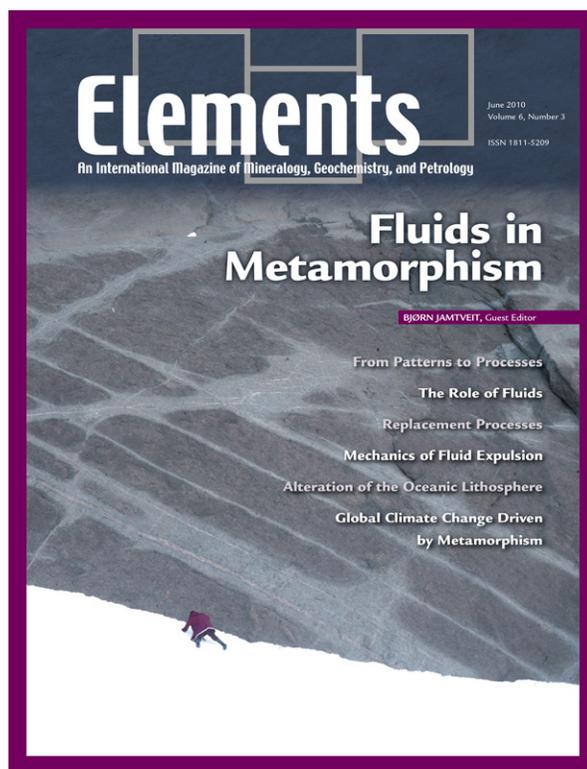


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Replacement Processes in the Earth's Crust

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A fundamental question in metamorphism is: What is the mechanism that converts one mineral assemblage into another in response to a change in the physical and/or chemical environment? The fact that aqueous fluids must be involved in such large-scale re-equilibration has been demonstrated by petrological, mineralogical, micro-structural and isotopic data. Fluid–mineral reactions take place by dissolution–precipitation processes, but converting one rock into another requires pervasive transport of reactive fluid through the entire rock. The generation of reaction-induced porosity and the spatial and temporal coupling of dissolution and precipitation can account for fluid and element transport through rocks and the replacement of one mineral assemblage by another.

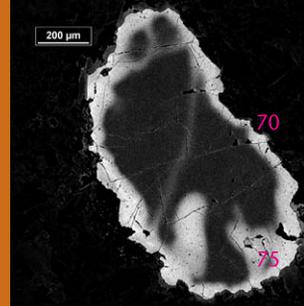
KEYWORDS: mineral replacement, crustal fluids, metasomatism, fluid–rock interaction, dissolution–precipitation

INTRODUCTION

Metamorphic petrology is often concerned with assigning a specific range of pressure and temperature (P , T) conditions over which an observed mineral assemblage is stable. From a sequence of stable mineral assemblages, usually interpreted from micro-structures, textures and inclusions, a schematic pressure–temperature–time (P – T – t) path can be derived that provides valuable constraints on the large-scale geodynamic processes that drive the metamorphism. The metamorphic response to a geodynamic process does however depend on the mechanism of the various phase transitions and on the relative roles of solid-state diffusion (where the rock is considered to be dry) and dissolution–precipitation (in the presence of a free fluid phase). In this context, the mechanism of the metamorphic reactions that take place with increasing metamorphic grade, for example, the isochemical reaction from kyanite to sillimanite, was considered by Carmichael (1969). From a textural study of thin sections, he noted that sillimanite does not grow directly from kyanite but forms by a sequence of dissolution–transport–precipitation sub-reactions. First the kyanite reacts with quartz and K^+ -bearing fluid to form a solution through which the components diffuse a short distance in the rock and precipitate muscovite. The muscovite in turn reacts with the fluid to form sillimanite and quartz. More complex reactions were explained by similar schemes involving fluid and mass transport, albeit on a small scale.

Carmichael (1969) points out that, even in a closed isochemical system, local mass transport must occur during the re-equilibration of a rock. Thus on a small spatial scale

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A partially replaced garnet from the Bergen Arcs, Norway, where granulite has been eclogitised by a fluid. The dark core has the original composition of a granulitic garnet, while the pale rim has the lower Mg/Fe ratio of an eclogitic garnet. COURTESY OF K. POLLOK

the system is chemically “open,” while on a larger scale it may be closed. Metamorphism accompanied by a change in rock composition is referred to as metasomatism and is normally assumed to be the response to fluid-controlled mass transfer, rather than purely to changes in P – T conditions. However, Carmichael’s example illustrates that the spatial scale at which a system is claimed to be open might be somewhat arbitrary.

Thus, one may ask whether the distinction between metamorphism and metasomatism is really useful, or even valid? Is it only a matter of spatial scale or degree of compositional change? Can we recognise the difference between a reaction driven by a change in P – T conditions and one driven by the infiltration of a fluid out of equilibrium with the parent assemblage?

In this article, we focus on reactions that occur when an essentially dry, low-permeability rock is infiltrated by a fluid that induces re-equilibration of the mineral assemblage. Such rocks make up most of the continental crust. Fluid infiltration may or may not be associated with a tectonic event characterized by changing pressure and temperature, and the effect of the fluid composition in changing the mineral assemblage of the rock can vary over a wide spectrum. In a fluid-saturated sedimentary basin undergoing progressive burial, diagenesis and metamorphism, the scale of mass transfer and fluid transport may be limited (Yardley 2009). Here we are not explicitly concerned with the scale of mass transport, but rather with the mechanism of re-equilibration at the fluid–mineral interface.

To determine the mechanism of metamorphic reactions, we need to find examples of interfaces and reaction textures that contain both the “before” (the protolith) and the “after” mineral assemblages – in other words, case studies where the process of conversion is “frozen in”. In the following examples, we illustrate some aspects of the role of fluids in metamorphic reactions and discuss how reactive fluids can pervasively infiltrate a rock. We argue that fluids not only trigger sluggish isochemical reactions but also may drive reactions through compositional changes of the affected system at constant P and T ; further, we contend that the common mechanism for replacing one rock type by another is dissolution–precipitation. We use examples

from crystalline rocks and include reactions from the lower continental crust, subducting oceanic crust and continental upper crust. We start with observations made at the outcrop scale and then zoom in to examine at the nanometre scale the mechanisms occurring at the mineral-mineral interface.

REPLACEMENT PROCESSES AT LOWER CRUSTAL CONDITIONS AND IN SUBDUCTION ZONES

Metamorphism, fluid flow and mass transfer play a major role in processes in the deep crustal roots of mountain belts and in subduction zones (Austrheim 1987; Philpotts and Ague 2009). For example, the conversion of crustal rocks into eclogite is a very important transformation that takes place along low geothermal gradients. It is associated with changes in rheology, with earthquakes and with arc magmatism. However, geophysical measurements of subducting oceanic lithosphere have shown that eclogitisation of lower crustal rocks (e.g. oceanic gabbro) does not always take place as one would expect from the ambient P - T conditions (Rondenay et al. 2008), and the same observation has been made for the roots of mountain belts (Jackson et al. 2004).

FIGURE 1 shows a well-studied example of a partial reaction in which granulite is transformed into eclogite in the Bergen Arcs region of western Norway, where the root zone of the former Caledonian mountain belt outcrops today. The eclogite formation is associated with fractures in the rock, and Austrheim (1987) argues that the interface between the eclogite and granulite represents the limit of infiltration of the fluid that promoted the eclogitisation. This suggests that the surrounding granulite was preserved within the stability field of eclogite because element mobility by solid-state diffusion was not possible at the relevant temperature and timescale (Jamtveit et al. 1990).

Many studies of exhumed slices of formerly subducted oceanic rocks have shown that eclogitisation occurred exclusively in the parts of the outcrop, rocks and minerals where fluids infiltrated (e.g. John and Schenk 2003). In the case of a gabbro under low strain, this replacement occurred pseudomorphically, retaining the texture of the gabbro



FIGURE 1 Eclogite band (dark) following a fracture in granulite (pale), Bergen Arcs, western Norway

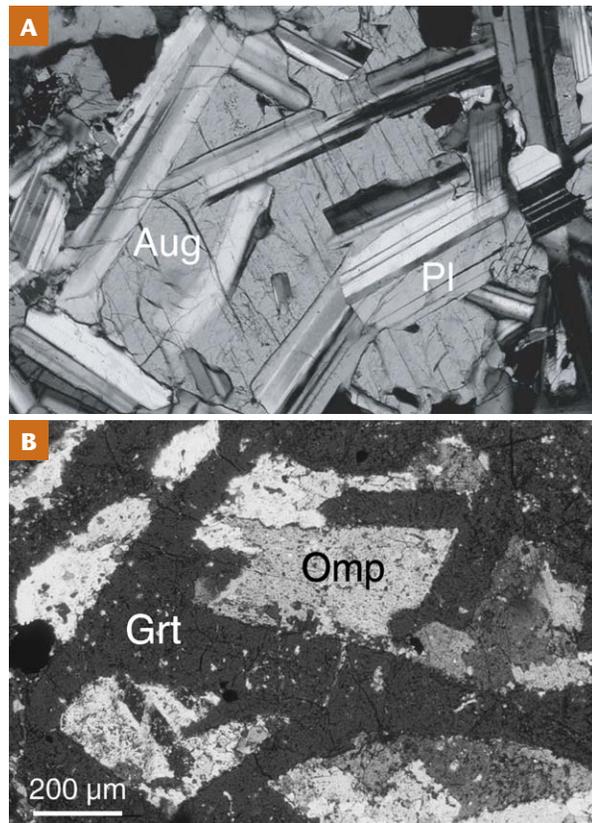


FIGURE 2 (A) Photomicrograph of a gabbro with typical ophitic texture (Aug = augite; Pl = plagioclase). (B) Pseudomorphic replacement of a gabbro, such as in A, by eclogite. Omphacite (omp) pseudomorphically replaced augitic pyroxene, and garnet (Grt) replaced plagioclase, preserving the magmatic texture. See JOHN AND SCHENK (2003)

(FIG. 2). Only the eclogitisation itself and the reaction textures indicate fluid infiltration; the conversion of dry gabbro to essentially dry eclogite only locally resulted in the formation of hydrous minerals. The conclusion is that the gabbro-to-eclogite transformation was facilitated by fluid, which provided a faster means of material transport than solid-state diffusion. The process was dissolution, element transport through the fluid and re-precipitation of a more stable assemblage.

Further examples of how fluids affect metamorphic reactions are provided by the blueschist-to-eclogite and eclogite-to-blueschist transformations that are associated with well-known dehydration and hydration reactions (e.g. Peacock 1993). Field evidence shows that the flow field of fluids released from subducting slabs is channelized and that these fluids tend to react with their wall rocks (Breeding and Ague 2002; John et al. 2008). In the Tianshan mountains (China), initial eclogitisation (i.e. dehydration) of blueschists takes place along well-developed reaction selvages associated with veins several metres in length formed by external fluids. In our case study, a profile sampled perpendicular to a vein shows a transitional conversion from blueschist to eclogite towards the vein, which is accompanied by a gradual change in composition from Ca-poor to Ca-rich (Beinlich et al. 2010). Thermodynamic calculations for the two distinct bulk compositions – the Ca-poor blueschist (6–7 wt% CaO) and the Ca-rich eclogite (up to 16 wt% CaO) – indicate that both mineral assemblages are stable at the same peak P - T conditions (21 ± 1.5 kbar and $510 \pm 30^\circ\text{C}$); this is also confirmed by conventional geothermobarometry (Beinlich et al.

2010). In this example the transformation of blueschist to eclogite is driven by the change in bulk composition through interaction with the Ca-rich fluid, not by differences in lithostatic pressure or ambient temperature. The eclogite formed where the reactive fluid infiltrated the precursor blueschist. The progress of the reaction, manifested by the replacement of glaucophane by omphacite, as well as the progressive change in the bulk composition of the rock are dependent on the distance to the fluid conduit.

The fluid phase may play two roles in a metamorphic reaction. First, by providing a dissolution–transport–precipitation mechanism for an essentially isochemical reaction, it acts as a catalyst that plays only a kinetic role. On the other hand, the fluid can also affect the thermodynamics of a reaction by changing the chemical potential of so-called “mobile” components, and hence can affect the bulk composition of the system.

This is further illustrated by the case where a subducting slab becomes partly dismembered; then, some eclogite is exhumed and becomes (re)hydrated, and transforms back into blueschist (e.g. van der Straaten et al. 2008; Miller et al. 2009). FIGURE 3 shows part of an eclogitised pillow lava that has been transformed into blueschist along a pillow rim during retrograde metamorphism. Field observations and petrologic data indicate migration of a free fluid phase into the pillow interiors, forming a reaction zone. The interfaces between the precursor eclogite and the product blueschist (FIG. 3C, D) show a well-defined reaction front. At higher magnification, the parts that are almost completely converted to blueschist illustrate the replacement character of the transformation. FIGURE 3B shows the replacement of omphacite by glaucophane, caught in the

act, with only small patches of omphacite left in the core. Mass-balance calculations for this reaction front and zone, using immobile trace elements as a reference frame, show an overall mass loss and a corresponding volume loss during the eclogite-to-blueschist transformation. During transformation, the rock gained Mg, Ni and Co and lost Si and Ca, implying that the fluid was in equilibrium with rocks of peridotitic composition prior to infiltration (van der Straaten et al. 2008).

Since the precursor eclogite had a lower water content than the blueschist, fluids had to be involved. Furthermore, the chemical changes across the reaction interface demonstrate that this was not an isochemical reaction. The interaction between the eclogite and the infiltrating fluid caused a significant mass loss to the fluid phase, resulting in an overall volume loss that allowed fluid infiltration and diffusion to proceed.

THE REPLACEMENT OF ROCKS IN THE UPPER CONTINENTAL CRUST

In our case study from the upper continental crust, we examine how fluid can change a rock composition, producing pseudomorphs of initial minerals and retaining the overall texture. We also show that replacement processes that reproduce natural textures can be achieved in very short times in laboratory hydrothermal experiments.

In the Bamble sector of southeastern Norway, outcrops of albitite and unaltered granite and gabbro allow detailed studies of reaction mechanisms (FIG. 4A). Albitisation is estimated to have taken place at 350–450°C and 2–4 kbar (Nijland and Touret 2001).

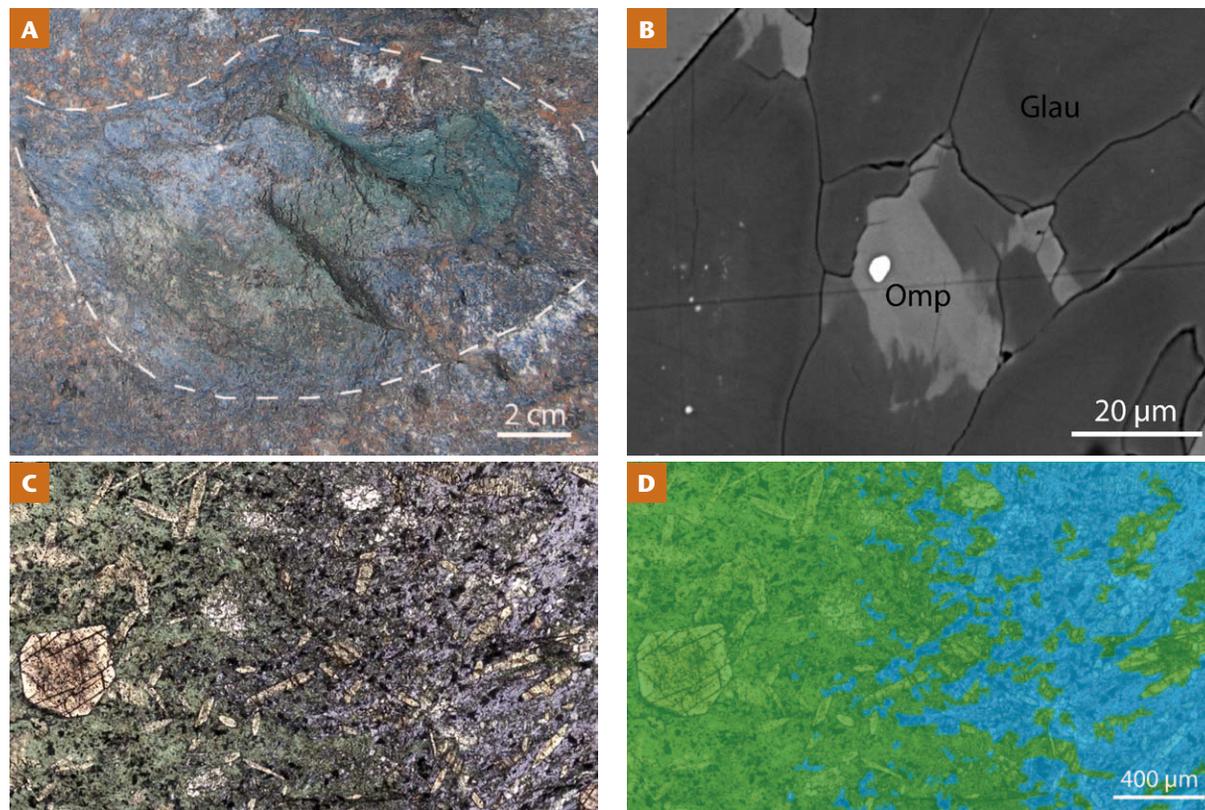


FIGURE 3 Eclogite-to-blueschist transformation (van der Straaten et al. 2008). (A) Field image showing an eclogite pillow lava relict (green) that is partly replaced by blueschist (blue). The dashed line highlights the former outline of the pillow structure. (B) Back-scattered scanning electron micrograph showing the

replacement of omphacite (Omp) by glaucophane (Glau), along sharp and irregular interfaces. (C) Thin section image showing the reaction interface, (D) A simplified representation of B showing the blue rock (blueschist) replacing the green rock (eclogite) along an irregular interface.

Individual grains of plagioclase feldspar in the protolith (composition $\sim\text{An}_{20}$) were pseudomorphically replaced by albite (Engvik et al. 2008) (FIG. 4B). The reaction interface lies within each partially replaced single crystal and proceeded both through the solid mineral and along microfractures. The micro-structure shows a number of characteristic features of mineral replacement reactions:

- Isovolumetric replacement, i.e. the external dimensions of the parent plagioclase grains are preserved;
- A sharp reaction front, indicating that volume (lattice) diffusion played an insignificant or minor role in the reaction;
- Porosity (assumed to be interconnected) developed in the albite product, which allowed fluid and mass transfer by diffusion through the pores in albite to and from the reaction front;
- Preservation of the crystallographic orientation of the feldspar across the reaction interface.

Hydrothermal experiments on feldspar–alkali chloride equilibria have been carried out for many years (e.g. Orville 1972; Moody et al. 1985), but the replacement mechanisms have only recently been clarified (Labotka et al. 2004; Niedermeier et al. 2009; Hövelmann et al. 2010). The albitisation reaction shown in a natural example from the Bamble sector (FIG. 4B) was reproduced experimentally in a hydrothermal reaction (600°C, 2 kbars, 18 days) between plagioclase (composition $\sim\text{An}_{22}$) and an aqueous solution containing Na and Si (Hövelmann et al. 2010). FIGURE 4C is a cross section through a partially replaced crystal. Replacement takes place at the rim as well as along fractures. Quantitative compositional data indicate the loss of Ca, Al, K and trace elements to the fluid phase. If the experimental solution is enriched in ^{18}O , this isotope can be used as a tracer for oxygen exchange during the replacement. Raman spectroscopy confirms that the ^{18}O is incorporated into the silicate framework of the albite; thus, all elements are exchanged in this dissolution–precipitation process (Hövelmann et al. 2010).

An important issue arises from an interpretation of images such as FIGURES 4B AND C. Partial replacement is one of the micro-structural criteria considered to be reliable indicators of a metamorphic reaction in P – T space, with the implication that the parent and product phases represent a ‘frozen-in’ stable coexistence at the reaction boundary (Vernon et al. 2008). However, in the case of the albitisation reaction, the parent plagioclase and product albite clearly are not an equilibrium pair, and the interface between them represents the reaction between the plagioclase and an Na,Si-bearing fluid, with which it is out of equilibrium. The partial dissolution of plagioclase in this fluid generates an interfacial solution supersaturated with respect to albite, and equilibrium, if it exists at all, would be between this solution and the precipitating albite.

INTERFACE-COUPLED DISSOLUTION–PRECIPITATION

The examples above show that one mineral can be replaced by another in the presence of a fluid with an appropriate composition. A large number of experiments of salt systems, oxides, sulphides and silicates show that, at temperatures too low for solid-state diffusion to be effective on the observed length scales, micro-structures are produced by coupled dissolution and precipitation at a reaction interface (Putnis 2009).

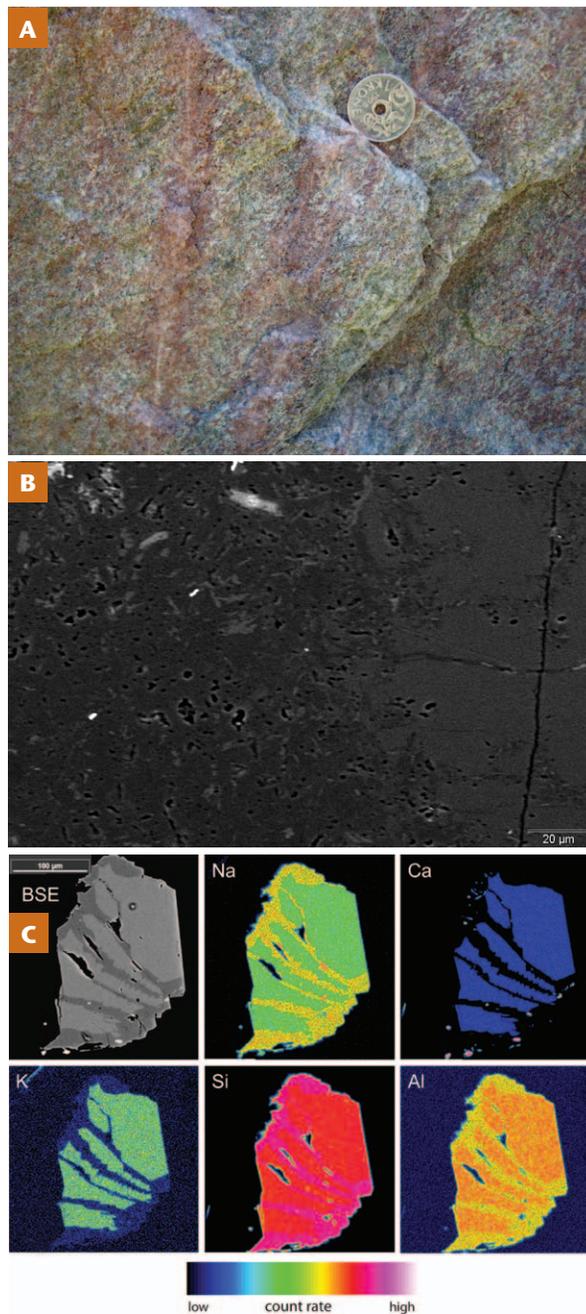


FIGURE 4 (A) Field image from the Bamble sector, southeastern Norway, showing reddening due to hematite precipitation, which is associated with albitisation around fractures. (B) Back-scattered electron SEM image of a sample from the edge of an albitised zone similar to that in A. The parent plagioclase (anorthite content An_{22}) is partially replaced by albite (An_2) (darker grey, on the left). The plagioclase has a smooth texture while the albite is full of pores (black) and small sericite mica inclusions. (C) Cross sections of experimentally albitised plagioclase (dark grey in the BSE image). The element maps show replacement by albite along the rim and fractures. IMAGES B AND C COURTESY OF A. ENGVIK AND J. HÖVELMANN, RESPECTIVELY

When a fluid interacts with a mineral with which it is out of equilibrium, dissolution begins. At the fluid–mineral interface, even the dissolution of a few monolayers of the parent may result in a new fluid composition that is supersaturated with respect to a more stable phase. The precipitation of this phase on the surface of the parent phase depends on the kinetics of nucleation. If the parent and

potential product phase have some common crystallographic relationships, this favours epitaxial nucleation. In the case of a feldspar replaced by a feldspar, the parent and product share the same orientation across the reaction interface.

Where there is a lower degree of lattice matching, the product phase is likely to be polycrystalline with no obvious epitaxy. Nucleation of the product is also favoured if there is a high value of supersaturation at the fluid–mineral interface (i.e. a low solubility of the product phase). Dissolution and precipitation may be very closely coupled, resulting in an exact pseudomorph preserving nano-scale features of the parent, or they can become spatially separated, depending on whether the overall reaction is dissolution controlled (the first case), or precipitation controlled (the second case) (Xia et al. 2009).

Once the reaction interface between the parent and product phase is established, its propagation through the parent depends on the continued availability of pathways for fluid transport to and from this interface. The generation of porosity in the parent phase is therefore an integral requirement for the reaction to continue beyond producing a superficial layer. The generation of porosity depends on two factors: the change in the molar volume of the solid phases, and the relative solubilities of the solid phase, in the fluid phase. The second factor determines how much of the parent is dissolved relative to how much of the product is precipitated, and it can outweigh the first factor (i.e. a porosity can still be generated) if there is an overall molar volume increase. This is discussed in more detail in Putnis (2009).

The hydrothermal replacement of albite by K-feldspar in an aqueous solution of KCl is a good example of an interface-coupled dissolution–precipitation reaction (Labotka et al. 2004; Niedermeier et al. 2009). FIGURE 5 shows partial replacement in an experimental sample, with a sharp reaction interface between the parent albite and the product K-feldspar. The diffraction contrast in the TEM image mosaic shows that the K-feldspar is defect rich and suggests nano-channels normal to the interface. Nano-pores in the product phase have also been imaged in a TEM study of albitised plagioclase (Engvik et al. 2008). Diffraction patterns in both cases confirm that the crystallographic orientations are preserved when feldspar is replaced by feldspar.

In metamorphic reactions the replacement of one mineral by another need not be pseudomorphic, and as in the examples given by Carmichael (1969) the dissolution of one phase may not be spatially coupled to the precipitation of a product. The degree of spatial coupling depends on the relative rates of dissolution, diffusive transport through the fluid, and precipitation (Xia et al. 2009).

FLUID TRANSPORT THROUGH ROCKS

The mechanisms of fluid transport in metamorphic rocks have been widely discussed in the literature (e.g. Oliver and Bons 2001; Ague 2003). However, the low permeability of metamorphic rocks measured in the laboratory is not consistent with the estimates of time-integrated fluid fluxes inferred from metamorphic reactions (Ingebritsen and Manning 2003; Jamtveit et al. 2008). This suggests that permeability must be enhanced during metamorphism.

A number of fluid-transport pathways have been proposed: (1) pre existing as the intrinsic rock porosity (e.g. grain boundaries), (2) created by deformation (e.g. grain-scale dilatancy), or (3) transport by the fluid event itself (hydraulic fracturing from fluid overpressure during devol-

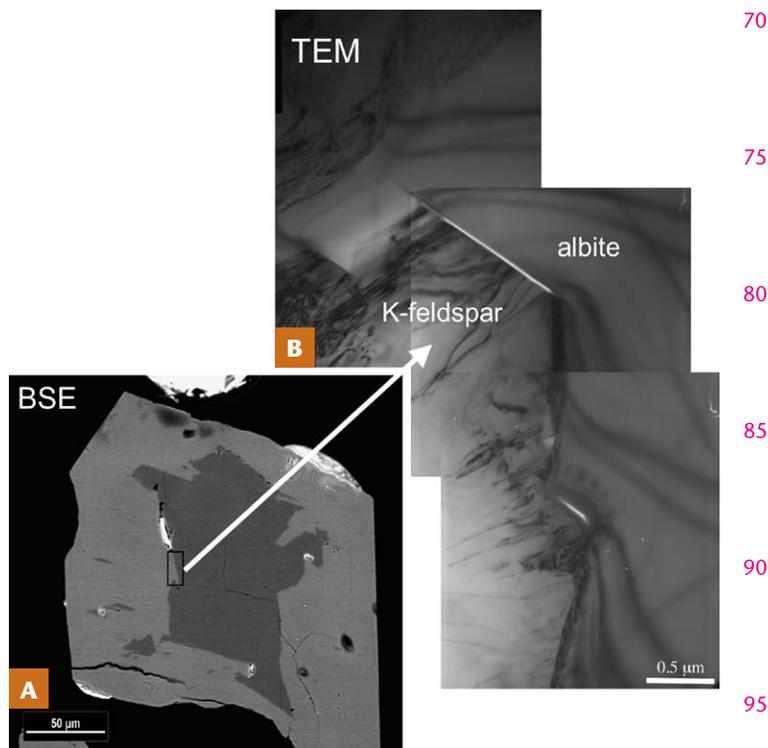


FIGURE 5 (A) BSE SEM image of a cross section of an albite crystal (dark core) partially replaced by K-feldspar (pale grey rim). (B) TEM image mosaic of the sharp chemical and structural interface between the albite parent and the K-feldspar product. IMAGE COURTESY D. NIEDERMEIER

atisation). A volume decrease between parent and product phases is also frequently cited as a cause of reaction-enhanced permeability (e.g. Cartwright 1997; Ferry 2000). However, development of new flowpaths does not explain how re-equilibration of an entire crystal could take place. Diffusion through the volume between closely spaced micro-fractures has usually been invoked as an explanation.

Porosity generated by interface-coupled dissolution–precipitation – allowing pervasive fluid transport through mineral grains, dissolving the parent at the reaction front and precipitating the product in its wake – eliminates the need to invoke solid-state diffusion at any stage of re-equilibration. Establishing interconnected porosity allows diffusion to and from the reaction interface through the fluid phase.

IMPLICATIONS

Metamorphic reactions can be driven by changes in P – T conditions, changes in chemical environment resulting from fluid infiltration, or both, through the processes of dissolution, transport and precipitation. This has implications for a number of other aspects of metamorphism which we have not addressed. Some of these provide topics for future research.

1. Interpreting micro-structures in terms of metamorphic events carries with it the implication that parent and product phases represent an equilibrium pair. This is not necessarily the case, either in partial replacement textures or in other reactions such as coronas formed at grain boundaries between two adjacent minerals (Putnis and Austrheim 2010). When fluids are involved, such reactions need not be isochemical, and the most likely equilibrium is between an interfacial fluid phase and the product phase(s).

2. In a dissolution–precipitation reaction, the partitioning of trace elements between parent and product phases may be influenced more by the nature and transport properties of the interfacial fluid than by any intrinsic closed-system equilibrium partitioning coefficient. In an open system, diffusion and advection in the fluid determine how much of the trace element content of the parent may be incorporated into the product. Fluid–mineral partition coefficients are valid, but the effective concentration of a specific element in solution has to be carefully evaluated.

3. When solid-state diffusion is not the principal mechanism for re-equilibration and when fluid composition rather than temperature is the driving force for metamorphic change, the concept of a “closure temperature” – used in isotope geochronology to determine when a mineral is effectively closed to further element exchange by solid-state diffusion – requires re-evaluation. Recognition that both temperature-dependent and fluid-dependent processes

may operate during re-equilibration opens the possibility of dating both the thermal history and the “hygrometric” history of a rock (Villa 2006).

4. Experiments on mineral-replacement reactions indicate that, under hydrothermal conditions, reactions are very fast on a laboratory timescale and instantaneous on a geological timescale. This suggests that metamorphic reactions involving fluids may be fast even under conditions where the fluid and parent rock are not far from being in equilibrium.

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