Fluid-induced processes: metasomatism and metamorphism

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ABSTRACT

Metamorphism and metasomatism both involve the reequilibration of mineral assemblages due to changes in pressure, temperature and/or chemical environment. Both processes involve material transport but on different length scales, so every metamorphic reaction is metasomatic on a local scale. Fluids provide a transport mechanism which is orders of magnitude faster than solid state diffusion and induce reequilibration through dissolution of parent phases and reprecipitation of products. Chemical weathering (kaolinitization and serpentinization), and albitization are used as examples to describe the coupling between dissolution and precipitation. Albitization of feldspars in nature and in experiments is a pseudomorphic replacement which generates porosity in the albite. Porosity generation associated with interface-coupled dissolution-precipitation allows rapid material transport and together with fluid induced fracturing, is the mechanism of pervasive fluid flow through reacting crystals. Examples of metamorphic reactions in granulite-eclogite rocks illustrate the role of fluids in inducing chemical changes along fluid pathways. Microstructural criteria for a metamorphic event (i.e. change in P, T) are critically reviewed by describing the corona formed by reaction between kyanite and garnet, as well as partial replacement textures. We conclude that both corona structures and partial replacement textures are equally indicative of a metasomatic reaction (driven by a fluid-induced compositional change) as they may be of a metamorphic reaction driven by a change in P and/or T. This raises the question of the extent to which fluids play not only a catalytic role but also a thermodynamic role in determining the course of a metamorphic reaction.

Key words: dissolution–precipitation, fluid–rock interaction, metamorphism, metasomatism

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INTRODUCTION

Metasomatism is traditionally defined as metamorphism which involves a change in the chemical composition, excluding the volatile components. This distinction between metasomatism and metamorphism may appear to be well defined, but as no reaction can occur without transport, it appears that this definition requires that we specify an arbitrary length scale of mobility to distinguish the two processes. The fundamental question is therefore whether the two processes rely on completely different reaction mechanisms, that is, does metamorphism occur without the presence of a fluid phase, as opposed to metasomatism where fluid is ubiquitous. Within the general context of mineral–fluid interaction the distinctions become less clear, both in terms of the spatial scale

involved as well as the extent of chemical change between the protolith and the product mineral assemblage. If metamorphism is defined as the process by which a mineral assemblage reequilibrates in response to changes in pressure and temperature (P, T), then metasomatism is the reequilibration of a rock involving a change in the chemical composition. The latter clearly implies an external source and flux of material over a significant distance and this can only be achieved through the interaction of the parent rock with a fluid phase. Metasomatism may be driven by a tectonic event and so be associated with a change in P, T conditions, but as will be shown from the following examples, fluid-driven events need not be associated with tectonism. For a broad understanding of the response of a rock to changes in physicochemical conditions we therefore need to consider not only changes in pressure and temperature

but also the availability and chemical composition of fluids which may be associated with a metamorphic or metasomatic event. Implicit in any such discussion is the question of the mechanism of reequilibration of a solid mineral assemblage to form a new assemblage, in the presence of a fluid phase.

The major difference between the reequilibration of a rock with and without the presence of a fluid phase is the relative kinetics of the mechanisms for mass transport and reaction. In a 'solid state' reaction, mass transport can occur by grain boundary diffusion or volume diffusion through crystal grains, both slow mechanisms with large activation energies which are unlikely to have a significant effect on rock textures except perhaps at the highest temperatures. The common observation of microstructures in chemical and isotopic disequilibrium illustrates the fact that equilibration by solid state diffusion can only operate on a length scale much shorter than the scale of the microstructure. In the presence of a fluid phase, mass transport can take place by advection and diffusion through an interconnected fluid with activation energies typically 10 orders of magnitude faster, so that mass transport continues to operate at low temperatures. Reequilibration by dissolution and precipitation becomes a viable mechanism and as we shall see below, the rates of such processes are fast even on a laboratory time-scale. Reaction rates are therefore dependent on the availability of fluid, a point which will be emphasized throughout this paper. Thus on kinetic grounds, it has become clear that fluid flow and mass transport play fundamental roles in both metasomatism and metamorphism (Philpotts & Ague 2009).

Metasomatism is clearly recognized on the outcrop scale when a reaction interface can be seen between the protolith and a rock with a different mineralogy, often with a distinct mineral assemblage and chemistry. An example is the albitization of granitic rocks from the Bamble Sector of SE Norway where albitization of a preexisting plagioclase feldspar ($\sim$An$_{21-23}$) occurs normal to fractures in essentially unaltered rock (Fig. 1A). In the field such a reaction front can be recognized by a reddening of the rock due to hematite precipitation associated with the albitization (Engvik *et al.* 2008). Such reaction fronts represent the limits of fluid infiltration, and allow a detailed study of the 'before' and 'after' compositions and textures. In the reaction front region, reaction interfaces in individual crystals can be studied by scanning and transmission electron microscopy and mechanisms of reactions inferred. However, such albitization occurs on a regional scale in the Bamble Sector, but in the absence of a clear reaction front, metasomatized rocks may not be recognized as such, and may merely be mapped as 'albitites' with no specific genesis, or even assigned the wrong origin (Elliott 1966; Bodart 1968).

In the Curnamona Province in the Olary Domain of South Australia, similar reaction fronts are common (Fig. 1B), often indicating several episodes of fluid infiltration and reaction (Clark *et al.* 2005). Albitized rocks in this area cover many hundreds of square kilometres, and, as in the Bamble Sector, are spatially related to ore deposits. Perhaps one of the best-studied examples of large-scale sodic metasomatism is in the Mary Kathleen Fold Belt in the Mount Isa Inlier (Queensland, Australia) involving scapolitization and albitization as a result of infiltration of large volumes of highly saline brines at high temperatures (500–700°C) (Oliver *et al.* 1994). Again, these alteration systems are associated with extensive mineralization and evidence of the passage of fluids through rocks, stripping them of their metal content which is reprecipitated from the fluid elsewhere. These and many other examples provide evidence for long-distance mass transfer. Albitization is not however restricted to high temperatures nor to any specific rock type or tectonic setting (Perez & Boles 2005) and can take place at temperatures as low as those in early diagenesis (Saigal *et al.* 1988; Lee & Lee 1998; Holness 2003; Lee *et al.* 2003).

Regional-scale metasomatism is not confined to sodic alteration, and regional Ca-metasomatism, K-metasomatism,
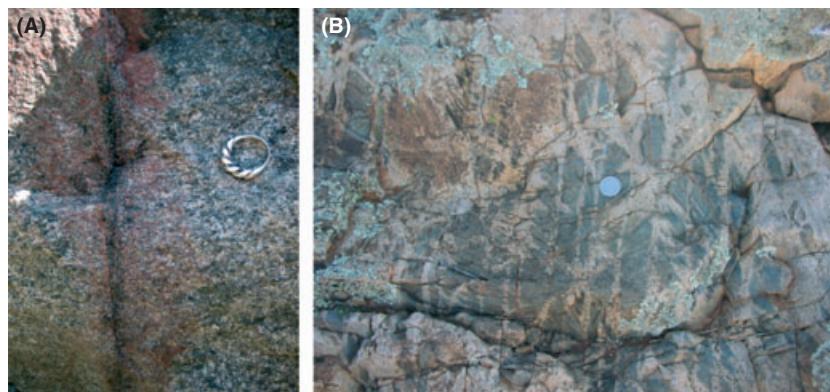

Fig. 1. Field photographs of albitization. (A) Alteration of grey tonalite to red albitite in the Bamble Sector, SE Norway. (B) Albitization (pale) of grey metasediments in the Curnamona Province, Olary Domain, South Australia.

Mg-metasomatism, Fe-metasomatism, Si-metasomatism have all been proposed to account for unusual rock compositions which have no chemical equivalents among sedimentary or igneous parent rocks (Schreyer 1977; Munz *et al.* 1994; John *et al.* 2004a; Jöns & Schenk 2004). In the absence of a clear transition zone from unaltered to altered rock, an unequivocal metasomatic origin may be debatable, but there are sufficient well-documented examples to indicate that metasomatism is *not* merely a local process confined to selvedges and skarns around veins and igneous intrusions (Vernon & Clarke 2008) or blackwall between ultramafic and felsic lithologies (Winter 1998). Metasomatized rocks can also have compositions and mineral assemblages indistinguishable from metamorphic rocks which could have formed isochemically on a relatively large scale, and only a careful textural study of replacement fronts in the field and in individual grains may determine the nature of the protolith. For example, metasomatic fronts have been identified to propose crustal scale Mg-rich fluid infiltration associated with biotite-chlorite formation during metasomatism within the Mont Blanc granite (Rossi *et al.* 2005, 2007).

One of the key issues in any discussion about metasomatism is the mechanism of mass transfer. Mass transfer over the distances observed in metasomatic reactions requires advection of fluid through a parent rock, and diffusion through this fluid. It is generally assumed that the fluid phase can only occupy fractures, pore spaces and intergranular boundaries within the rock, which leaves the problem of how equilibrium can be established within the individual crystals. In the absence of understanding mechanisms of equilibration of solids in the presence of a fluid phase, volume (solid state) diffusion through the crystals has been proposed to be necessary to establish local equilibrium between grains (e.g. Mueller 1967; Vernon & Clarke 2008). However, except at high temperatures solid state diffusion is negligible compared with fluid-induced reaction mechanisms (Putnis 2002; John & Schenk 2003). Understanding the mechanism by which a rock can change its composition and mineralogy at a fluid front is crucial.

Although metasomatism can take place on a regional scale, the mechanism takes place on the scale of individual grains, by a coupled dissolution–precipitation process which is explained in more detail in this paper. The link between the mechanism of metasomatism and metamorphic reaction mechanisms was established some time ago by Carmichael (1969) who demonstrated that even in a closed isochemical system, the textural development of a metamorphic rock on a thin section scale can be explained by a sequence of dissolution and precipitation sub-reactions. These 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 it may be closed. However, the fundamental mechanism of metasomatism and metamorphism at the reaction interface is the same.

A further important observation in this context is that there are well-documented examples where metamorphism has been inhibited except where fluid has been introduced. A very well-studied example is the eclogitization of Precambrian anorthositic granulites of the Bergen Arcs, western Norway (Austrheim 1987; Jamtveit *et al.* 1990; Austrheim *et al.* 1997; Bjørnerud *et al.* 2002). In this case eclogitization does not involve a major chemical change, but is a function of fluid access and deformation, rather than being controlled by changes in P, T conditions alone. Figure 2 shows a rock outcrop in which a dark band of eclogite associated with a shear plane and fluid infiltration cuts across the paler granulite. The eclogitization is limited by the extent of fluid infiltration laterally from the shear plane. In the absence of fluid the granulite remains essentially unreacted. Assuming that the whole rock outcrop experienced the same P, T conditions, we must conclude that the presence of fluid is responsible for the eclogitization reaction. Fluid-induced reactions are also crucial for converting the lower oceanic crust to eclogite in old and cold subduction zones (Yuan *et al.* 2000; John & Schenk 2003).

The role of chemically reactive aqueous fluids in driving reactions during contact metamorphism is well established (Jamtveit *et al.* 1992a,b; Ferry *et al.* 1998, 2002). While the formation of skarns is an unequivocal example of metasomatism associated with fluids mobilized by an igneous intrusion, the formation of wollastonite ($CaSiO_3$) from

Fig. 2. Eclogitization (dark) along a fracture in the paler anorthositic granulite, Bergen Arcs, western Norway.

reaction between calcite and quartz is a very common metamorphic reaction in contact aureoles, and also driven by an infiltrating fluid which transports the CO_2 from the reaction site (Ferry & Gottschalk 2009):

$$CaCO_3 + SiO_2 \Rightarrow CaSiO_3 + CO_2(aq) \qquad (1)$$

The porosity generated by such a reaction, taken simply as the molar volume change in the solid phases, allows fluid transport through the rock. As we shall see below, porosity development also depends on the relative solubilities of the parent and product phases in the specific interfacial fluid, and the thermodynamic stability of wollastonite in the above reaction implies that it is less soluble than a mixture of calcite + quartz in the fluid driving the reaction. This suggests that Ca and Si as well as CO_2 may be transported by the fluid, resulting in an even higher porosity generation. The difference between typical skarn formation and wollastonite formation is then a matter of degree rather than principle. Taken a step further, the contact metamorphic facies variations defined in metapelitic assemblages in an aureole around a pluton, usually attributed to decreasing temperature, rarely include the effect of the fluid composition which drives these reactions.

In this paper we focus on situations where an essentially dry, low permeability rock is infiltrated by a fluid which induces reequilibration 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 with changing pressure and temperature, and the effect of the chemistry of the fluid in changing the chemistry of the rock can vary over a wide spectrum. In the cases we consider, the temperature during infiltration is typically lower than the formation temperature of the parent rock. The situation in a fluid-saturated sedimentary basin undergoing progressive burial, diagenesis and metamorphism may be different, and the scale of mass transfer and fluid transport will be limited. The role of fluids in such a setting has been recently reviewed by Yardley (2009). Here we are not explicitly concerned with the scale of mass transport, but rather with the mechanism of reequilibration at the fluid–mineral interface.

With this background linking the mechanism of metasomatism with metamorphism via the interaction of fluids with minerals at the grain scale, we will explore aspects common to both processes. If we take into account the spatial scale of the mass transfer and the extent of chemical change it becomes not merely convenient, but conceptually obvious that in comparing metamorphism in general, with metasomatism, we are dealing with a spectrum of responses of a rock to fluid reaction. The distinction between a metasomatic reaction and a metamorphic reaction at the reaction interface scale will be explored using both natural and experimental examples. The aim of this paper is to give examples of mineral–fluid reactions and their atomic-scale

mechanism and hence to describe how fluids move through rocks.

CHEMICAL WEATHERING AS A METASOMATIC PROCESS

Chemical weathering is the *in situ* response of a rock exposed to the atmosphere. Although the ultimate breakdown product is soil, the early stages of weathering in which a rock retains its integrity, yet changes its mineralogy, are no different, in principle, to the processes which take place during metasomatism. The extent of chemical change can also vary in degree, such as in the breakdown of feldspars to either kaolinite at temperate conditions, or to bauxite under harsher weathering conditions. Long before a rock literally falls apart, chemical weathering alters the mineralogy. Weathering of silicate minerals to clays involves the transport of aqueous solutions to and from the reaction interface. High-resolution transmission electron microscopy of such a reaction interface (Banfield & Barker 1994) in the case of the breakdown of amphibole to smectite shows that the reaction is pseudomorphic, i.e. the volume occupied by the parent and product phases is unchanged (Fig. 3). This is typical of a mineral replacement reaction in which there is a coupled dissolution of the parent and precipitation of the product. The preservation of crystallographic orientation in isovolumetric mineral replacement reactions has been recently discussed by Putnis (2009).
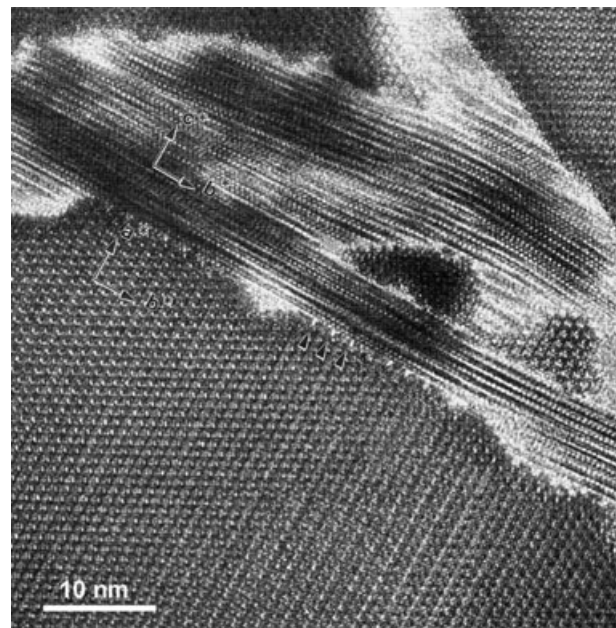

Fig. 3. High-resolution transmission electron microscope image of amphibole isovolumetrically replaced by smectite. Note the crystallographic relationship between the parent and product phases (from Banfield & Barker 1994).

For the case of amphibole weathering to smectite in the presence of an acidic aqueous solution, Banfield & Barker (1994) have shown that, to preserve volume of the solid parent and product phases, the reaction must involve the removal of Mg, Fe, Si and Al from the reaction interface.

SERPENTINIZATION AND RODINGITIZATION – SEA FLOOR WEATHERING AND METASOMATISM

Serpentinization is a common weathering/hydration reaction in ultramafic rocks, often associated with alteration near mid-ocean ridges, in which olivine and pyroxene are replaced by serpentine minerals and Fe in the parent minerals is released and forms iron oxides.

In detail, such reactions are difficult to define precisely, as we need to know the composition of the reacting fluid, how this fluid changes composition as the reaction proceeds and then the composition of the fluid moving out of the 'system'. For example, the serpentinization of olivine may be written as an isovolumetric replacement reaction:

$$2Mg_2SiO_4 + 2H^+ + H_2O \Rightarrow Mg_3[Si_2O_5](OH)_4 + Mg^{2+} \quad (2)$$

Figure 4 shows the typical 'mesh structure' of partially serpentinized olivine, associated with both the precipitation of hematite (from the Fe component in the olivine) as well as magnesite, consistent with the liberation of Mg (as well as the presence of dissolved carbonate in the fluid). The interpretation of the replacement texture in Fig. 4 in terms of volume changes is equivocal. The dark grey areas of serpentine could be considered as an isovolumetric replacement of olivine or could be infilling cracks associated with volume expansion. Without some physical reference frame a case could be made for either interpretation.
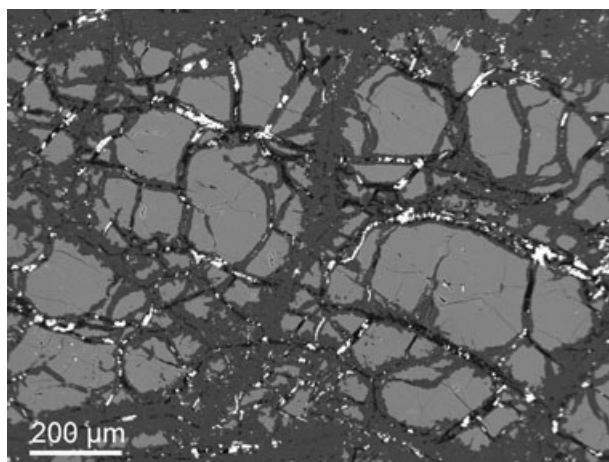

Fig. 4. Back-scattered SEM image of a typical mesh texture in serpentinized olivine. The dark grey areas are serpentine, the lighter grey areas are olivine and the black material in the veins is magnesite. The brightest phase in the veins is hematite.

In general, hydration reactions are thought to increase the solid volume, but this depends totally on the assumptions made about the composition of the fluid into and out of the system. For example, in the serpentinization of orthopyroxene, the reaction could be written as

$$2MgSiO_3 + Mg^{2+} + 3H_2O \Rightarrow Mg_3[Si_2O_5](OH)_4 + 2H^+ \quad (3)$$
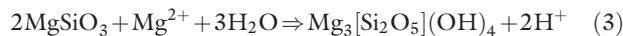
which preserves the silica composition but implies a 50% increase in volume. Alternatively, the reaction

$$4MgSiO_3 + 2H^+ + 5H_2O \Rightarrow Mg_3[Si_2O_5](OH)_4 \\ + Mg^{2+} + 2H_4SiO_{4(aq)} \quad (4)$$
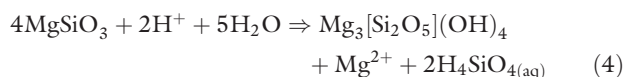
is balanced on volume but involves loss of silica. (The approximate molar volumes of enstatite and lizardite are 25 and 100 cm^3 mol^{-1} respectively). Isovolumetric serpentinization of orthopyroxene can be illustrated by the preservation of undisturbed lamellar structure when in exsolved intergrowths of orthopyroxene and clinopyroxene, only the orthopyroxene is serpentinized (Viti et al. 2005), while in other cases there is evidence of textural disruption and hydraulic fracturing (Shervais et al. 2005).

When the rock being serpentinized contains calcium-bearing phases such as clinopyroxene, the Ca is released to the fluid phase, which in turn can migrate to react with other mafic or felsic rocks to form *rodingites*. Rodingitization is a type of Ca-metasomatism leading to assemblages including grossular garnet, diopside, prehnite and chlorite with other minor phases. Assuming that serpentinization and rodingitization take place contemporaneously, Bach & Klein (2009) have used geochemical reaction path modelling to first calculate how seawater composition would change when reacted with peridotite, and then calculate what happens when this new fluid composition reacts with gabbro. The results support the hypothesis that typical rodingite mineral assemblages only form in areas where the composition of the fluids is controlled by serpentinization reactions. Austrheim & Prestvik (2008) observed that the rodingitization of the Leka ophiolite in Norway occurs through mineral replacement reactions and listed six reactions including replacement of olivine by clinopyroxene.

In addition to serpentinization and rodingitization which are assumed to involve hydrothermal fluids at temperatures above 150°C, pervasive low temperature interaction of peridotites with sea water results in lower MgO and higher SiO_2 content relative to unweathered peridotite (Snow & Dick 1995). This type of sea floor weathering is attributed to the incongruent dissolution of olivine and pyroxene, releasing Mg^{2+} into solution and leaving an enriched silica surface phase behind (Iyer et al. 2008). The mechanism of incongruent dissolution is not well understood, although it is reasonable to assume that it has much in common with other examples of mineral–fluid reaction mechanism described below.
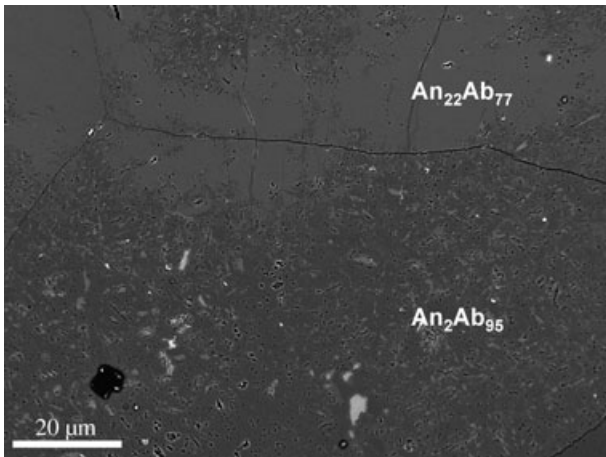
Fig. 5. Back-scattered SEM image of natural oligoclase (An content $\sim An_{22}$) partially replaced by albite ($\sim An_2$). The parent oligoclase has a smooth textures surface, while the albite (darker grey) is full of small sericite mica inclusions (pale) and pores (black) (from Engvik *et al.* 2008).

Fig. 6. Back-scattered SEM image of a cross-section of oligoclase crystals (ol $\sim An_{22}$) partially replaced by albite (ab) in hydrothermal solution containing Na and Si (image: J. Hövelmann).

ALBITIZATION – FROM DIAGENESIS TO AMPHIBOLITE FACIES METASOMATISM

As mentioned above, albitization of feldspars, and ultimately of all other minerals in a rock can take place over a wide range of temperatures and pressures, and indicates a reaction between a felsic rock and a saline fluid. A detailed study of a reaction front between a more calcic plagioclase ($\sim An_{20}$) and albite reveals some important features of metasomatism and mineral–fluid reaction mechanisms in general. Figure 5 (Engvik *et al.* 2008) shows that the interface between the parent oligoclase feldspar and the albite is sharp, that the albite is porous, and that the albitization is also associated with precipitation of hematite and sericitization, indicating introduction of K as well as Na and Si in the fluid phase.

Albitization can be readily reproduced experimentally. Hövelmann *et al.* (2010) replaced calcic plagioclase (oligoclase $\sim An_{22}$) by albite in aqueous solutions containing both Na and Si at 600°C within weeks. Figure 6 shows a partially replaced grain with a sharp reaction interface between the parent and product phase. Compositional data indicate extensive mobilization of trace and minor elements, as well as Al, into the fluid phase. Using ^{18}O-enriched aqueous solution as a tracer for the mineral–fluid reaction results in the incorporation of ^{18}O in the product albite, demonstrating that all elements are exchanged, as would be expected from a coupled dissolution–precipitation mechanism (Putnis 2002, 2009). Although the porosity is not obvious in low magnification images such as Fig. 6, higher magnifications and especially transmission electron microscopy show that in experimental feldspar–feldspar replacements the porosity is on a nanoscale (see e.g. Niedermeier *et al.* 2009). The coarser porosity in the
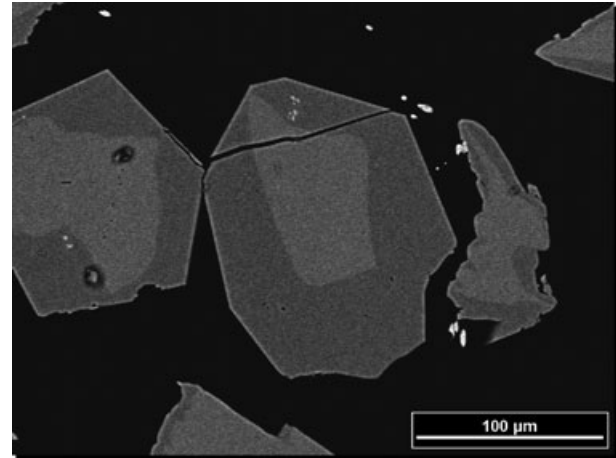
natural sample (Fig. 5) may also be due to porosity coarsening over time, a phenomenon observed in salt replacement analogues (Putnis *et al.* 2005).

The Engvik *et al.* (2008) and the Hövelmann *et al.* (2010) studies indicate that albitization is a pseudomorphic replacement reaction in which the dissolution of the parent feldspar is spatially and temporally coupled to the precipitation of albite. Although such coupling is not a prerequisite for a metasomatic reaction, when it does take place it is characterized by a number of distinctive features:

(1) The replacement is isovolumetric, i.e. the external dimensions of the parent grains are preserved.
(2) A sharp reaction front indicating that volume (lattice) diffusion plays an insignificant or minor role in the reaction.
(3) Porosity (assumed to be interconnected) developed in the albite product which allows fluid and mass transfer *through* the albite product, to the reaction front.
(4) Transfer of crystallographic information from the parent to the product. In the case of an isostructural replacement, the crystallographic orientation is preserved across the reaction interface, even though the parent is dissolved and the product reprecipitated. When the replacement is not isostructural some crystallographic features are preserved as in the orientations shown in Fig. 2.

In the Bamble Sector, SE Norway albitization affects rocks with a range of lithologies. The example in Fig. 5 is from partially albitized granitic rocks. In the same area, gabbro has also been pervasively affected by Na metasomatism resulting in a complex sequence of replacement processes. From observations across reaction zones between the gabbro protolith and the final assemblage, a complex sequence of progressive replacements can be identified. Feldspars are replaced by Cl-scapolite which is itself replaced by albite.
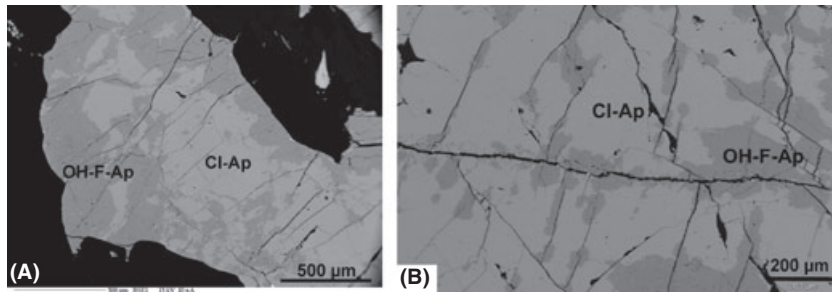
Fig. 7. Back-scattered SEM images of Cl-rich apatite, (A) partially transformed to OH-rich apatite in patches around the rim of the former phase and also along fractures (B). Note that the replacement is not uniform along fractures but is more extensive near fracture intersections (from Engvik *et al.* 2009).

Phlogopite replaces ilmenite and hornblende (see also Fig. 10 and the discussion below), while Cl-rich apatite is replaced by OH- and F-rich apatite (Austrheim *et al.* 2008; Engvik *et al.* 2009). The replacement of the chlorapatite by hydroxyapatite (Fig. 7) is initiated at grain boundaries and fractures and it is clear from the microtextures that a simple ion-exchange diffusion process cannot be invoked to explain the replacement. However, the microtexture is consistent with a dissolution–precipitation mechanism. It is unclear if the multiple replacement textures observed represent the migration of metasomatic fronts through the rock caused by a single fluid event. All replacement textures document that the chemical inheritance between the parent and product phases may be limited.

In the examples above the dissolution of the parent and precipitation of the product are spatially coupled and the textures suggest that the replacement process is at least approximately isovolumetric (apart from the porosity generated in the product). However, as already mentioned in the case of serpentinization, volume changes depend on the composition of the fluid moving into and out of the system. There are numerous documented examples, based on whole rock chemical analyses, where fluid flow through rocks has apparently resulted in compositional and whole-rock volume changes (Ague 1994a, 2003a,b; Bucholz & Ague 2010 and references therein). Note that in assessing mass and volume transfer from whole-rock chemical analyses a fundamental issue is the definition of a geochemical reference frame. The usual procedure is to assess changes in bulk chemistry of a rock relative to 'immobile' reference elements (see Philpotts & Ague 2009 for a discussion). In experiments or textural studies where it is evident that replacement has been isovolumetric, mass balance calculations are based on preservation of solid volume as in Hövelmann *et al.* (2010) and Banfield & Barker (1994).

METAMORPHIC REACTIONS ALONG FLUID PATHWAYS

Eclogite–granulite facies reactions

In the Western Gneiss Region of South Norway, eclogite facies rocks have partially reacted to form granulite facies
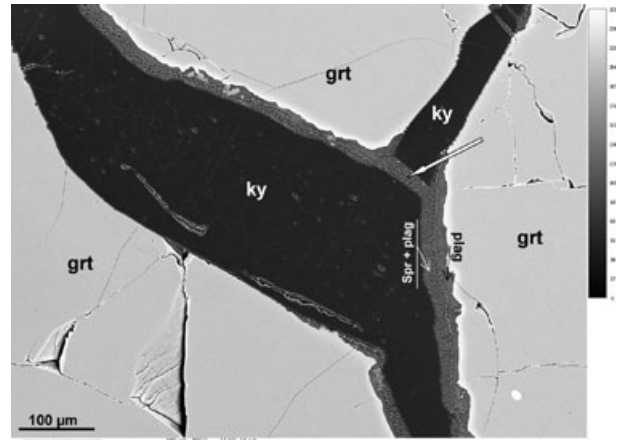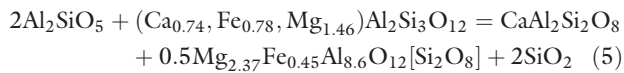

Fig. 8. Back-scattered SEM image of a grain boundary between garnet (light) and kyanite (dark grey). A fracture follows part of the grain boundary from lower right to upper left. The reaction products (plagioclase adjacent to the garnet and sapphirine-plagioclase symplectite adjacent to the kyanite) only form where the fracture is present and not on all garnet-kyanite boundaries. The kyanite-kyanite grain boundary (large arrow) is filled with the sapphirine + plagioclase symplectite (see also Straume & Austrheim 1999).

assemblages during decompression (Straume & Austrheim 1999) and a detailed study of the textures associated with these reactions illustrates how fluid transport pathways along fractures control the extent of reaction. This is well illustrated by Fig. 8 (Straume & Austrheim 1999) which shows a garnet-kyanite contact boundary in the eclogite, reacting to sapphirine + plagioclase. These granulite facies reaction products do not form on all garnet-kyanite grain boundaries, only on those along which fractures have propagated, and along which fluid has been able to pass. The reaction is not isochemical, as the presence of ∼10% albite component in the plagioclase clearly shows that the reaction is not only between garnet and kyanite but must involve a sodium source (Straume & Austrheim 1999).

The texture in Fig. 8 indicates that not all grain boundaries contained free fluid, and that under fluid-absent conditions the reaction did not proceed. Solid state reaction with volume diffusion was not a significant mechanism. Although grain boundaries are often cited as important transport paths for fluids, there must be a fundamental

difference between fluid transport along grain boundaries and along fractures. The origin of fractures is usually ascribed to deviatoric stresses generated by large-scale tectonic processes, or by local stresses developed during differential expansion of the various minerals during uplift. Grain boundaries are common sites for microfracturing creating a 'hydraulic permeability' (Etheridge *et al.* 1983; Cox & Etheridge 1989). A further origin of fractures may also be due to the highly localized stresses generated by volume changes associated with fluid-induced chemical reactions (Janssen *et al.* 2008; Jamtveit *et al.* 2009).

Based on the composition of the reactants and products given by Straume & Austrheim (1999), and neglecting for the moment, the Na-content of the plagioclase, we can estimate the volume change for the reaction balanced on Si and O and approximately balanced for the other cations:

$$2Al_2SiO_5 + (Ca_{0.74}, Fe_{0.78}, Mg_{1.46})Al_2Si_3O_{12} = CaAl_2Si_2O_8$$
$$+ 0.5Mg_{2.37}Fe_{0.45}Al_{8.6}O_{12}[Si_2O_8] + 2SiO_2 \quad (5)$$

Using molar volume data from standard databases, the above reaction is very close to isovolumetric if the silica is removed in solution. If the introduction of Na from the fluid into the plagioclase is taken into account, some of the Si will also be consumed by the plagioclase also reducing its Al content.

In Fig. 8, the sapphirine + plagioclase product assemblage of the reaction rim has a symplectite texture. The origin of symplectites in metamorphic rocks is also a highly debated topic as similar textures can form under a wide variety of conditions. The example given here shows that symplectite textures can form by reaction involving a fluid phase (i.e. dissolution) whenever two product phases co-crystallize (precipitation) within a restricted environment.

Granulite–eclogite facies reactions

The granulite to eclogite reaction in the Bergen Arcs of Western Norway has already been mentioned as a well-studied example of fluid-induced metamorphism (Fig. 2). A detailed study of the transition zone between essentially unreacted granulite and eclogite, i.e. at the limit of fluid infiltration, gives further insights into the reaction mechanisms, specifically on the mechanism of the conversion of diopsidic clinopyroxene in the granulite to omphacitic clinopyroxene in the eclogite. This is an especially important reaction as the jadeite content in omphacite is commonly used as a geobarometer (Holland 1980).

Figure 9 shows a polarized light and a back-scattered SEM image of the reaction zones between granulitic clinopyroxene with composition $\sim Di_{0.70}CaTs_{0.20}Jd_{0.10}$ (labelled zone 1) and omphacitic clinopyroxene with composition $\sim Di_{0.45}CaTs_{0.05}Jd_{0.5}$ (labelled zone 4). The granulitic clino-

pyroxene can be found free of inclusions and lamellae in the most pristine granulite, but near the eclogites it contains fine amphibole lamellae typically 0.2–0.4 µm in width. Zone 2 is a symplectite which replaces the pyroxene in zone 1. The symplectite is an intergrowth of a pargasitic amphibole with (Na+K)/Ca ~ 0.75 and Ca/(Mg+Fe) ~ 0.5 and a clinopyroxene $\sim Di_{0.65}CaTs_{0.10}Jd_{0.25}$, significantly more sodic than in zone 1. This zone contains numerous small pores. Zone 3 is a coarser amphibole-clinopyroxene symplectite apparently replacing zone 2. The proportion of amphibole in the zone 3 symplectite is reduced but has the same composition as that in zone 2. The pyroxene is more sodic with composition $\sim Di_{0.60}CaTs_{0.10}Jd_{0.30}$. Zone 3 has large, apparently open pores. The final stage (zone 4) is almost end-member omphacite ($Di_{0.45}CaTs_{0.05}Jd_{0.5}$) with little amphibole and a reduced, though still present, porosity.

Two possible interpretations of this texture can be suggested. The texture could have evolved during changing *P* and *T* conditions so that the higher Jd content corresponds to the maximum *P*, and the symplectite subsequently formed during uplift. Alternatively the zonal distribution reflects the changing composition of the fluid phase at the extended interfacial region between the granulite and eclogite. The sequence also suggests that the fine amphibole lamellae in zone 1 are the first indication of fluid infiltration associated with the reactions to form the eclogite. Realizing that the reactions take place through a fluid phase may require a modification of the *P*–*T* paths suggested for these rocks.

HOW DO FLUIDS MOVE THROUGH ROCKS?

It has been recognized for many years that substantial quantities of aqueous fluids are involved in low- and medium-grade metamorphism, in amounts greater than can be supplied by dehydration of surrounding rocks (Fyfe *et al.* 1978; Etheridge *et al.* 1983; Ferry 1994; Rumble 1994; Oliver 1996). The driving forces for fluid flow through low permeability rocks have been variously attributed to (i) a response to regional thermal gradients and/or (ii) deformation-induced hydraulic head gradients (Oliver 1996). In either case, fluid flow depends on the availability of pathways, either preexisting in the intrinsic porosity of the rock, or created by the deformation/fluid event associated with the metamorphism. In the latter case, dilatancy (the volume change resulting from deformation) is considered to be a key requirement for fluid movement both on a local and a long-range length scale. Hydraulic fracturing, arising from fluid overpressure during devolatilization reactions, has also been recognized as an important mechanism for fluid flow (Thompson & Connolly 1992; Ague 1994b, 2003a; Davies 1999; Oliver & Bons 2001; Zack & John 2007; Lyubetskaya & Ague 2009). Similar considerations of fluid flow paths apply in the case of metasomatism.
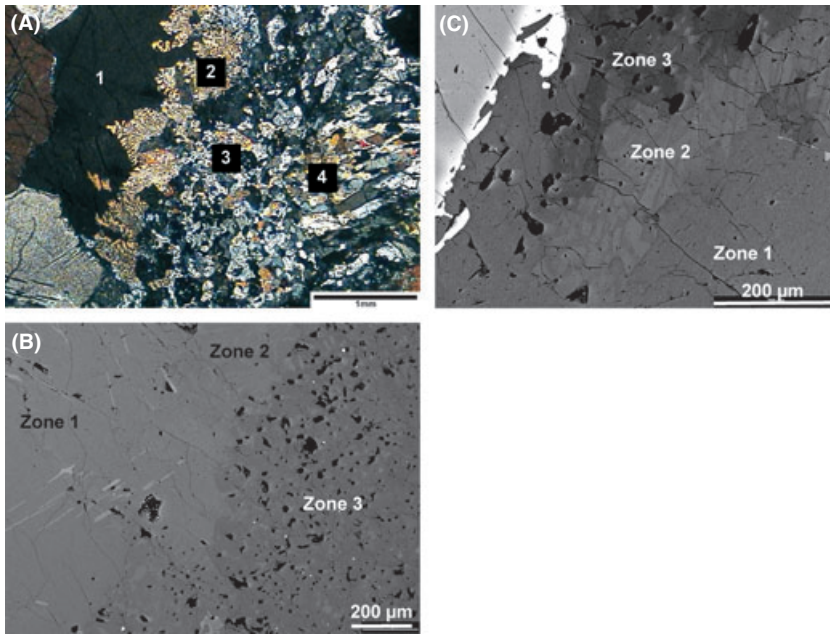
Fig. 9. The reaction zones between diopsidic pyroxene in granulite (zone 1) and omphacite in eclogite (zone 4). Zones 2 and 3 are amphibole-sodic pyroxene symplectites in which the omphacite component of the pyroxene increases in a step-wise manner, while zone 4 contains stoichiometric omphacite. (A) Transmitted light micrograph showing the symplectite in zone 2 replacing the diopsidic pyroxene in zone 1. A coarser symplectite (zone 3) with a high porosity [black spots in the BSE SEM image in (B)] replaces zone 2. (C) A higher magnification BSE SEM image showing the successive zones 1–3 (images F. Casarin).

Apparent permeabilities of rocks have been estimated from time-integrated fluid fluxes inferred from measured progress of metamorphic reactions, and are invariably higher than the permeabilities of similar rocks measured in the laboratory (Oliver 1996; Ingebritsen & Manning 2003). This suggests that during metamorphism and metasomatism, permeability is enhanced. The most popular mechanisms cited are grain-scale dilatancy and hydraulic fracturing. Thus porosity and permeability are transient phenomena associated with the process itself and not necessarily dependent on intrinsic properties of the rock.

The concept of 'reaction-enhanced permeability' has been discussed for some time and is considered to be dependent on a volume decrease between parent and product solid phases in a metamorphic reaction (Rumble & Spear 1983; MacDonald & Fyfe 1985; Cartwright 1997; Ferry 2000). For example, the reaction between quartz and calcite to wollastonite, written in the form of Eqn 1 would result in a molar volume reduction of ~33% and hence very significant permeability generation and probable compaction of the wollastonite (Balashov & Yardley 1998). However, a literal mole-for-mole interpretation of such a reaction may not be valid, as reactions may be isovolumetric and therefore reaction equations are more appropriately written to preserve volume, as discussed above, and in more detail in Putnis (2009).

Recent advances in understanding the mechanism of pseudomorphic mineral replacement processes (Putnis
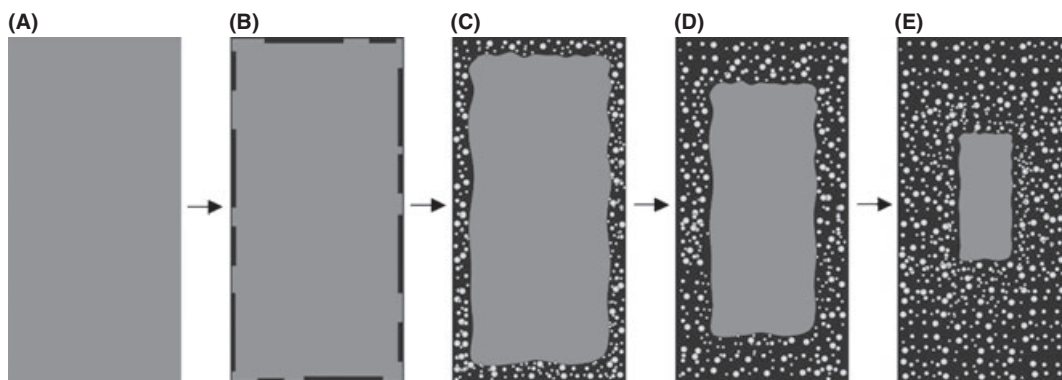

Fig. 10. When a solid (A) comes into contact with a fluid with which it is out of equilibrium, dissolution of even a few monolayers of this parent may result in an interfacial fluid which is supersaturated with respect to a product phase, which may nucleate on the surface (B). (C)–(E) Continued dissolution and precipitation at the parent-product interface depends on the generation of interconnected porosity in the product phase allowing mass transport through the fluid phase and the migration of the reaction interface from the surface through the parent.

2002, 2009; Putnis & Mezger 2004; Putnis *et al.* 2005; Putnis & Putnis 2007; Xia *et al.* 2009a) have shown that reactive fluids can pass through individual crystal grains by a mechanism termed interface-coupled dissolution-precipitation. In the context of fluid flow, porosity generation is a key feature of this mechanism. Figure 5, the replacement of a more calcic plagioclase (oligoclase) by albite, shows that interconnected porosity and hence permeability must have been generated by the replacement process. This allows continuous contact between the fluid and the reaction interface as it moves through the crystal, allowing advective transport of fluid through the pores and providing diffusional pathways for element transport. For example, albitization of plagioclase involves addition of Na and Si and removal of Al and Ca, as well as trace elements all of which are transported through the fluid phase in the pores (Hövelmann *et al.* 2010). The porosity is not only a consequence of a reduction in solid molar volume, which in the case of albite replacing oligoclase is too small to account for the observed porosity, but also depends on the relative solubilities of parent and product phases in the reactive fluid. In other words, more parent material may be dissolved than product reprecipitated, thus generating porosity. Indeed, it has been shown that even in a pseudomorphic reaction in which there is a molar volume increase, porosity may still be generated by the reaction (Putnis *et al.* 2007; Xia *et al.* 2009b).

The generation of porosity during mineral replacement reactions has been reported in a large number of studies on both natural and experimental samples (Putnis 2009 and references therein). The general principle that some material may be lost to the fluid phase due to solubility differences is not restricted to pseudomorphic replacement, and may equally apply to a metamorphic reaction where dissolution and precipitation are not as spatially coupled as in a pseudomorphic reaction.

The recognition of porosity generation in a metasomatic reaction creates a further link between permeability and reaction progress. Combined with hydraulic microfractures it provides a mechanism for the pervasiveness of fluid flow and element transport. The fact that a reactive fluid can move through a single crystal, dissolving the parent at the reaction front and precipitating the product in its wake, eliminates the need to invoke volume diffusion as a mechanism of chemical interaction between fractures and the adjacent 'wallrock', as proposed by Cox & Etheridge (1989). Porosity generation associated with contact metamorphism of limestone has recently been quantified using small angle neutron scattering techniques which can be applied to bulk samples, and confirms the micro-scale observations above, that a metasomatic/metamorphic front is associated with a high permeability zone that moves outwards with the aureole as metamorphism progresses (Anovitz *et al.* 2009).

THE ROLE OF THE FLUID IN METAMORPHIC AND METASOMATIC REACTIONS

If we accept all the petrological, mineralogical, textural, microstructural and stable isotopic data supporting high water fluxes in regional metamorphic belts and metasomatized terrains (Ferry 1994; Ague 2003b; John *et al.* 2004b; Rossi *et al.* 2005; Beinlich *et al.* 2010), then a fundamental question is what is the mechanism by which a mineral or mineral assemblage in a rock equilibrates in the presence of an aqueous fluid.

Despite the perhaps obvious proposition that solid state diffusion cannot compete kinetically with dissolution-precipitation as a mechanism of mineral reequilibration (except at temperatures approaching the melting point), the replacement of one mineral by another has often been considered as an essentially solid state reaction, even when the reequilibration involved chemical exchange with a fluid phase. Part of the reason for this is the historical over-reliance that mineralogists placed in materials science (e.g. metallurgy and ceramic science, solid state chemistry and physics) for the development of an understanding of phase transformations and reactions between solids. The geological time-scales invoked for metamorphic reactions also suggested that even slow volume diffusion on enormous time-scales could bring about a complete change in mineral assemblage.

At a crystallographic level, replacement processes which preserved both the external shape and internal crystal structure (such as the replacement of one feldspar by another) were obvious candidates for a solid state ion-exchange mechanism. Early experimental work using ^{18}O in the fluid phase in feldspar-fluid equilibration reactions (O'Neil & Taylor 1967; O'Neil 1977) established that oxygen was also exchanged, which suggested the dismantling and reassembly of the whole alumino-silicate framework. Recent work has shown that the preservation of crystal structure in an interface-coupled dissolution–precipitation mechanism is an inevitable consequence of the close coupling when the crystal structures of the parent and product phase are the same. In such a case, the epitaxial relationship between the nucleating phase and the substrate greatly enhances the rate of precipitation (nucleation). When the crystal structures of parent and product are different the parent phase may be polycrystalline, with some degree of lattice matching across the interface, yet may still retain the external shape and volume of the parent.

The isochemical nature of many metamorphic reactions implied in the metamorphic facies concept also suggested that a reaction could be achieved by solid state reactions and relatively localized diffusion. Again stable isotope studies demonstrated that metamorphism involved reaction with a fluid which was not in isotopic equilibrium with the parent assemblage. The ability to map oxygen isotope

distributions with high spatial resolution has confirmed that oxygen isotope reequilibration in individual minerals follows replacement involving the major elements (van Haren *et al.* 1996; Cole *et al.* 2004; Bowman *et al.* 2009).

The mechanism of mineral replacement by interface-coupled dissolution-precipitation is illustrated schematically in Fig. 10. In an open experimental system the reequilibration of a mineral in the presence of a fluid with which it is out of equilibrium first involves some dissolution of the parent phase(s). Even the dissolution of a few monolayers of the parent will result in a fluid which is supersaturated with respect to a more stable phase. The precipitation of this phase on the surface of the parent phase is dependent on the kinetics of nucleation: existence of epitaxial (crystallographic) relations between parent and product will favour nucleation, as will a high value of supersaturation at the fluid–mineral interface (i.e. a low solubility of the product phase). Autocatalysis (the feedback between surface nucleation and dissolution rate) also contributes to the overall balance between dissolution and precipitation rates (Anderson *et al.* 1998a,b). Dissolution and precipitation may be very closely coupled, resulting in an exact pseudomorph preserving nanoscale features of the parent, or they can become spatially separated, depending on whether the overall reaction is dissolution controlled or precipitation controlled respectively (Xia *et al.* 2009a).

In a mineral assemblage in a rock, the reactions will be controlled by the fluid pathways available and the mineralogy through which initial hydraulic or tectonically induced fractures propagate. Although the individual dissolution-transport-precipitation steps are much more difficult to evaluate (see Carmichael 1969), as are the spatial relationships and coupling between dissolution and precipitation, the basic principles remain the same. In the early stages of a metamorphic or metasomatic reaction when there is the possibility of seeing relationships between reactants and products, the reaction mechanisms are related to fluid pathways (e.g. Fig. 8). When the final mineral assemblages have been formed there may be little textural evidence of the former assemblage. In some special cases where the parent assemblage contained ilmenite with zircon rims, the metasomatism completely removed all the ilmenite, but the zircon rims were unaffected and were thus physical markers of the former existence of the ilmenite, now replaced by phlogopite (Fig. 11) (Austrheim *et al.* 2008). In this case a Fe-Ti oxide has been replaced by an Mg-silicate, indicating addition of Mg, Si, Al and removal of Fe, Ti from the former site of the ilmenite grain.

In a subsequent replacement process prehnite which replaces the phlogopite contains inclusions of titanite, suggesting that the Ti from the phlogopite reacts with Ca and Si from the fluid to form titanite (Fig. 12A). The replacement of the prehnite by albite (Fig. 12B) leaves the titanite inclusions intact within the albite. Such observations of the
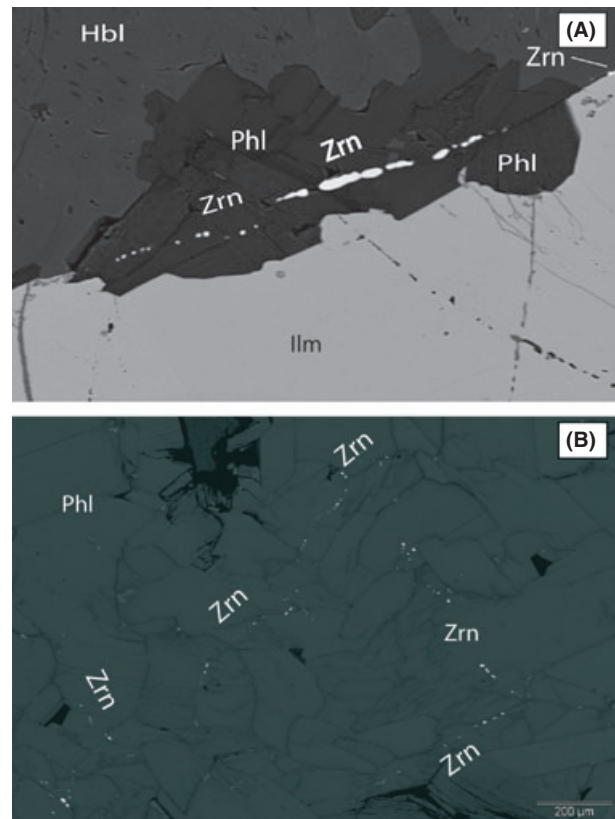

Fig. 11. (A) BSE image showing the early stages of replacement of ilmenite and hornblende by phlogopite. The bright phase is zircon which marks the original ilmenite grain boundary. (B) After total replacement of all phases by phlogopite, the 'necklace' of zircons is the only indication of the grain boundary of the replaced ilmenite grain (from Austrheim *et al.* 2008).

microstructural evolution record fluid-induced replacement processes and as pointed out by Vernon *et al.* (2008) can be misinterpreted as indicating parageneses along a specific *P*, *T* path.

Dissolution–transport–precipitation is a very efficient mechanism of mineral reequilibration and can be driven by very small free energy differences between the parent and product phases. This has been demonstrated by Nakamura & Watson (2001) who showed that reduction in interfacial free energy is sufficient to drive recrystallization. A reduction in strain energy also drives the dissolution of fine-scale coherent intergrowths of cryptoperthite and the reprecipitation of patch perthite (Parsons & Lee 2009). Wood & Walther (1983) and Walther & Wood (1984) have also shown that rates of dissolution of a wide range of minerals under near-equilibrium conditions are very fast on a geological time-scale even at a 1°C temperature overstep. The transport and nucleation steps are much more difficult to quantify and depend on the distribution of fluid and its supersaturation. Wood & Walther (1983) argue that the nucleation step is not rate limiting and therefore in the presence of a fluid phase the extent of disequilibrium in
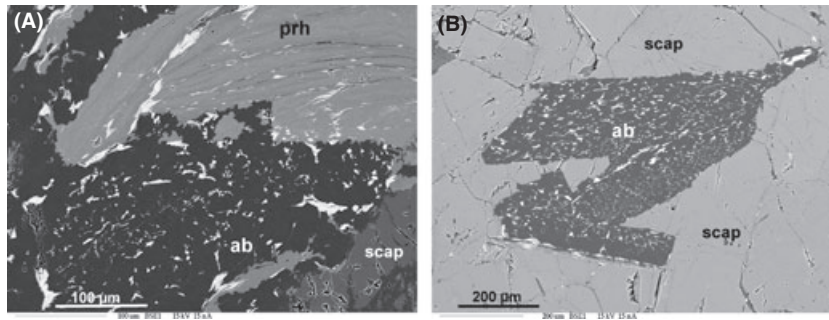
Fig. 12. (A) Replacement of prehnite (prh, upper right) by albite (ab, dark). The titanite inclusions in prehnite (white) are also present in the albite, suggesting that titanite was insoluble in the albitizing fluid. The grain in the lower right corner is scapolite. (B) BSE image showing scapolite (grey) and albite (dark). The bright spots in albite are inclusions of titanite. The albite has completely replaced prehnite. Note that albite preserves the form of a former mica, indicating the following sequence of replacements: phlogopite – prehnite + titanite – albite + titanite.

metamorphic rocks is likely to be small. More recent textural evidence suggests that nucleation problems may require reactions to be considerably overstepped (Wilbur & Ague 2006) but that subsequent growth is likely to be rapid. However, in the absence of fluid, metamorphic reactions may not occur at all.

The fact that fluids increase the rates of reactions is well known, so that there is a tendency to consider the fluid as a catalyst which plays no role in the thermodynamics of the reaction. A catalyst, in the strict sense, makes available a different mechanism with a lower activation energy. Rather than relying on vague concepts such as 'fluid-enhanced solid state diffusion' to explain why 'solid-state' reactions are faster in the presence of the fluid, we suggest that fluids inevitably provide a dissolution-precipitation mechanism for a reaction and this then competes kinetically with solid state diffusion. The fact that the fluid phase is not pure water but contains dissolved CO_2 as well dissolved ions suggests that the fluid must play a thermodynamic as well as a kinetic role in the reaction. However as data on fluid thermodynamics over the range of compositions, temperatures and pressures are very limited, this aspect of the role of fluids is usually conveniently ignored. The question of determining whether a reaction is driven by changes in temperature, pressure or chemistry due to infiltration of fluid is a major challenge for the future.

REACTION INTERFACES AND COEXISTING MINERALS

In a metamorphic event $P-T$ paths are inferred from sequences of reactions assumed to take place as a rock crosses univariant reaction lines in $P-T$ space. The replacement of one mineral assemblage by another is taken as an indication that such a reaction has or is taking place in a rock. However, the use of mineral microstructures to infer metamorphic events is subject to misinterpretation, as pointed out by Vernon *et al.* (2008). To define a metamorphic paragenesis requires that the assemblage consists of minerals which 'have grown simultaneously or have stably coexisted' (Vernon *et al.* 2008). Vernon *et al.* (2008) consider corona structures to be among the most reliable indicators of a metamorphic reaction. A corona in this sense is a reaction rim between a core mineral and its surroundings, representing an arrested metamorphic reaction which captures a time-frame where the minerals in the corona are in equilibrium with the two reacting minerals on either side.

However, the reliability of corona structures as indicators of a metamorphic event is called into question if we consider in more detail the reaction between kyanite and garnet shown in Fig. 8. The reaction rim is no different in principle to a corona. However, the plagioclase in the reaction rim contains 10% albite component and Na is not present in either kyanite or garnet. Furthermore, the reaction rim is not equally developed on all kyanite–garnet interfaces, indicating the reaction has only taken place where the interface coincided with a fracture allowing infiltration of fluid. Equilibration by solid state diffusion of components between the two phases played no significant role in the development of the rim. The dissolution of both garnet and kyanite by the fluid created a compositional gradient in the interfacial fluid, with the fluid at the garnet interface more Ca-rich than the fluid at the kyanite interface. The zonation of the reaction rim, with a layer of plagioclase nucleating on the garnet, indicates a chemical potential gradient in the fluid phase. The importance of the boundary layer of the fluid at the dissolving interface in controlling the precipitation of the product has been emphasized by Putnis & Mezger (2004) and Putnis *et al.* (2005). The residual fluid containing other components of the dissolution (Ca, Mg, Fe, Al, Si), together with Na from the infiltrating fluid, co-crystallize to form the sapphirine + plagioclase symplectite. The 'reaction rim' continues through a kyanite–kyanite contact (arrowed in Fig. 8) where the space is filled with the symplectite, demonstrating the mobility of these elements in the fluid phase through the fracture. Note that the presence of a fluid phase in a reaction does not necessarily imply the

formation of hydrous minerals even when the fluid components may play a significant role in the thermodynamics.

The equilibrium (if any) established in this reaction is between the fluid at the interface (formed from both the infiltrating solution and the dissolving parent) and the product phases in the reaction rim. If the infiltrating solution is out of equilibrium with the parent kyanite + garnet assemblage, then the corona, or rim in this instance, does not represent a reliable indicator of a metamorphic reaction, as the reaction is not isochemical. Although we may infer that the infiltrating fluid contains Na, we can make no assumptions about the composition of the outgoing fluid. The determination of P, T conditions for the reaction becomes problematic, as the fluid is an integral component in the reaction and its thermodynamics must be taken into account. Furthermore, the presence of Na in the plagioclase requires that both the thermodynamic mixing properties of the cations, as well as the change in Al,Si ordering, be taken into account (Carpenter & Ferry 1984) when determining the thermodynamics of the reaction.

When a fluid is involved in a metamorphic reaction, the interpretation of the microstructure and phase assemblage in terms of a metamorphic paragenesis becomes highly problematic. Among the microstructural criteria which have been used to infer a sequence of metamorphic reactions in P–T space, partial replacement of one mineral by another has been used to indicate a 'frozen-in' metamorphic reaction with the implication that the parent and product phases coexist (Vernon *et al.* 2008). However, as we have seen from studies of albitization, as just one example (Engvik *et al.* 2008; Hövelmann *et al.* 2010), metasomatism and interface-coupled dissolution-reprecipitation results in precisely such a partial replacement (Figs 5 and 6). Albitization of labradorite proceeds in the same way as oligoclase (Hövelmann *et al.* 2010) and in both cases the parent plagioclase and product albite are clearly out of equilibrium. The interface between them represents the reaction front between the plagioclase and an Na-Si-bearing fluid. As in the case of coronas, equilibrium, if it exists at all, would be between the interfacial fluid (resulting from the dissolution of the plagioclase) and the precipitating albite.

CONCLUSIONS AND FURTHER IMPLICATIONS

From the brief examples above, we can conclude that at the reaction interface level, there is no fundamental mechanistic difference between metasomatism and metamorphism. Except at the highest temperature grades of metamorphism, where solid state diffusion may have a significant role to play in mass transport, or where melting begins, metamorphism involves aqueous solutions. Both metasomatism and metamorphism take place by a sequence of dissolution-transport-precipitation reactions, which in the case of metasomatism

involves a significant change in the bulk chemistry of the rock on a (undefined) macroscopic scale. In cases where the dissolution and precipitation are closely coupled, reaction interfaces can be recognized as partial pseudomorphs. The interpretation of partial pseudomorphs is ambiguous – when do reaction interfaces indicate crossing a reaction line in P, T space and when do they indicate a reaction between an infiltrating fluid out of equilibrium with the parent mineral? In the former case the mineral paragenesis is used to determine a reaction defined in P, T space, treating the fluid as a catalyst which does not alter the thermodynamic relations between parent and product solids. In the latter case the reaction is dominated by the composition of the fluid rather than the P, T conditions, and the extent of reaction by the relative solubilities of the parent and product phases in that fluid. The recognition of when a mineral pair is 'coexisting' in the thermodynamic sense requires a detailed study of textural and chemical relations from the field scale to the micron scale.

In a system which evolves by dissolution and precipitation, the reaction rates will depend on the kinetics of both processes. Although measured dissolution rates in an open system under laboratory conditions are fast on a geological time-scale (Wood & Walther 1983; Walther & Wood 1984), there is ample evidence of chemical and isotopic disequilibrium on the grain scale (Abart & Sperb 1997; Cole *et al.* 2004; Villa 2006). Understanding the importance of porosity generation is vital. If a reaction of a parent mineral with a fluid produces an impermeable product, this may effectively isolate the parent against further reaction. Some minerals in the assemblage may react with a fluid and be replaced, while others remain unreacted, although all minerals in the parent assemblage may have been out of equilibrium with the fluid.

As pointed out by Vance *et al.* (2003) and Villa (2006), this opens new possibilities in the dating of geological events, based on the possibility of high spatial resolution isotopic measurements, but most importantly on understanding microtextures, mechanisms of mineral reactions and mass transport on the microscale. A further implication in this context is the continuing debate about the meaning of isotopic 'closure temperatures' (Dodson 1973; Glodny *et al.* 2002). In the examples discussed above, we have proposed that temperature is not the only parameter needed to describe a metamorphic/metasomatic reaction. In the context of geochronology, Villa (1997) recognized that two entirely different processes affect element (and isotopic) transport: temperature-dependent volume diffusion and fluid-assisted recrystallization, opening new avenues for dating both the thermal history as well as the 'hygrometric' history of a rock.

A further implication of the role of fluids in metamorphism/metasomatism is the interaction between deformation, fluid infiltration and induced chemical reactions. The

various possible feedbacks, in which fluid infiltration causes rock weakening and shear deformation related to metamorphism, have been explored for some time (Austrheim & Griffin 1985; Wintsch 1985; Wheeler 1987; Wintsch & Yi 2002). The realization that fluids can pervasively infiltrate impermeable rocks by reaction-induced porosity formation opens the possibility that fluids are far more than merely an initiator of chemical reactions, but may in fact be the principal driver for geodynamics.

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