement reaction creates this permeability behind the reaction front and as long as there is sufficient fluid and mass transport through the created porosity, rocks can be reequilibrated on a large scale. The fluid can literally react its way through a rock, by-passing some minerals with which there may be no reaction, or with which a reaction generates a non-porous product which effectively seals the mineral off from the fluid.

Fluid passing through rocks can result in large scale element mobilization in the earth (Oliver et al. 2004; Putnis et al. 2008). For example, albitization affects large volumes of rock in many parts of the crust, stripping the parent rock of major and trace elements, leaving behind pure porous albite. This "charged fluid" can migrate large distances before encountering conditions conducive to precipitation (Clark et al. 2005) and forming ore and mineral deposits.

How to recognize mineral replacement

In most of the examples above, a replacement interface could be recognized in the field, on the thin-section scale, and at the electron microscope scale in natural rocks, as well as in experimental samples. In these cases of partial replacement where the limit of fluid infiltration can be well defined, there is no doubt about the nature of the parent and product phases. However, in a rock which has been totally replaced, it is often not possible to determine the protolith, and there is a lot of scope for misunderstanding the petrogenesis of a mineral assemblage. At a thin section scale it is very important to study the textural relationships between minerals as well as internal microstructures. Porosity and the presence of mineral inclusions within pores is an indication that the host mineral is a replacement product. Porosity produces turbidity, especially in feldspars, and turbid feldspars are all secondary, whereas primary feldspars are clear and glassy. This has been recognized for many years (e.g., Folk 1955; O'Neil and Taylor 1967; Parsons and Lee 2009), but still deserves emphasis. Fluids can also preferentially move along cleavage planes and other defects leaving trails of fluid inclusions strung out along their length. It is a common observation that more calcic cores of zoned plagioclase crystals in igneous rocks are sericitized (i.e. forming an alteration product of fine mica + albite – e.g., Plümper and Putnis 2009) while more sodic rims are unaltered.

Replacement rims are often mistaken for and referred to as "overgrowths" representing a change in the chemical or physical conditions in the fluid from which the crystal is growing. While it is not always straightforward to distinguish between an overgrowth and a replacement, the presence of pores and inclusions in the rim is an indication for replacement.

An interesting example of recognizing the metasomatic origin of rocks has recently been described by Austrheim et al. (2008). Zircon rims around ilmenite occur in a wide variety of mafic igneous and granulite facies rocks (Bingen et al. 2001; Morisset and Scoates 2008). The rims may be continuous or may be trails of discrete single crystals along the oxide grain boundary. These rims and trails may serve as inert markers which remain in place after the ilmenite is replaced during a metasomatic or metamorphic event. In scapolitized gabbros from the Bamble and Kongsberg sectors in Norway, these markers can be seen in both the unaltered gabbro where the ilmenite is preserved, as well as in the scapolitized rock where the ilmenite is totally replaced by a new mineral assemblage. Only the unreacted zircon trails are evidence for the former ilmenite boundary and provide a physical reference frame which can be used to quantify the mobility of elements during replacement as well as to identify fluid involvement in the replacement mechanism (Austrheim et al. 2008). Again this study emphasizes the importance of studying the mineral and rock textures.

Replacement textures and "co-existing compositions"

An understanding of replacement textures aids in identifying when minerals are in equilibrium in a rock or when they represent a frozen-in parent-product relationship. The ease with which feldspars are partially replaced leads to many possibilities for very different feldspar compositions existing in a single hand specimen or thin section. If interpreted as "co-existing" from a thermodynamic point of view, this can lead to incorrectly proposed miscibility gaps.

"Leaching" and the formation of depleted surface layers

Many minerals and glasses, when exposed to aqueous solutions, do not dissolve congruently, so that the release of ions into solution is not in proportion to their composition in the solid. Such non-stoichiometric dissolution results in the development of chemically and structurally altered surface layers relative to the bulk. These are commonly referred to as "leached layers" and the prevailing view is that some components are selectively removed from the solid, and the depleted layer then may become structurally reorganized by a solid state mechanism.

Many of the examples above could be referred to as "leaching": the conversion of pentlandite $(Fe,Ni)_9S_8$ by violarite $(Ni,Fe)_3S_4$ involves removal of Fe and Ni; the reaction of natural pyrochlore $(Ca_{1.23}Na_{0.75})Ta_{1.78}O_{6.28}F_{0.57}$ with fluids results in the selective removal of Na and Ca; the reactions of REE-bearing zircon and monazite with fluid result in the removal of the REEs and the precipitation of secondary REE minerals within the replaced zones.

However, we have seen that using ^{18}O as a tracer in the fluid, this isotope has been *added* to the depleted layer, demonstrating an interaction between the whole fluid and the whole solid, and interpreted in terms of a coupled dissolution-reprecipitation mechanism.

Leached layers, depleted in metal ions, are commonly formed during incongruent dissolution of silicate minerals and glasses. Whether a silicate mineral dissolves congruently or incongruently depends on both the structure of the solid, and the composition of the fluid. Materials with the same chemistry but different crystal structure may dissolve differently, for example of the two forms of $CaSiO_3$, wollastonite dissolves incongruently while pseudo-wollastonite dissolves congruently (Casey et al. 1993). In feldspars, the pH determines whether dissolution is congruent (at high pH) or incongruent (at low pH) (Casey et al. 1989a,b; Petit et al. 1990).

If we consider the balance of free energies for such solid-fluid interactions, the overall reduction in free energy is achieved by considering the free energies of solids and fluids. Therefore it should not be surprising that as the structure and composition of either changes, a reaction Solid(1) + Fluid(1) → Solid(2) + Fluid(2) may be favoured over a reaction Solid(1) + Fluid(1) → Fluid(3). The thermodynamic argument is the same as that for congruent and incongruent melting – the phase diagram is merely a consequence of the relative positions of free energy curves for the phases involved, e.g., enstatite melts incongruently at atmospheric pressure but congruently at pressures above about 3 kbar. Small differences in the free energies of each phase can lead to very different phase equilibria.

However the mechanism of incongruent dissolution in silicate minerals has been the subject of much research and controversy. The generally accepted view is that H^+ ions from the solution diffuse into the structure and exchange for the metal cations which diffuse out of the crystal, leaving behind a silica-rich leached layer. This interdiffusion is accompanied by a spontaneous reconstruction of this layer to form amorphous silica (Casey et al. 1993). Weissbart and Rimstidt (2000) re-emphasized the role of the reconstruction of the leached layer in limiting the release of cations into solution, and summarize much of the earlier work on incongruent dissolution of wollastonite.

However, Hellmann et al. (2003) studied the interface between experimentally altered (i.e., leached), and non-altered plagioclase feldspar by high resolution transmission electron microscopy, and concluded that the interface was chemically and structurally sharp on an atomic scale, and did not show the compositional profiles that would be expected from a solid state interdiffusion mechanism. They concluded that the data were better explained by an interfacial dissolution-reprecipitation mechanism. In other words, the dissolution is initially stoichiometric, but is coupled with the precipitation of amorphous silica from a supersaturated boundary layer of fluid.

The mechanism of dissolution of glass is also a hotly debated topic, especially for glass which is used for the containment of radionuclides from spent nuclear fuel. The arguments are similar to those generally proposed for crystalline silicates: interdiffusion of H^+ and alkali cations in the glass to form a leached layer, accompanied by a structural reorganization of this layer to form glass with a different structure from the parent. The reaction with aqueous solution and production of a leached layer is generally referred to as “corrosion.” While in contact with the fluid, the leached layer continues to get denser with time, leading to pore closure and a sharp drop in the migration of the reaction interface (Cailleteau et al. 2008). Geisler et al. (2008) have proposed a new mechanistic model to explain the same data, based on congruent dissolution of the glass which is spatially and temporally coupled to the precipitation of amorphous silica at an inward moving reaction interface.

The debate on the mechanism of silicate mineral and glass corrosion is reminiscent of the debate about cation exchange between feldspars and alkali and alkali-earth chloride solutions, a debate which was definitively quashed by O'Neil and Taylor (1967) by their concept of a dissolution-reprecipitation model. It is tempting to interpret all of the examples of fluid-mineral interaction given in this chapter in a similar way. The example of the replacement of KBr by KCl after contact with a saturated KCl solution at room temperature is one in which interface-coupled dissolution precipitation cannot be seriously questioned. A slightly undersaturated KCl solution in contact with a crystal of KBr immediately completely dissolves the crystal, while in a saturated KCl solution a virtually perfect pseudomorph is formed, preserving crystallographic orientations, and with a porosity which depends on both molar volume changes and relative solubilities of parent and product in the fluid. Subsequent coarsening and loss of connectivity of porosity by continued textural equilibration slows the reaction with time (Putnis and Mezger 2004; Putnis et al. 2005). These common features in the other examples given above outweigh the differences. When the parent and product crystal structures are different, the product is polycrystalline, but in the few cases where any crystallographic orientations have been measured, a degree of topotaxy has been found (Glover and Sippel 1962).

Many of the observations made on the incongruent dissolution of silicate minerals could also be interpreted in terms of a coupled dissolution-precipitation model as suggested by Hellmann (2003), with subsequent textural reequilibration of leached layers by continued dissolution and reprecipitation. However, at the present time, the most commonly accepted explanation of leaching is related to interdiffusion of protons which form Si-OH bonds in the silicate network, and release weakly bound cations which diffuse through the structure and into the solution. Exactly how this interdiffusion is accomplished at room temperature remains a matter of some conjecture.

Determining the mechanism of the incongruent dissolution which results in these depleted layers is not merely an academic issue. The main point of understanding mechanisms is to be able to model experimental results and extrapolate these to long time-scales appropriate to understanding weathering reactions, in the case of silicate minerals, or to the long-term aqueous durability of materials used to encapsulate nuclear waste.

Another interesting example of the formation of "depleted layers" is found in the gold-rich rims on electrum (Au-Ag alloy) nuggets in placer gold deposits (see Fig. 21). The Au-rich, Ag-depleted rims vary in thickness and may have a convoluted, lobate interface with a core of less-pure gold. The interface between the core and rim is chemically sharp and the rim is porous. It is also a well known observation that alluvial gold becomes richer in Au-content the further it is from the lode from which it was derived (Groen et al. 1990) and the general consensus is that the Ag-depletion takes place at low temperatures. The enhancement of gold content on the surfaces of impure gold objects ("depletion gilding"), has been known since the pre-Columbian cultures of Central and South America, who treated the surfaces with naturally-derived organic fluids (Lechtmann 1984). The literature on the origin of the Ag-depletion has generally used

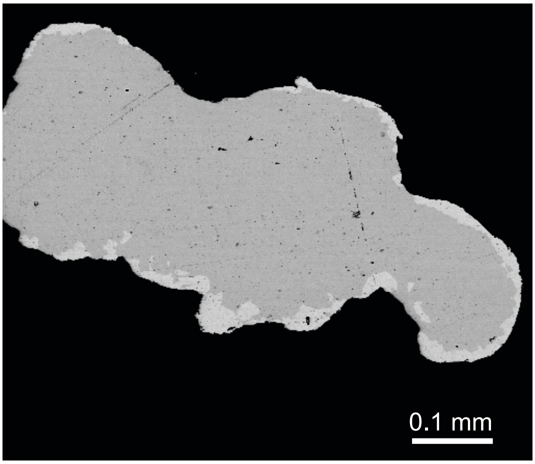


Figure 21. Reflected light image of a nugget of gold alloy (electrum Au-Ag), which has an Au-enriched rim (light grey). (Image: B. Grguric)

the terminology of "selective dissolution," whereby "the less noble element is preferentially removed from the alloy, leaving a gold-rich residue" (Fortey 1981). However, Groen et al. (1990) rejected a diffusion-based leaching mechanism to remove Ag as far too slow to account for the rim thicknesses (which would take between 10^{17} and 10^{18} years to form by solid state diffusion of Ag), and also inconsistent with the sharp compositional gradient at the interface between rim and core. Groen et al. (1990) invoke a mechanism termed self-electrorefining (Fontana 1986) (also used to explain "dezincification" of brass), where the electrum at the solid-fluid interface dissolves and the purer gold immediately precipitates back onto the surface of the grain. The porosity generation, due to the lower solubility of gold, allows continued contact between the fluid and the reaction interface. More recent crystallographic studies (Hough et al. 2007) have also shown that there is no variation in crystallographic orientation between the core and rim.

Solid state and dissolution-precipitation mechanisms: what's the difference?

This may seem a rather trivial question. In the extreme cases there is no ambiguity. As pointed out early in this Chapter, Cardew and Davey (1985) made the distinction between a polymorphic transformation in a dry system, in which all atomic motion is by volume or "solid state" diffusion and in a wet system where dissolution of the less stable polymorph is followed by precipitation of a more stable polymorph. Where there is no coupling between the dissolution and precipitation (i.e., the two processes are separate in both space and time) then the terminology of dissolution-precipitation has a well understood meaning. However, as these two processes become more closely coupled, a pseudomorphic replacement, which retains various degrees of crystallographic information, begins to have characteristics attributed to solid state reactions. Even in recent papers "structure inheriting solid state reactions under hydrothermal conditions" is a terminology in use (Eda et al. 2005, 2006) for reactions which preserve external morphology and aspects of the crystal structure. However, the degree of coupling between dissolution and precipitation can be manipulated by changing the fluid composition (e.g., Xia et al. 2009b) emphasizing that although the texture of the final product is very different, the fundamental mechanism remains the same.

There is an historical tendency to interpret the mechanisms of reactions in solid state terms even when fluids are present and other mechanisms are available. In the debate on the formation of leached layers in silicate minerals and glasses, a solid state terminology is also used, but modified to include terms such as "hydrolysis" of bonds and "condensation" of leached layers. On a nanoscale these terms may have similar meanings to "dissolution" and "precipitation." There is also, in general usage, the vague concept of "fluid-enhanced solid-state diffusion" (i.e., that "solid state" reactions are faster in the presence of fluid).

An example where a comparison between solid state diffusion and dissolution-precipitation has been made is in the reequilibration of cation distributions between coexisting minerals. In a perfectly dry system, when two minerals are in contact at high temperature, they may exchange cations across the contact by a volume interdiffusion process until the equilibrium cation distribution between the two phases is reached. For example, the interchange of Fe and Mg between two minerals, such as garnet and pyroxene, could be accomplished by a solid state diffusion mechanism which would initially produce a diffusion profile of Fe and Mg in each phase. However, if the two minerals were separated by a fluid, it is also possible that the same reequilibration could take place by a dissolution–precipitation process, retaining the morphology and crystallography but with a sharp interface between the parent and product compositions in both the garnet and the pyroxene. Analysis of experimental kinetic data and comparison with that expected from solid state diffusional exchange led Pattison and Newton (1989) to conclude that, in the presence of fluids, equilibration was by dissolution and precipitation. This has significant implications for the way thermodynamic data are extracted from experiments, as discussed by Pattison (1994).

It is well known that the presence of fluids enhances reactions which in a perfectly dry system would proceed at negligible rates. This suggests that the fluid acts as a catalyst, i.e. a substance that decreases the activation energy of a chemical reaction without itself being changed at the end of the chemical reaction. Thus in a reaction involving only anhydrous species

$$A + B \rightarrow X + Y \tag{12}$$

the thermodynamics of the solid phases will define the P,T slope of the univariant reaction curve. If water catalyses this reaction by providing a dissolution-precipitation mechanism, the P,T slope of the univariant reaction curve is not affected. This is the assumption made in petrology when determining P,T stability fields of a mineral assemblage, such as $X + Y$.

However, in an open system where a fluid with many dissolved components reacts with a rock, the fluid adds some components to the solids and removes others, such that the final assemblage $X + Y$ could have formed by a reaction such as

$$C + D + F_1 \rightarrow X + Y + F_2 \tag{13}$$

where F_1 and F_2 represent the compositions of ingoing and outgoing fluids. In such a case the fluid is not merely a catalyst but is a phase whose thermodynamics also needs to be considered, both before and after the reaction. It is therefore possible that an assemblage $X + Y$ could have formed at different P,T conditions by reactions (12) and (13).

A situation of this type has been discussed for the partial eclogitization of gabbros in Zambia, in which fluids not only enhance the reaction between anhydrous gabbros and anhydrous eclogites, but are also major contributors to the trace-element variations found in the reaction product (John and Schenk 2003; John et al. 2004).

Replacement processes in magma

In so far as a magma is a multicomponent solution from which minerals may precipitate or into which they may dissolve, the general principles of interface-coupled dissolution-precipitation are applicable. Tsuchiyama (1985) has described the reequilibration of plagioclase crystals of different compositions in melts in the system, diopside-albite-anorthite. Cross-sections of partially reequilibrated crystals show that the morphology is maintained while a sharp reaction interface moves into the crystal separating parent and product plagioclase compositions. The rim is porous, and is generally referred to as “dusty plagioclase,” due to the many melt inclusions trapped in the pores. The melts in such inclusions are in equilibrium with the product plagioclase composition (Nakamura and Shimakita 1998). Johannes et al. (1994), described such processes in terms of a “crystallographically oriented solution-reprecipitation mechanism.”

New strategies for materials synthesis

Synthesizing new materials with specific physical and chemical properties lies at the heart of materials science. Metal sulfide synthesis provides a good example of how coupled dissolution-precipitation replacement reactions can lead to new routes for synthesis of compounds. Many metal sulfides can be synthesized using traditional methods of reacting metal powders with molten sulfur at high temperatures (> 500 °C) in a vacuum. However, many sulfides are not stable at such high temperatures and their synthesis presents considerable problems. For example, violarite $(Ni,Fe)_3S_4$ is only stable below 373 °C, and below such temperatures the reaction rates are very slow and generate other unwanted impurities (Tenailleau et al. 2006b). However Xia et al. (2008) have demonstrated the synthesis of violarite and linnaeite (Co_3S_4) by replacement of pentlandite $(Fe,Ni)_9S_8$ and cobaltpentlandite (Co_9S_8) as precursors. The synthesis can be carried out at temperatures < 145 °C, and produces a much purer product in a fraction of the time.

Hydrothermal synthesis of materials is not new, but by using a suitable precursor phases and solution composition, the replacement route opens many new possibilities. Precursor phases in hydrothermal experiments have also been used by Eda et al. (2005, 2006) to synthesize alkali metal molybdenum oxides, but their interpretation of the mechanism is quite different. They define "structure-inheriting solid-state reactions under hydrothermal conditions" based on the fact that the product phase inherits the morphology of the parent (i.e., is a pseudomorph) as well as preservation of some aspects of the crystallographic structure. Structural models are then devised to explain how such a "solid state" reaction might be achieved. However, as we have seen above, preservation of morphology and structure is also a feature of the interface-coupled dissolution-precipitation mechanism.

The experimental conversion of sulfates to carbonates has also been interpreted in terms of a coupled dissolution-precipitation mechanism. Celestite ($SrSO_4$) can be readily converted to strontianite ($SrCO_3$) under hydrothermal conditions in carbonated solutions (Suárez-Orduna et al. 2004, 2007). The external morphology is preserved, the product is porous and there is a sharp reaction front between the parent and product phases. Since the crystal structures of the two phases are different, the product is polycrystalline. Similar experiments have been used to pseudomorphically replace celestite by $SrCrO_4$ (Rendón-Angeles et al. 2005), barite ($BaSO_4$) by $BaCO_3$ (Rendón-Angeles et al. 2008) as well as celestite by SrF_2 (Rendón-Angeles et al. 2006). In each case the features of the replacement are consistent with an interface-coupled dissolution-precipitation mechanism, although in earlier publications the pseudomorphism was thought to necessitate a solid state reaction.

In some cases the preservation of morphological and internal microstructural details of the parent becomes the main design rationale of materials synthesis. For example, in the conversion of leucite to analcime (see above), the very fine twinning common in leucite is preserved, and the reprecipitation reaction produces arrays of uniformly oriented analcime nanocrystals which inherit their crystallographic orientation from the leucite. There is considerable interest in developing methods of producing materials with self-assembled arrays of nanocrystals, and Xia et al. (2009a) have proposed that three-dimensional arrays can be produced by a suitable choice of parent phase and solution composition.

An early classic example of materials design using this principle of preservation of morphology during replacement was the conversion of natural coral to hydroxyapatite (Roy and Linnehan 1974) to produce porous material which would be compatible with bone for medical implants.

CONCLUSION

Understanding reaction mechanisms is a fundamental step for understanding processes in nature and in industry. In the examples described in this chapter we have seen that in the presence of a fluid phase, reequilibration processes in a wide range of materials are dominated by dissolution and reprecipitation mechanisms. The range of materials has included open framework structures where solid state ion exchange may have been expected, sulfides in which volume diffusion is relatively rapid, highly soluble salts and low solubility phosphates, oxides, silicates and metal alloys. The interaction of aqueous fluids with these materials results in a remarkable consistency of behavior, especially in the way that the dissolution and precipitation processes are coupled, and how the relative solubility and molar volume combine to create porosity which allows fluid to continuously migrate to the reaction interface. The recent discovery that the coupling can be manipulated by changing the fluid composition, not only emphasizes the role of the fluid in the coupling, but opens new avenues for materials syntheses.

The realization that fluids not only trigger metamorphic processes, but also contribute to the chemistry of the solids, introduces a new and largely unknown parameter into determining the thermodynamics of metamorphic and metasomatic reactions. The thermodynamics of the aqueous fluid phases, before and after the reaction must be included. However, before we can even begin on such a daunting task, we need to recognize the role of fluids in determining textures of rocks over a wide range of spatial scales.

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