



## Coupled dissolution and precipitation at mineral–fluid interfaces



E. Ruiz-Agudo <sup>a,\*</sup>, C.V. Putnis <sup>b</sup>, A. Putnis <sup>b</sup>

<sup>a</sup> Dept. of Mineralogy and Petrology, University of Granada, Fuentenueva s/n, 18071 Granada, Spain

<sup>b</sup> Institut für Mineralogie, Universität Münster, Corrensstrasse 24, 48149 Münster, Germany

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### ABSTRACT

Reactions occurring at mineral–fluid interfaces are important in all geochemical processes and essential for the cycling of elements within the Earth. Understanding the mechanism of the transformation of one solid phase to another and the role of fluids is fundamental to many natural and industrial processes. Problems such as the interaction of minerals with CO<sub>2</sub>-saturated water, the durability of nuclear waste materials, the remediation of polluted water, and mineral reactions that can destroy our stone-based cultural heritage, are related by the common feature that a mineral assemblage in contact with a fluid may be replaced by a more stable assemblage.

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### 1. Solid phase changes

There are two main mechanisms governing the phase changes occurring during the replacement of one solid phase by another:

- (i) First, the parent solid may exchange atoms with another phase by diffusion in the solid state. The resulting diffusion profile of

relevant diffusing elements indicates the progression of the diffusion interface within a solid phase. This type of transformation has been well studied historically, mainly due to the application to metals, alloys and refractory ceramics, where in a water-free environment structural transformations at high temperatures control changes in the solid state. The preservation of the morphology and crystallographic relationships during the replacement of one solid phase by another was always regarded as evidence for a solid-state transformation. However in the Earth, although solid-state diffusion is an on-going process, especially relevant

\* Corresponding author.

E-mail address: [encaruiz@ugr.es](mailto:encaruiz@ugr.es) (E. Ruiz-Agudo).

at increased temperatures deeper within the Earth, crustal and superficial reactions occur at a rate that is too fast to be explained by solid-state diffusion alone.

- (ii) When a solvent, such as water, is present, a different mechanism may take place, whereby the less stable phase dissolves and a more stable phase precipitates from the fluid phase. In the early 1950s, Goldsmith and Laves (1954) proposed that although at dry conditions and elevated temperatures feldspar–feldspar transformations occur by solid-state diffusive mechanism, under hydrothermal conditions such reactions could proceed by the dissolution of the parent mineral and the precipitation of the replacing phase. A few years later, Wyart and Sabatier (1958) mentioned that the alteration of labradorite under hydrothermal conditions in KCl solutions (which results in the formation of orthoclase and anorthite) could result from a dissolution–reprecipitation process. Studies by Mérigoux (1968) on hydrothermal alteration of K-feldspars showed that the kinetics of  $^{18}\text{O}$  incorporation into secondary Na-feldspar was best explained by such a mechanism, rather than by solid state diffusion. O'Neil and Taylor (1967) suggested an interfacial dissolution–reprecipitation mechanism as an alternative mechanism to the classical solid-state interdiffusion model for K feldspar–Na feldspar mineral replacement under hydrothermal conditions. This work constituted a significant breakthrough in the understanding of mineral replacement reactions. Furthermore, they state that the reaction front is associated with a thin fluid film at the interface between the parent and product phases. Later, Parsons (1978) suggested that the orthoclase to microcline transformation occurring in plutonic rocks may also take place through a dissolution–reprecipitation mechanism.

More recently the coupling of dissolution and precipitation at the reaction interface resulting in a pseudomorphic replacement and the conditions required for the generation of porosity in the parent phase have been reported (Putnis, 2002, 2009; Putnis and Putnis, 2007). The basic principle behind the interface-coupled dissolution–precipitation mechanism is that an aqueous fluid will induce some dissolution even in a highly insoluble phase, producing an interfacial boundary layer of fluid which may be supersaturated with respect to one or more stable phases. One of these phases may then nucleate at the surface of the parent phase initiating an autocatalytic reaction that couples the dissolution and precipitation rate. If an epitaxial crystallographic matching exists between the parent substrate and the product, the nucleation of the new phase transfers crystallographic information from parent to product.

In order to propagate a pseudomorphic replacement front, mass transfer pathways must be maintained between the fluid reservoir and the reaction interface. This requires that the replacement process is a volume deficit reaction, and that the resulting product is porous (discussed in more detail below) and hence allows continued infiltration of the fluid phase to the interface with the parent phase. This porosity results from both the molar volume differences between parent and product as well as the relative solubilities of the phases in the specific fluid at the interface (Pollok et al., 2011). During mineral replacement reactions, the external volume is preserved and pseudomorphs are formed as shown in Fig. 1. In the last decade a significant amount of research has been devoted to improve our understanding of such solvent-mediated phase transformations. Furthermore, in these years the development of techniques that allow direct in situ observations of reactions occurring at the mineral–fluid interface (such as in situ Atomic Force Microscopy (AFM) and various interferometry methods), as well as the significant advancements achieved in both solid sample preparation methodology and analytical techniques, have provided new

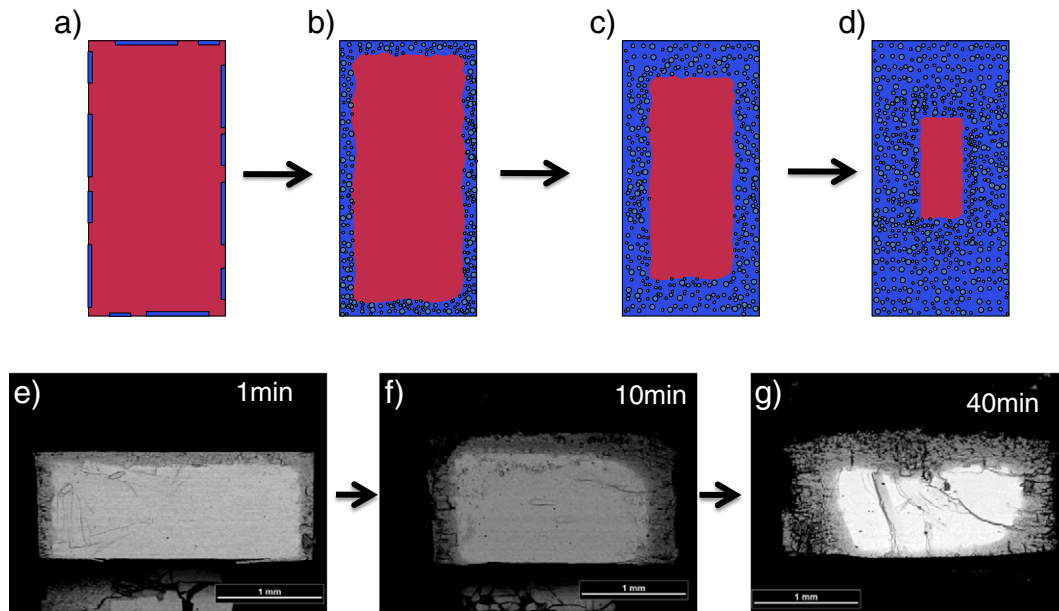
experimental evidence supporting a mechanism based on interface-coupled dissolution–precipitation reactions for mineral replacement reactions (Putnis and Ruiz-Agudo, 2013). This review attempts to summarize the most relevant aspects of the progress done on this topic.

## 2. How well do we understand dissolution mechanisms?

Bulk dissolution rates of minerals and inferred mechanisms have been determined for decades using relatively simple mixed flow reactors by measuring the composition of input and output solutions passing through the reactor containing the mineral powder. Rates are normalised relative to the initial total surface area and the aim has been to derive a rate equation which, with suitable material parameters, can be universally applied to different minerals. These dissolution rates have formed a large and useful database (Oelkers, 2001; White and Brantley, 2003; Brantley and Olsen, 2013). One well-recognised problem is the determination of reactive surface area, as opposed to total surface area, as the reactivity of different surfaces of the same crystal is likely to be different (Godinho et al., 2012). With the advent of nano-imaging in situ methods of directly observing dissolution, by techniques such as Atomic Force Microscopy (AFM) and Vertical Scanning Interferometry (VSI) it has become clear that surface topography, that can be equated qualitatively to a surface energy landscape, plays a major role in determining dissolution mechanisms. This has been more formally stated in recent articles (Fischer et al., 2012; Luttge et al., 2013) where the concept of a dissolution rate spectrum has been proposed as a way of contributing to a better understanding of the variability of dissolution mechanisms at sites with different reactivity. The significance of different energetic sites on a mineral surface to dissolution rates is also being explored computationally by molecular modelling (e.g. Stack et al., 2013).

Whatever the details of the actual mechanisms, dissolution is clearly a response of the mineral and the fluid to achieve a lower free energy state. In the trivial case e.g. the interaction of a pure end-member mineral (with no lower energy polymorphs) with pure deionized water, the mineral will continue to dissolve until the fluid reaches saturation. i.e. the ion activity product in the solution is equal to the equilibrium solubility constant of the mineral. One complication is that many multicomponent minerals dissolve “incongruently” or “non-stoichiometrically” which means that the measured elemental ratios in the solution are different from those in the solid phase, especially during the initial stages of the dissolution process.

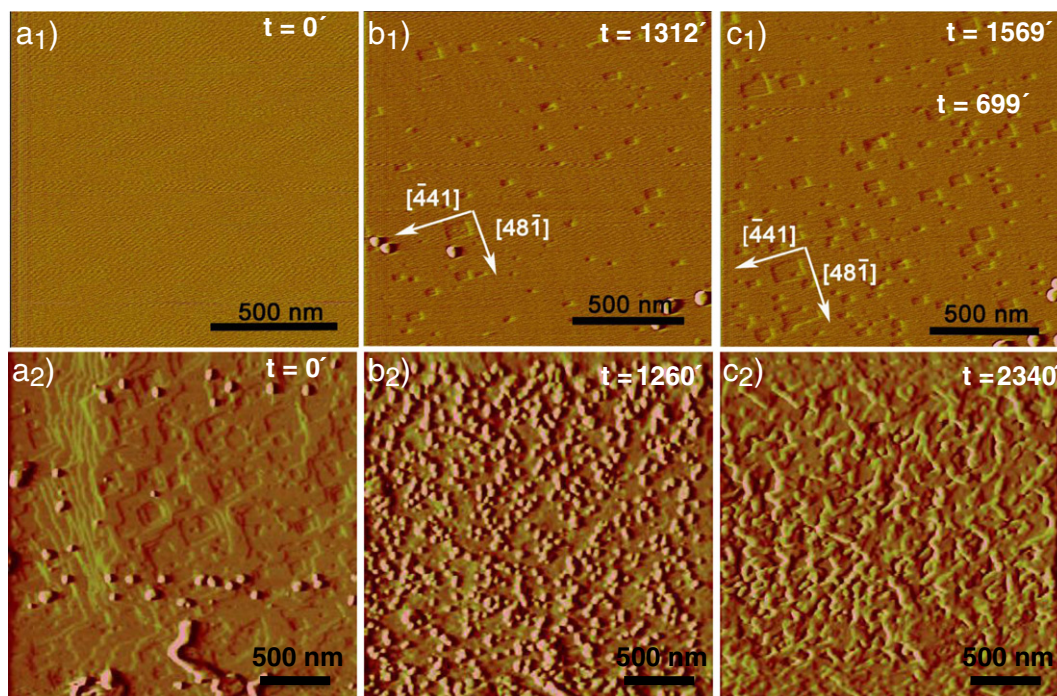
For example, the apparent non-stoichiometric dissolution of dolomite ( $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$ ) has been explained by the preferential release of calcium ions into the solution and therefore the formation of a Mg-enriched surface layer (Busenberg and Plummer, 1986; Pokrovsky and Schott, 2001; Zhang et al., 2007). The origin of such a phenomenon continues to be the subject of considerable debate. On the one hand, the invoked preferential dissolution of the calcium component has been attributed to the much lower hydration energy of the  $\text{Ca}^{2+}$  ion compared with  $\text{Mg}^{2+}$  and thus its lower stability at the dolomite/water interface (Pokrovsky and Schott, 2001). However, nanoscale observations by AFM of the in situ dissolution of dolomite cleavage surfaces reacting in acidic solutions show no experimental evidence that supports the hypothesis of a preferential release of calcium (Urosevic et al., 2012). Instead, the dissolution results in normal rhombohedral etch pits similar to those regularly observed in calcite (Ruiz-Agudo and Putnis, 2012) with spreading of etch pit steps parallel to the  $\langle -441 \rangle$  direction (Fig. 2). Dissolution at such step edges is necessarily a stoichiometric process, as equal amounts of calcium and magnesium ions are present along such steps. However, the dissolution is accompanied by the precipitation of an Mg-rich phase at the dissolving surface (Fig. 2), clearly demonstrating that this “incongruent” behaviour is the result of a coupled dissolution–precipitation process.



**Fig. 1.** Pseudomorphic replacement by interface-coupled dissolution–precipitation reaction. When a solid 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 that is supersaturated with respect to a product phase, which may nucleate on the surface (a). (b)–(d) Continued dissolution and precipitation at the parent–product interface and the generation of interconnected porosity in the product phase allows the migration of the reaction interface from the surface through the parent phase, which is pseudomorphically replaced by the product. (e)–(g) Pseudomorphic replacement of a KBr crystal by KCl, with the development of porosity seen in the product rim.

A similar mechanism has been proposed to explain the apparent non-stoichiometric dissolution behaviour of some silicate minerals, such as wollastonite ( $\text{CaSiO}_3$ ). The dissolution of most common multi-component silicate minerals and glasses is apparently incongruent, as shown by the non-stoichiometric release of the solid phase components. This results in the formation of so-called surface “leached” layers

enriched in one of the components of the parent phase. These layers will be referred to here as “surface altered layers” to avoid reference to a particular formation mechanism. The mechanism of surface altered layer formation is obviously related to apparent incongruent dissolution, but because “leaching” is such a common phenomenon particularly when referring to secondary enrichment processes in ore minerals,



**Fig. 2.** Sequential AFM deflection images of a dolomite (10–14) surface exposed to (a1)–(c1) deionized water and (a2)–(c2) pH 3 HCl solution for increasing periods of time. Note the dissolution of the dolomite cleavage surface by formation and propagation of etch pits with edges parallel to  $\langle\bar{4}41\rangle$  direction and the formation of a Mg-rich phase on the dolomite surface.

the term has become associated with a solid-state interdiffusion mechanism of protons and cations, with the implication that it is merely an element exchange through an otherwise inert crystal structure (Casey et al., 1989a,b, 1993; Petit et al., 1989, 1990). Due to the important effects these surface altered layers may have on mineral dissolution rates and secondary mineral formation, they have attracted a great deal of research.

Teng et al. (2001) questioned the theory of a solid-state interdiffusion mechanism for explaining the apparent non-stoichiometric dissolution of orthoclase, and attributed this behaviour to the formation of a silica gel. In the case of wollastonite, Green and Lüttge (2006) suggested from their Vertical Scanning Interferometry (VSI) study that a precipitation event could occur during dissolution of wollastonite at acidic pH. More recently, Ruiz-Agudo et al. (2012) reported in situ AFM observations of the dissolution of wollastonite,  $\text{CaSiO}_3$ , that provide, for the first time, clear direct experimental evidence that surface altered layers are formed in a tight interface-coupled two-step process: stoichiometric dissolution of the pristine mineral surfaces and subsequent precipitation of a secondary phase (most likely amorphous silica) from a supersaturated boundary layer of fluid in contact with the mineral surface.

These results differ significantly from the concept of preferential leaching of cations, as postulated by currently accepted incongruent dissolution models (e.g. Schott et al., 2012), and support an interface-coupled dissolution–precipitation model as the most probable mechanism for surface altered layer formation. One of the strongest pieces of evidence against a solid-state interdiffusion mechanism is the reported nm-sharp chemical boundaries that are spatially coincident with the sharp structural boundaries. Diffusion modelling, which shows broad sigmoidal profiles that are dependent on cation charge, is incompatible with TEM results from the past 10 years (e.g. Hellmann et al., 2003, 2012).

Furthermore, the significant advancements achieved in both sample preparation methodology and analytical techniques during the last 15 years have provided further evidence supporting a dissolution–precipitation mechanism. Ultramicrotomy and focused ion beam (FIB) techniques have permitted the nanometer-scale analysis of reaction interfaces in cross section with nm or sub-nm-sized TEM probes, thereby giving chemical maps with true nm-scale spatial resolution. Experimental work supporting an interdiffusion mechanism (e.g. Casey et al., 1989a,b, 1993; Petit et al., 1989, 1990) is based on the use of surface techniques where the beam impinges upon the reacted mineral surface, yielding artificially broadened chemical profiles that resemble diffusion profiles. Hellmann and co-workers have shown how analytical techniques can give chemical gradients orders of magnitude different for the same altered mineral-feldspar (Hellmann et al., 2004).

Despite all this evidence, the debate is still ongoing and in the last couple of years papers by Ruiz-Agudo et al. (2012) and Schott et al. (2012) propose two entirely different interpretations of surface altered layer formation. The ultimate resolution of this issue has important implications for understanding and evaluating dissolution kinetics of major rock-forming minerals as well as glasses. The latter case is particularly important for long term prediction of glass corrosion, specifically glass containing radioactive waste products (see below). We propose that incongruent dissolution is essentially the same as any other mineral–fluid equilibration process. As stated above, when a fluid interacts with a mineral phase with which it is out of equilibrium the mineral will tend to dissolve. However, depending on the fluid composition, dissolution of even a few monolayers of the parent surface may result in supersaturation of the interfacial fluid with respect to a secondary phase. This product phase may nucleate on the parent surface, within this interfacial fluid, depending on the fluid composition and the degree of epitaxy between parent and product phases. The dissolution and precipitation may be coupled in space and time (depending on the fluid composition) and result in the complete replacement of the parent mineral by the product.

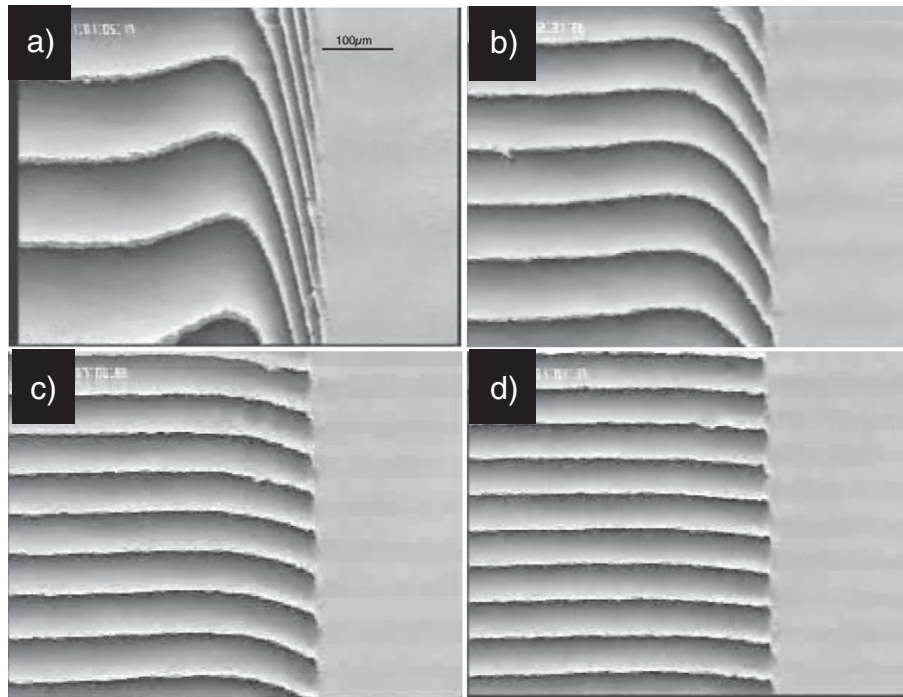
### 3. The role of the boundary fluid–mineral interface in the control of replacement reactions

In many replacement systems, the formation of the new mineral assemblage occurs despite the fact that the bulk solution is undersaturated with respect to the secondary phase/s that precipitate/s. This has been verified in an increasing number of in situ AFM experiments which have shown that growth on mineral surfaces can occur from solutions whose bulk (average) composition is undersaturated with respect to the precipitating phase. It has been suggested that interfacial fluids have thermodynamic and physical properties (e.g. diffusion rates, viscosity, solute adsorption, dielectric constant or pH) (Fenter and Sturchio, 2004; Kerisit and Liu, 2009) that differ from those of bulk fluids. This is related to the fact that mineral surfaces induce a strong order on fluid molecules over distances of a few molecular layers, as a result of reduced orientational and translational entropy, as shown by molecular dynamic simulations (Wang et al., 2006).

These differences in fluid parameters are thought to enhance solution saturation in thin fluid films (James and Healy, 1972; Putnis et al., 2005). While the actual value of the fluid composition at a replacement interface is very difficult to measure, real-time phase-shift interferometry has been used to show the steep compositional gradient existing at the surface of a KBr crystal while it is reacting in a KCl solution (Putnis et al., 2005, Fig. 3). This apparently simple salt system has been shown to be useful as a model for more complex Earth systems involving mineral–fluid reactions during such processes as metasomatism, metamorphism and weathering. The main implication of the presence of such a gradient at the mineral–solution interface is that the dissolution of even a few monolayers of the parent solid may result in the fluid at the interface (boundary layer) becoming supersaturated with respect to the product phase/s, while the bulk solution remains undersaturated. Dissolution and the release of elements from the solid phase to the interfacial fluid layer, coupled with the precipitation from this fluid, are kinetically faster than diffusion through the bulk fluid.

The existence of a supersaturated fluid boundary layer has been inferred from experiments in a number of systems. For example, during the above-mentioned AFM flow-through dissolution experiments of wollastonite under acidic conditions, thermodynamic calculations indicate that the composition of effluent solutions is undersaturated with respect to amorphous silica (saturation indexes with respect to amorphous silica varied from  $-0.3$  to  $-1.23$ ), for both total Ca and the stoichiometric amount of Si, as well as the measured Si concentration. Yet, AFM observations, FESEM and MicroRaman spectroscopy analyses of the surface layers formed on wollastonite indicate that they are formed by an amorphous silica precipitate (Ruiz-Agudo et al., 2012). Hellmann and co-workers reported high undersaturation values with respect to different silica polymorphs during labradorite and wollastonite dissolution at acid pH conditions. Nevertheless, in both cases a Si-enriched layer is formed at the mineral surface (Hellmann et al., 2012). Similarly, when calcite is in contact with Se (IV)-bearing solutions during flow-through experiments, a precipitate forms while calcite is still dissolving. This occurs even though geochemical modelling shows that, even if the equilibrium with calcite was reached, the solution would be undersaturated with respect to any possible phase. Simulations, considering that the reaction process takes place in a series of small reaction steps in which a calcite monolayer dissolves in a thin layer of solution of defined thickness, show that for thicknesses smaller than  $10\ \mu\text{m}$ , this fluid layer in the Se(IV) solutions is supersaturated with respect to  $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$ , the phase that precipitates (Putnis et al., 2013).

Other examples where the partial dissolution of the substrate provides ions included in the new phase, include the growth of Ca phosphates (Wang et al., 2012; Klasa et al., 2013), and Ca phosphonates (Ruiz-Agudo et al., 2010) on calcite cleavage surfaces, and Ca phosphates (Pinto et al., 2010) on gypsum surfaces. The concept of a boundary layer becoming supersaturated with respect to another phase, that then precipitates, is essential for the understanding of coupled dissolution–



**Fig. 3.** Compositional gradients at the solid–fluid interface during replacement reactions. (a)–(d) A sequence of phase shift interferometry images recorded when a KBr crystal (on the right) is in contact with a saturated KCl solution. The fringes represent characteristic refractive index values of the fluid, and changes in refractive index indicate changes in the composition of the fluid. The curved interference fringes near the surface of the crystal show an initial steep compositional gradient at the surface, produced by the initial replacement reaction.

precipitation as a mechanism of mineral replacement. Similar phenomena which emphasise the importance of the interaction between the dissolved ions and the parent phase substrate in a two-dimensional interfacial zone, have also been described by [Murdaugh et al. \(2007\)](#).

The importance of understanding the properties of the fluid–mineral interface cannot be overestimated and has implications in every aspect of fluid–rock and fluid–mineral interaction as discussed in the further examples below.

#### 4. Environmental remediation through the formation of more stable phases

Coupled dissolution and precipitation can be an effective way of removing contaminants from polluted waters. For example, the dissolution of calcium carbonate releases calcium and carbonate ions to the solution which may react with anionic or cationic contaminants to precipitate a less soluble phase. When phosphate is present in solution the resulting precipitate would be one of the low solubility calcium phosphate phases such as apatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  or tricalcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$  ([Fig. 4](#)) ([Kasioptas et al., 2008](#); [Klasa et al., 2013](#)). If cadmium ions were present the reaction with carbonate ions released from the dissolving calcite would result in the precipitation of otavite,  $\text{CdCO}_3$ , which is 3 orders of magnitude less soluble than calcite ([Prieto, 2009](#); [Prieto et al., 2013](#)).

A similar strategy can be used to take up fluoride ions from aqueous solution by using hydroxyapatite as the reactant. In this case the dissolution of hydroxyapatite and reaction with fluoride in solution result in the precipitation of fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{F})$ , which is thermodynamically more stable in the presence of fluoride ions. The treatment is more effective when the reactants have a high surface area, and nanoparticle technology is being applied to such remediation treatments ([Sternitzke et al., 2012](#)). The use of hydroxyapatite for removal of Pb from contaminated soils is also a potentially effective method involving the dissolution of hydroxyapatite and the precipitation of the less-soluble pyromorphite,  $\text{Pb}_5(\text{PO}_4)_3(\text{OH})$  ([Miretzky and Fernandez-Cirelli, 2008](#)).

A similar strategy can be used with cerussite,  $\text{PbCO}_3$  as the reactant phase ([Wang et al., 2013](#)).

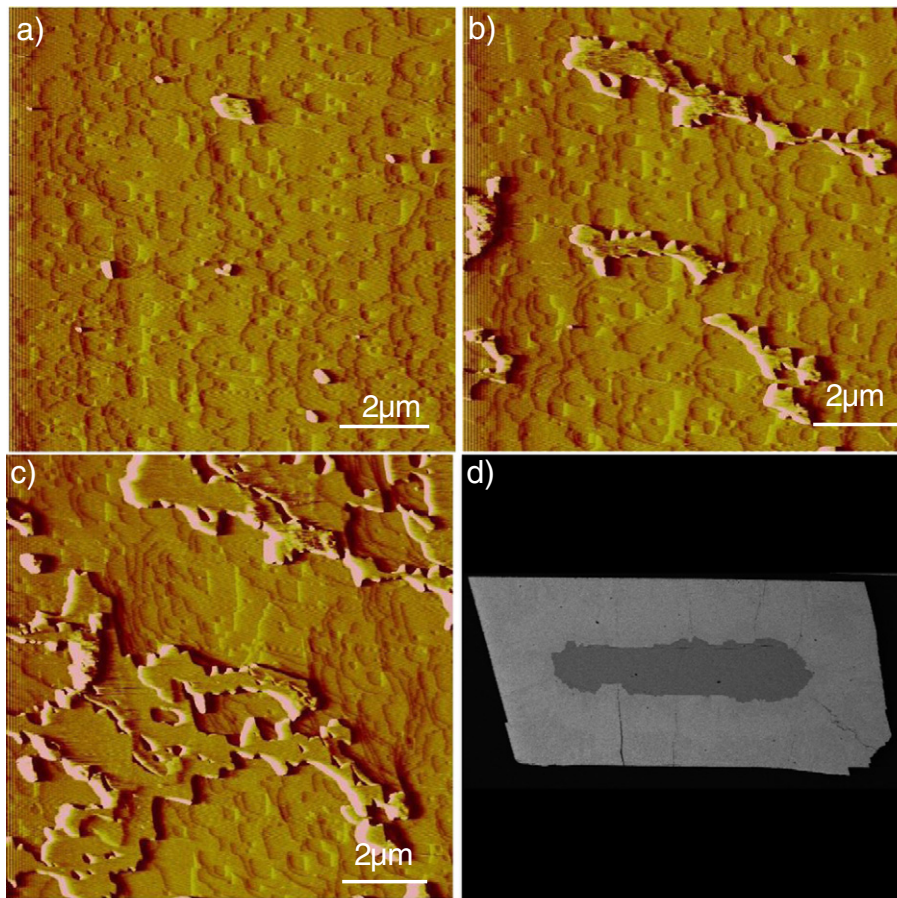
The use of apatite in this way highlights another important aspect of coupled dissolution–precipitation mechanisms, that is, that the parent reactant does not need to have a high solubility for the process to operate. The relative solubility of the parent and the product is the important parameter. All apatite compounds have a low solubility, but this is not a limitation for replacement because in a coupled process it is only the interfacial solution which needs to be supersaturated with respect to the product phase and so only small amounts of dissolved material need to be in this interfacial solution at a given time.

One potential problem with this remediation strategy is that the precipitating phase may form a layer over the surface of the calcite and effectively armour it against further dissolution and reaction. The continued availability of fluid pathways is therefore essential for the process to continue. This requires that the product precipitate is porous and also has a crystal structure sufficiently different from the substrate that it does not form an epitaxial film over the surface. The generation of porosity is discussed in more detail below.

#### 5. Element release and mobilization

While a coupled dissolution and precipitation process may immobilize some elements, other elements are released to solution ([Putnis and Fernandez-Diaz, 2010](#)). This aspect of coupled processes is the major mechanism for the redistribution of elements in the Earth's crust and hence the formation of many types of mineral and ore deposits. It is also highly relevant when considering the mechanism of glass corrosion by interaction with fluids, the main issue of current interest in that case being the durability of glass used to encapsulate nuclear waste.

We illustrate this with two examples. First, albitization, which is the reaction between minerals and Na-bearing aqueous solutions to form albite,  $\text{NaAlSi}_3\text{O}_8$ . The usual case considered is the albitization of potassic and calcic feldspars. This process can take place in detrital feldspars at low temperatures during diagenesis but is also common in the

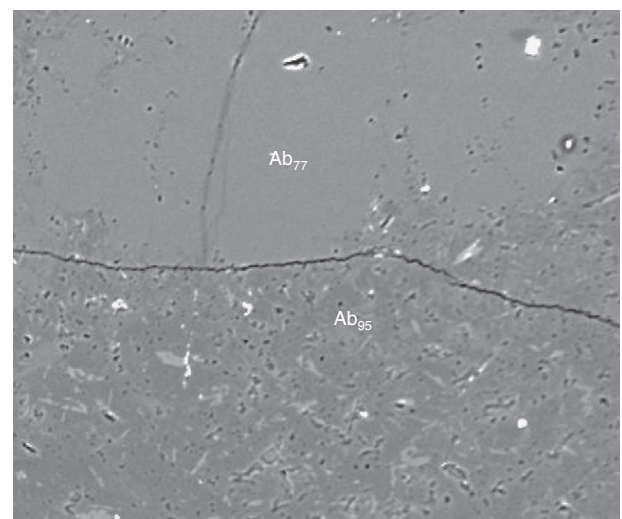


**Fig. 4.** (a)–(c) AFM deflection images of the initial stages of the replacement of calcite by calcium phosphate, showing the growth of a Ca-phase on the simultaneously dissolving calcite surface upon contact with phosphate bearing solutions at concentrations higher than 5 mM phosphate. At longer reaction times, the reaction proceeds so that calcite is pseudomorphically replaced by calcium phosphate. (d) Cross-section of an Iceland spar crystal partially replaced by hydroxyapatite.

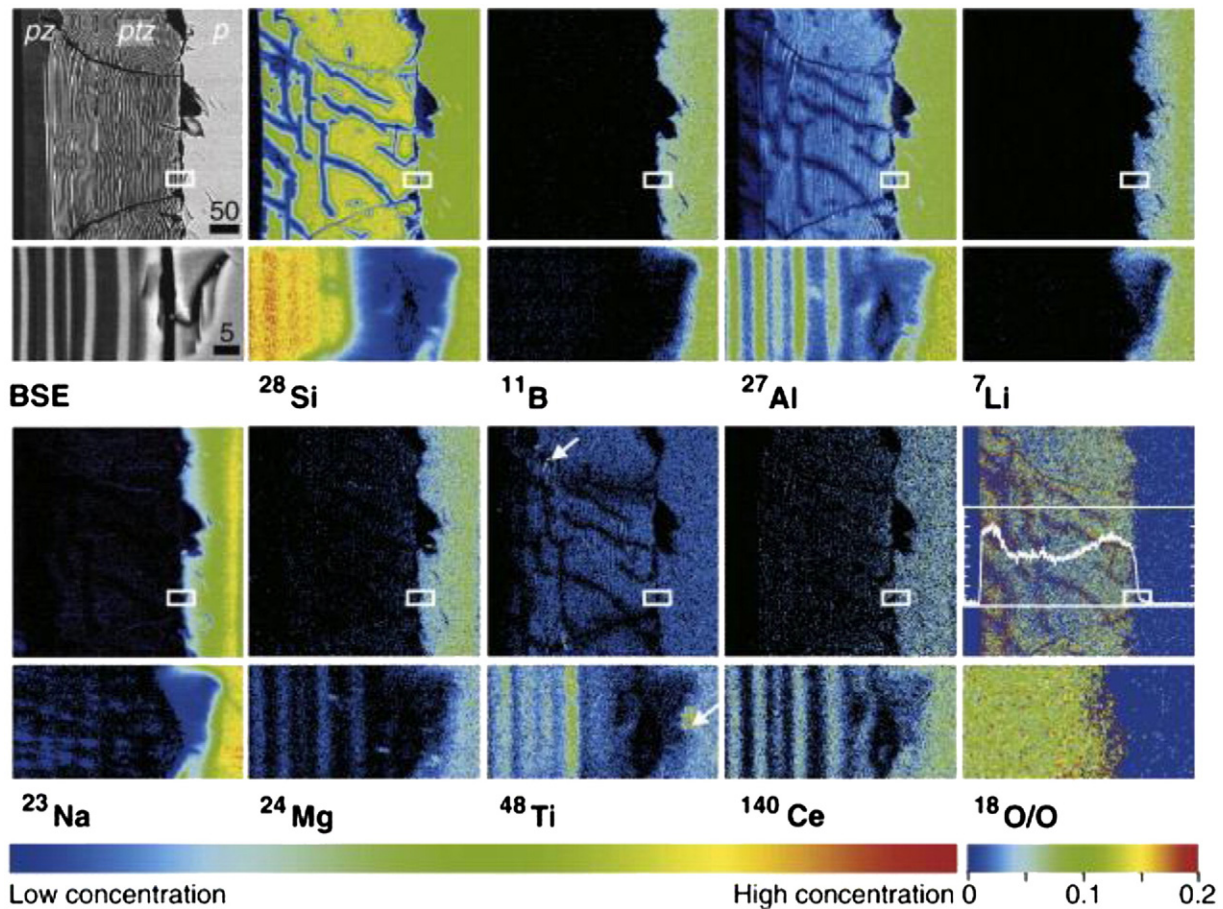
hydrothermal alteration of feldspar-bearing rocks. Although the albitization of potassic feldspar  $\text{KAlSi}_3\text{O}_8$  only seems to involve only the exchange of  $\text{K}^+$  and  $\text{Na}^+$ , the actual mechanism involves a dissolution of the parent phase and reprecipitation of the albite (Niedermeier et al., 2009). The same interface-coupled dissolution–precipitation mechanism has also been demonstrated experimentally for the albitization of plagioclases (that also involves the mobilization of Al and Si) (Hövelmann et al., 2010). The texture and porosity of the albite formed are similar to that in natural albitization (Fig. 5) (Engvik et al., 2008). Albitization can also be pervasive and replace all the minerals of a rock, resulting in “albitites”, essentially monomineralic rocks. In the Bamble sector of southern Norway, the formation of albitites is also associated with ore deposits in the region. The question of the fate of the fluid which has stripped the rock of all but Na, Al and Si has been addressed in the Curnamona region of South Australia by Clark et al. (2005) where extensive albitization is also associated with ore deposits. The origin of the major ore deposit at Mt Isa Queensland, Australia has also been linked to extensive albitization of the country rock, with the source of Na being evaporite rocks in the sequence (Oliver et al., 2004).

The second example, of the mechanism of interaction of glass with an aqueous solution is rather more contentious, particularly when applied to glass for radioactive waste storage. The prevailing view is that the release of elements from glass during corrosion is by “leaching” whereby protons in the aqueous solution diffuse into the glass and exchange for metal cations, which diffuse out into the solution, forming silanol ( $\text{Si-OH}$ ) groups. The subsequent formation of a silica ‘gel’ layer is then explained by a solid-state recondensation of this hydrolysed

network which then forms the residual polymerised porous hydrated silica-enriched layer (Bunker, 1994; Cailleteau et al., 2008). An alternative view has been proposed (Geisler et al., 2010; Dohmen et al., 2013) based on experimental data using isotopically enriched aqueous solutions as tracers, as well as on an interpretation of oscillatory laminar



**Fig. 5.** BSE image of a partly albitised natural feldspar. The albitised part ( $\text{Ab}_{95}$ ) has high porosity (black) and bright inclusions of hematite, while the parent feldspar ( $\text{Ab}_{77}$ ) is homogeneous.



**Fig. 6.** BSE and TOF-SIMS images from two areas of a corrosion rim formed around a borosilicate glass cuboid after reaction in an  $^{18}\text{O}$ -enriched solution of an initial pH of 0 at 150 °C.  $^{18}\text{O}$  is strongly enriched in the reaction zone, this representing strong evidence that the corrosion rim directly precipitated from the solution. Note also that the TOF-SIMS images of  $^{18}\text{O}$ , Na, B, Li, and Mg indicate a sharp drop at the reaction interface towards the pristine glass and no apparent diffusion profiles are observed. Abbreviations: p pristine glass, ptz patterned zone, and pz plain zone.

Geisler et al. (2010) reprinted with permission from Elsevier.

patterns formed during hydrothermal alteration (Fig. 6). Significantly, the laminar patterns formed experimentally are very similar to those observed in naturally altered, ancient glasses. These authors propose that silica-enriched alteration layers form by congruent dissolution of the glass network, which is coupled in space and time to the precipitation of amorphous silica at an inwardly moving reaction interface. Although the feedback mechanisms which control the oscillatory fluctuations in porosity and chemical composition in the alteration layers are not well understood, the new mechanistic model is essentially similar to the interface-coupled dissolution-precipitation model described above.

Clearly, any long-term prediction of the aqueous durability of nuclear waste glass and the potential mobilization of radioactive elements depend on correctly modelling the mechanism of glass corrosion and this remains the most challenging task.

The controversy over glass corrosion mechanisms is reminiscent of the arguments concerning the formation of silica-rich layers when silicate and aluminosilicate minerals react with aqueous solutions. Ion-exchange mechanisms by diffusion through an essentially inert framework structure were considered to be an essential aspect of the dissolution mechanism (Casey et al., 1989a,b, 1993), until high resolution transmission electron microscopy of experimentally altered plagioclase showed that the chemical and structural interface between the unaltered plagioclase and the silica-rich rim was too sharp to be accounted for by solid-state diffusion (Hellmann et al., 2003) and that the mechanism was consistent with coupled dissolution-precipitation, even when the product phase is amorphous. This also demonstrated

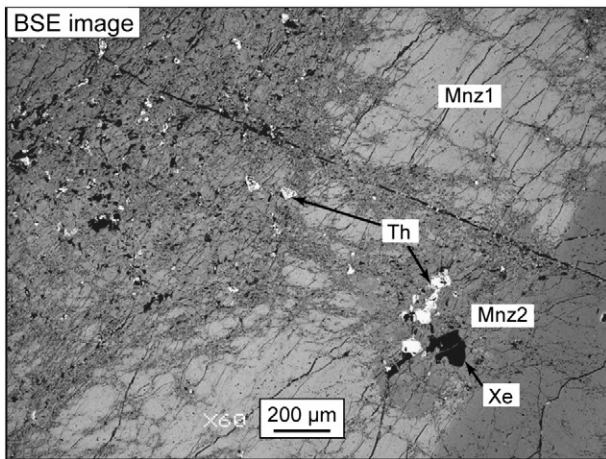
the essentially non-equilibrium nature of dissolution under the conditions of the experiment.

Since that time many more experimental studies have demonstrated that silica-rich layers on altered silicate minerals are the result of reprecipitation rather than leaching (Daval et al., 2011; King et al., 2011; Hellmann et al., 2012). One significant observation which mitigated against such an interpretation was that the bulk fluid in the experiments was not necessarily supersaturated with respect to amorphous silica. However, as explained above, only a thin layer of interfacial fluid needs to become supersaturated and when the dissolution and precipitation are coupled at the interface, the bulk fluid only acts as a reservoir for continuing the dissolution of the parent.

## 6. Fluid transport during replacement reactions: porosity, fractures and grain boundaries

The access of fluids to reactive surfaces during replacement reactions is critical for the advancement of the reaction boundary, and may be maintained by the development of porosity due to molar volume and relative solubility differences, the formation of fractures, and/or the presence of grain boundaries.

The generation of porosity during replacement processes has been reported in many systems both in experiments and in nature (e.g. see Putnis and Putnis, 2007; Putnis, 2009) including feldspars (Worden et al., 1990; David et al., 1995; Putnis A. et al., 2007; Putnis C.V. et al., 2007), KBr-KCl-H<sub>2</sub>O (Putnis and Mezger, 2004; Putnis et al., 2005), fluorapatite (Harlov et al., 2005), monazite-monazite (Seydoux-



**Fig. 7.** Backscattered secondary electron image of an unaltered monazite (Mnz1) partially replaced by a secondary, Th–U(Y)-depleted, high-Th/U, monazite (Mnz2) by a low-temperature, fluid-mediated coupled dissolution–precipitation mechanism. Note the formation of porosity in the secondary phase. Image courtesy of A.-M. Seydoux-Guillaume.

Guillaume et al., 2012), sulphide (Tenailleau et al., 2006; Zhao et al., 2014) and calaverite (Zhao et al., 2009) (Fig. 7). Parameters contributing to the overall volume change in a replacement reaction are the molar volume of parent and product and their relative solubility in a given fluid (Putnis, 2002; Pollok et al., 2011). In general, when more solid volume is dissolved than reprecipitated, some material is lost to the fluid phase and the result is the generation of porosity in the product. This mechanism allows the reaction interface to move through the crystal, with mass transport through the fluid-filled micro-porosity generated as the interface moves within the solid phase. If more solid volume is precipitated than dissolved, the reacting phase would quickly become isolated from the fluid phase by a layer of the reaction product(s), and the replacement process would cease. The solubility of the solid phases is generally determined by a number of variables, including fluid composition, temperature, pressure, and pH. Thus, theoretically the magnitude (and the sign) of the volume change may be different in the same system depending on the conditions of the solution (Ruiz-Agudo et al., 2013a). Additionally, it has to be considered that the composition of the solution will evolve continuously during the dynamic replacement process, thus potentially affecting the solubility of the different phases and, as a consequence, the resulting porosity.

The porosity is an integral part of the microstructure associated with the replacement mechanism, and as with any microstructure it is a transient feature (Putnis et al., 2005; Raufaste et al., 2011). Whereas in solid state transformations, where microstructures are preserved below some closure temperature, dissolution–precipitation reactions can continue at significant rates down to earth surface temperatures, as in the case of chemical weathering. Thus porosity developed due to a replacement process at higher temperatures may be annealed out while fluid remains in contact with the mineral. Such textural equilibration is an example of “annealing” by fluid-induced rather than by temperature-induced recrystallization. Textural equilibration (a form of Ostwald ripening) is driven by the large interfacial energy associated with the porous structure and generally results in porosity coarsening and the possible loss of interconnectivity of the pore distribution, and hence reduction in permeability. As a result, evidence of porosity may be erased. However, some residual porosity, such as fluid inclusions, may remain. Porosity can also be on a nanoscale as seen in most cloudy feldspars, the cloudiness resulting from the nanoporosity. In the case of pink-coloured feldspars, often present in granites, the nanoporosity contains nano-crystals of haematite giving the mineral its pink/red colour (Putnis A. et al., 2007).

The growth mechanism of the product phase is also a key variable to be considered during the analysis of porosity generation in replacement reactions. If a good epitaxial fit, formed by some crystallographic continuity, exists between the parent and product phases, the product will grow as a thin film (layer-by-layer or Frank-van der Merwe growth mechanism, Mutaftschiev, 2001) homogeneously covering the parent phase (Prieto et al., 2003). In contrast, if the structure of the product is appreciably different from that of the substrate, it will tend to precipitate by three-dimensional heterogeneous nucleation (Pérez-Garrido et al., 2007). The distribution of the precipitated volume will be different in these two opposite cases, and while in the first case, full coverage of the substrate surface may be achieved, in the second case some pore space will be generated at the interface between the parent phase and the product (Fig. 8).

The significance of the differences in growth mechanisms on a carbonate substrate has been shown, for example, for the case of the replacement of calcite and aragonite by  $(\text{Cd,Ca})\text{CO}_3$  solid solutions with a calcite-type structure (Prieto et al., 2003). The better structural matching with calcite results in the oriented overgrowth of thin crystallites, which quickly spread to cover the whole surface by a layer a few nanometers thick. This layer isolates the substrate from further dissolution, so that the replacement process stops when just a small amount of product has precipitated. However when aragonite undergoes a reaction in the presence of Cd solutions, 3-D growth on the aragonite surface occurs as the crystallographic structural matching is lower. In this latter case, growth of the new  $(\text{Cd,Ca})\text{CO}_3$  phase continues as long as Cd solutions are available since the surface does not become passivated by a precipitated layer. Therefore aragonite provides a better remediation surface for removing Cd from contaminated solutions (Prieto et al., 2003).

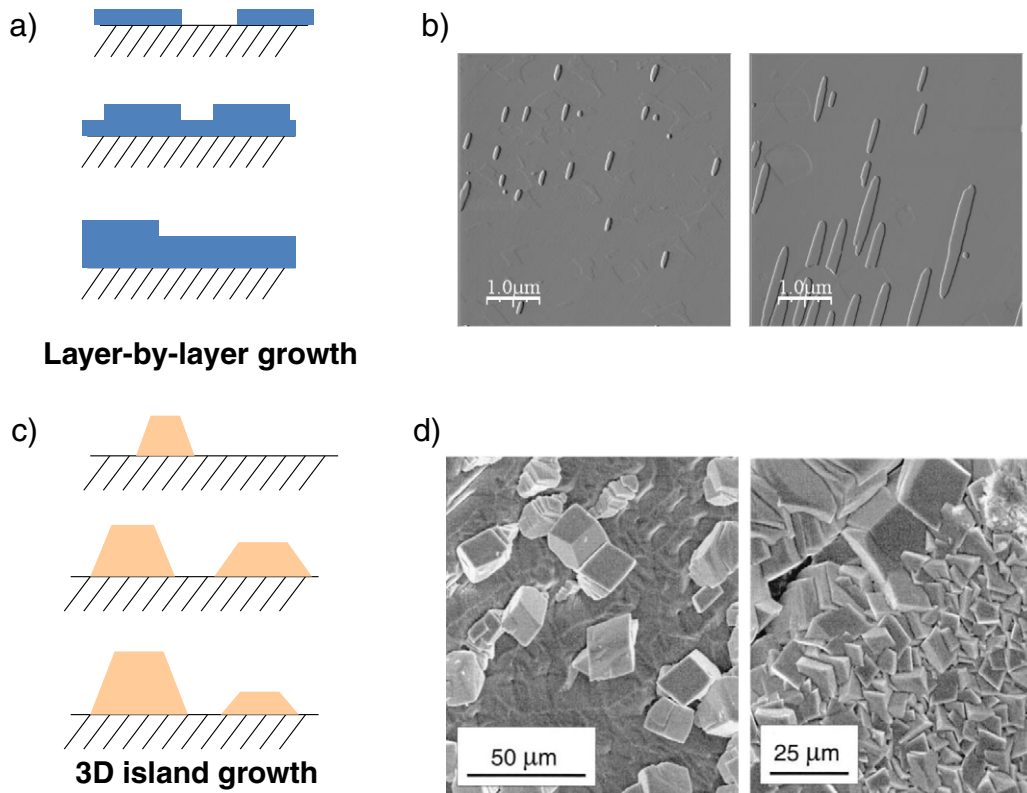
When replacement reactions involve significant volume changes, both positive (expansion) and negative (shrinkage), sufficient stresses can be generated to induce fracturing in parent and product phases. These fractures may be critical for the progress of the replacement reaction, particularly in those systems where the overall volume change (considering molar volumes and relative solubility differences) is positive, as they provide pathways for the fluid to reach unreacted surfaces and thus allow the advancement of the reaction interface. An example is the pseudomorphic replacement of leucite ( $\text{KAlSi}_2\text{O}_6$ ) by analcime ( $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ ) in which fluid transport to the reaction front takes place through sets of hierarchical fractures as well as porosity generation (Putnis C. V. et al., 2007; Jamtveit et al., 2009). Other examples of fracture formation during replacement reactions include the replacement of ilmenite by rutile (Janssen et al., 2010), aragonite by calcite (Perdikouri et al., 2011, 2013) and calcite by calcium oxalate (Ruiz-Agudo et al., 2013a) (Fig. 9).

Grain boundaries are also important fluid pathways which enable the reaction front to progress (Jonas et al., 2013, 2014). Hydrothermal experiments of the pseudomorphic replacement of Carrara marble by calcium phosphates in solutions enriched in  $^{18}\text{O}$  show that grain boundaries present in the rock are effective pathways that allow the fluid to penetrate the rock more than one order of magnitude faster than through the newly formed porosity (Fig. 10). Grain boundaries may allow the fluid to progress relatively large distances in short times, without developing broad reaction fronts perpendicular to those boundaries. However the slower replacement reactions within the mineral grains allow for a more complete element exchange between parent and fluid phases.

## 7. Cation (and anion) exchange mechanisms

Ion exchange involves an exchange of ions between a solid phase and an aqueous solution while keeping the crystal structure and morphology intact. Therefore it has the basic features of a replacement reaction, except that when applied to crystal structures which are in themselves microporous such as zeolites, it is generally accepted that

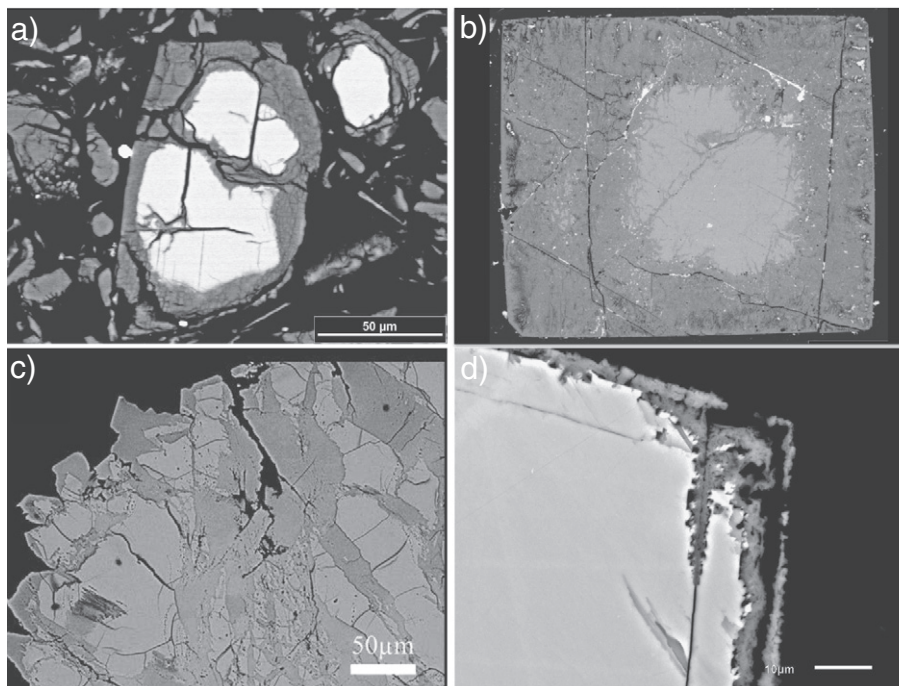




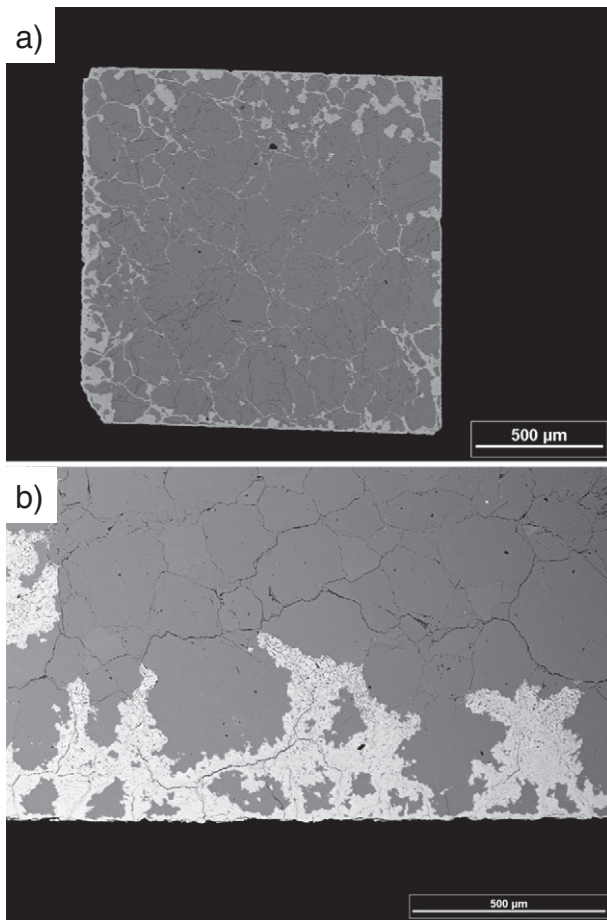
**Fig. 8.** Influence of the growth mechanism on the porosity development during replacement reactions. (a) If a good structural matching exists between the parent and product phases, the product will grow as a thin film homogeneously on the parent phase and full coverage of the substrate surface may be achieved. This occurs when a  $(\text{Cd,Ca})\text{CO}_3$  solid solution grows on calcite (b) (Prieto et al., 2003 reprinted with permission from Elsevier). (c) In contrast, if the structure of the product is appreciably different from that of the substrate, it will tend to precipitate by three-dimensional heterogeneous nucleation and some pore space will be generated at the interface. This occurs when a  $(\text{Cd,Ca})\text{CO}_3$  solid solution grows on aragonite (d) (Pérez-Garrido et al., 2007 reprinted with permission from Elsevier).

counterdiffusion of ions through the solid is the exchange mechanism. However, the possibility that it may involve a dissolution–precipitation mechanism has not been excluded (Rivest and Jain, 2013)

simply because most studies are mainly concerned with cation exchange capacities and are not specifically designed to investigate the mechanism.



**Fig. 9.** Examples of reaction-driven fracturing during replacement reactions: (a) leucite–analcime, (b) ilmenite–rutile, (c) aragonite–calcite and (d) calcite–whewellite.



**Fig. 10.** Backscattered secondary electron image of a Carrara marble cube partially replaced by calcium phosphate. The fluid moves towards the interior of the marble cubes along grain boundaries replacing the parent calcite, while developing reaction fronts perpendicular to those boundaries.

Although leucite ( $\text{KAlSi}_2\text{O}_6$ ) and analcime ( $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ ) can only marginally be called “zeolitic” they nevertheless have relatively open crystal structures and it might be expected that ion exchange of K and Na might be by solid state diffusion. However, the replacement of leucite by analcime mentioned above has been shown to take place by a coupled dissolution–precipitation mechanism (Putnis C.V. et al., 2007; Xia et al., 2009a). Furthermore, a recent study on the reaction between the zeolite scolecite ( $\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$ ) and NaOH solutions resulted in pseudomorphic replacement rims that contained the isostructural zeolite, mesolite ( $\text{Na}_2\text{Ca}_2\text{Al}_6\text{Si}_9\text{O}_{30} \cdot 8\text{H}_2\text{O}$ ) as well as the non-isostructural phase tobermorite (Dunkel and Putnis, 2014). This suggests that coupled dissolution–precipitation has to be considered as a viable mechanism even in the case of zeolites. Note however, that this reaction took place at high pH where the zeolite solubility is high.

## 8. Polymorphic transitions by a coupled dissolution–precipitation mechanism

The concept of coupled dissolution–precipitation as a general mechanism of converting one phase to another, with the main features explained above, is gaining general acceptance in both Earth and materials science, with applications to metamorphism and metasomatism as well as new material synthesis. This is a general mechanism of re-equilibration of solids in contact with an aqueous fluid and allows interpretation of many textural observations made in experimental studies and in natural rocks. Furthermore, it provides a framework for the

description and understanding of many transformation processes that occur in the presence of a fluid phase.

Examples of these processes are polymorphic transitions. Many substances can exist in two or more structurally different phases, depending on the temperature and pressure conditions prevailing during their formation. This is known as polymorphism, and examples are diamond and graphite, or calcite and aragonite. Although polymorphs have identical chemical composition, they have differences in bioavailability, solubility, dissolution rate, chemical stability, physical stability, melting point, colour, filterability, density, flow behaviour, and many other physical and chemical properties (Llinas and Goodman, 2008). This is relevant for many technological applications in which polymorphs are involved, such as the production of pharmaceuticals or explosives, as they may transform from one crystal structure to another during storage and/or processing. Moreover, in many cases, precipitation of crystals from solution results initially in the formation of an unstable polymorph, which subsequently may transform into another – more stable – polymorph. The study of polymorphic phase transformations aims at determining the thermodynamics (which phase is more stable under which conditions), and the kinetics (why metastable phases exist outside their stability field) of the transformation of one polymorph to another. While the thermodynamic parameters of most phases are comparatively straightforward to determine either experimentally or by computation, determining the kinetics is more problematic and requires detailed information on the reaction mechanisms. In general, a polymorphic transition is commonly regarded as a solid-phase transformation. However, in the presence of a solvent, the transition of one polymorph to another may take place by the dissolution of the initial phase and the subsequent precipitation of the new polymorph. Comparatively, this latter mechanism has received little attention in the literature.

The transformation of aragonite to calcite is an example of a polymorphic transformation in which the presence or absence of fluid is critical in interpreting the presence of aragonite in metamorphic rocks. In nature, aragonite is a stable phase in high pressure rocks but may transform to calcite during uplift. The preservation of aragonite in such rocks is evidence that no fluid was present (Carlson and Rosenfeld, 1981). In the presence of aqueous solutions the transformation takes place very rapidly, even on laboratory time scales. Perdikouri et al. (2011, 2013) have experimentally converted aragonite to calcite in timescales of weeks at temperatures between 160 °C and 200 °C, similar to the inferred temperatures when crossing the aragonite–calcite phase boundary during uplift.

Under conditions where calcite is more stable than aragonite it is less soluble and for the transformation to be pseudomorphic, porosity should be generated. However calcite has a larger molar volume than aragonite which would tend to close porosity and induce fracturing. In the experiments (Perdikouri et al., 2013) both porosity and fractures are generated during replacement, suggesting a more complex interplay between stress generation and the textures associated with dissolution–precipitation processes.

In a closed system, such as in the dry transformation of aragonite to calcite, the increased molar volume would result in fracturing. Such phenomena have been described in many other examples, the best known of which is the transformation of coesite to quartz in inclusions trapped at high pressure within garnet (Chopin, 1984, 2003). The enclosing garnet is extensively radially fractured around the partially transformed coesite inclusion. The preservation of the coesite is attributed to the strength of the garnet which can sustain a high internal pressure during uplift and decompression of the rock. However, another factor in the preservation of metastable phases is the absence of a fluid phase, which if present would initiate a much more rapid transformation by dissolution–precipitation (Mosenfelder et al., 2005).

Another example of polymorphic transition by a dissolution–precipitation reaction is the formation of retergerite ( $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) after nickelhexahydrate ( $\beta\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ ), phases that occur in the

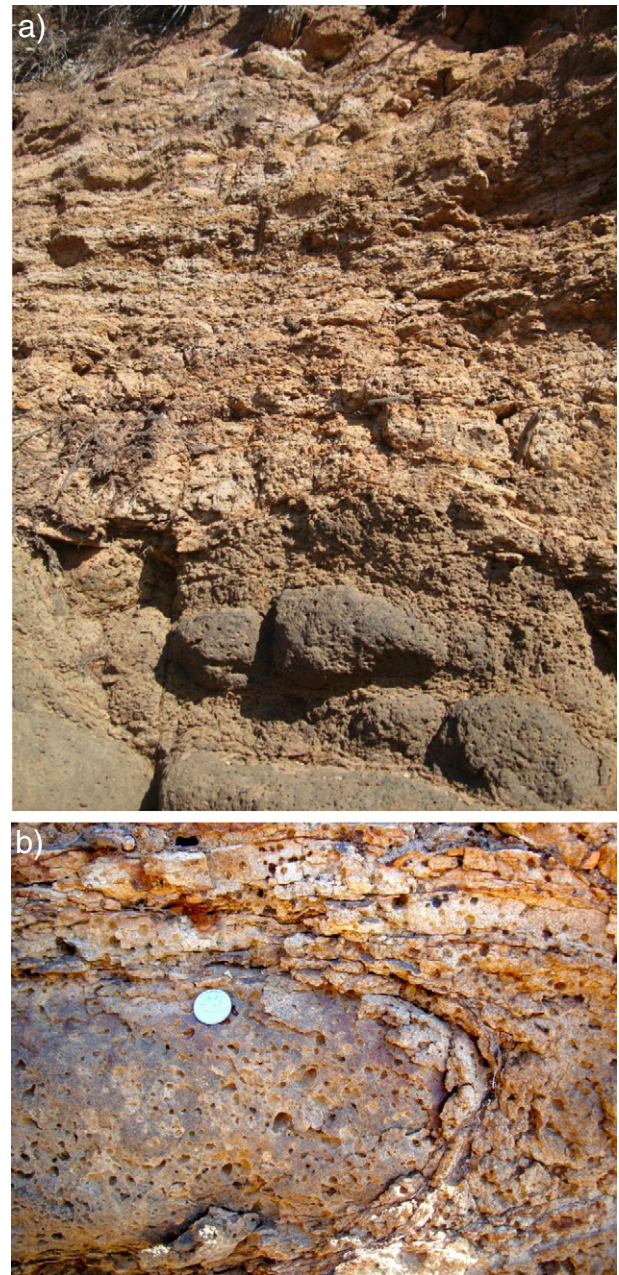
oxidation zone of Ni deposits and are formed in  $\text{H}_2\text{SO}_4$ -bearing aqueous solutions (Kul'kov and Klikin, 2007). Single crystal pseudomorphs of retergite were obtained when nickelhexahydrite dissolves and reprecipitates from the condensation water adsorbed on the surface of the initial phase. Thus, very limited amount of solution is needed for mineral replacement to proceed by a dissolution–precipitation reaction. Milke et al. (2013) have studied experimentally how much water is necessary to change the mechanism from solid state to dissolution–precipitation. In the reaction of olivine + quartz = orthopyroxene only a very few ppm of excess water on grain boundaries is needed for the reaction to proceed in solution. Recently, Ruiz-Agudo et al. (2013b) have suggested also the replacement of portlandite ( $\text{Ca}(\text{OH})_2$ ) by calcite to proceed by the dissolution of portlandite in its surface adsorbed water (7 monolayers of adsorbed  $\text{H}_2\text{O}$ ). Similarly to other replacement reactions reviewed here, fractures that penetrate into the unreacted nickelhexahydrite, which may contribute to fluid migration during the replacement process, are observed to form and seal during the reaction.

In an open system the question of volume expansion or reduction during replacement also depends on the extent of element mobility in the system, as any reaction can be written to balance the solid phases on volume, with the balance of the chemical components either added or subtracted by the fluid phase. The problem of volume changes during replacement reactions has been debated since Lindgren (1912) with further examples in a review by Putnis and Austrheim (2012). An example of chemical weathering of basalt provides a further interesting example of textural preservation during hydration. Fig. 11 shows an outcrop of weathered vesicular basalt where solid basalt boulders remain as remnants of severe weathering resulting in a very soft clay-rich lateritic soil. Although such hydration reactions result in the formation of less dense phases and hence an expected increase in volume, Fig. 11 shows that the vesicles in the basalt are preserved in the friable soil throughout the several metre thick soil layer. This suggests volume preservation and the loss of material to the fluid phase, a factor that should be taken into account in reactive transport modelling.

### 9. Fluid-mediated replacement processes in the Earth's crust

During a metamorphic event, the overall chemistry (excluding volatile compounds) is preserved, and metamorphic assemblages and textures in rocks are normally interpreted in terms of the specific range of pressure, P and temperature, T conditions over which the observed mineral assemblage is stable. However, a critical question in metamorphism is the mechanism by which a mineral assemblage can be converted to another (Putnis and John, 2010). Petrological, mineralogical, microstructural and isotopic data have demonstrated that aqueous fluids are involved in mineral reequilibration during metamorphism and that reactions that are considered to be driven by changes in P,T conditions may only occur if a fluid, that is out of equilibrium with the parent assemblage, infiltrates the rock (Putnis and Austrheim, 2010). Observations made on natural rocks that show the preservation of the magmatic texture in the gabbro–eclogite transformation or the replacement of plagioclase by albite are consistent with a reaction mechanism that involves coupling of dissolution and precipitation at a reaction interface.

Eclogitization of oceanic gabbro provides an example of how fluids affect metamorphic reactions (Austrheim, 1987; Jamtveit et al., 1990). The observation in the field is that the eclogitization is associated with fractures, local shear zones and fluid infiltration with preservation of granulite in the same outcrop. The general consensus is that fluid is required for the reaction to take place and that granulite can be preserved within the stability field of eclogite in those areas where the fluid does not reach (John and Schenk, 2003). The process itself and the reaction textures are the only evidence for fluid infiltration, as the conversion of a gabbro to an eclogite only rarely leads to the formation of hydrous minerals. Garnet replaces plagioclase and omphacite replaces augite,

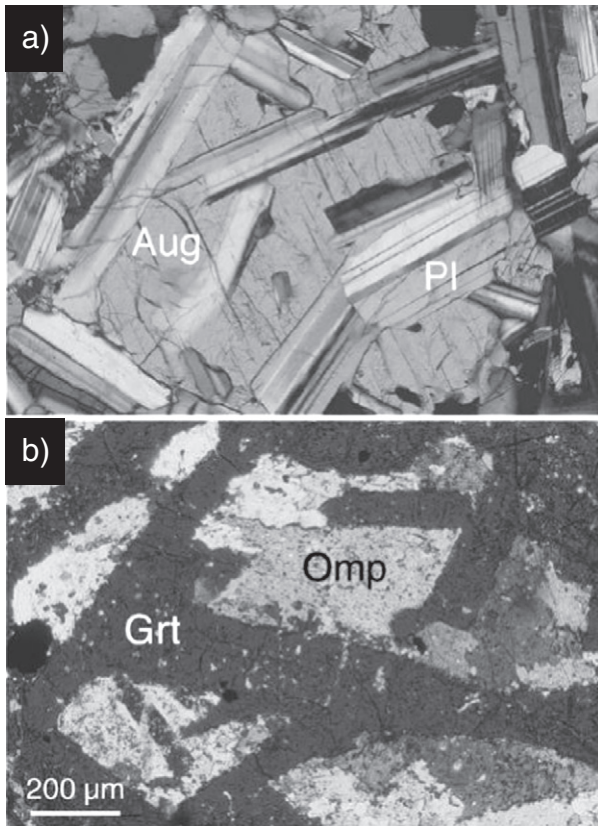


**Fig. 11.** (a) Photograph of an intensely weathered basalt outcrop (SE coast Australia) with relict solid boulders in a matrix of soft clay (image width approximately 2 m). (b) The basalt is vesicular and the vesicles are retained in the clay horizon, despite the complete replacement of the basalt minerals by less dense clay minerals.

and the igneous texture of the gabbro is preserved in the eclogite (Fig. 12).

The distinction between metamorphism (assumed to be a closed system) and metasomatism (an open system in which the bulk composition of the rock is changed) is not one of mechanism but depends on the spatial scale over which a closed system and an open system are defined (Putnis and Austrheim, 2010). This is somewhat arbitrary, for as Carmichael (1969) pointed out, every metamorphic reaction is metasomatic if one chooses a small enough volume, because metamorphic reactions involve the dissolution of some minerals and the growth of others and therefore involves element transport over some scale.

The factors that control the degree to which dissolution and reprecipitation are closely coupled are not well understood, especially in



**Fig. 12.** Microphotograph of the pseudomorphic replacement of a gabbro with typical ophitic texture (a) by eclogite (b). The omphacite (bright) pseudomorphically replaced augitic pyroxenes and garnet (dark) replaced plagioclase, preserving the magmatic texture.

John and Schenk (2003), reprinted with permission.

nature. In experimental studies on the replacement of sulphide minerals (pentlandite by violarite), the degree of coupling between dissolution and precipitation could be controlled by changing the pH of the fluid (Xia et al., 2009b). This defined a “length scale of pseudomorphism” in terms of the extent to which the microstructural features of the parent phase were preserved in the replacement process. The degree of epitaxy is also another important factor and in nature, deformation would also play a major role. The rate limiting step in a pseudomorphic replacement is most likely to be dissolution (i.e. surface reaction) although as the reacted rim gets thicker, the transport of components through the porous parent may ultimately control the rate.

Metasomatic rocks are most frequently recognised as such when the mineralogy does not conform to any known rock or melt precursor, as in the case of albitization. In the early stages of albitization, the pseudomorphic replacement of calcic plagioclase by albite is evident (Engvik et al., 2008), although, when the whole rock is replaced, such textural details may be lost. On the other hand, inert markers in the parent rock can sometimes provide a physical reference frame that indicates the texture of a precursor rock, even when it is totally replaced. This is the case when zircon coronas, initially defining the external form of ilmenite grains in a gabbro are preserved, even after the gabbro is totally replaced by hydrous minerals (Austrheim et al., 2008).

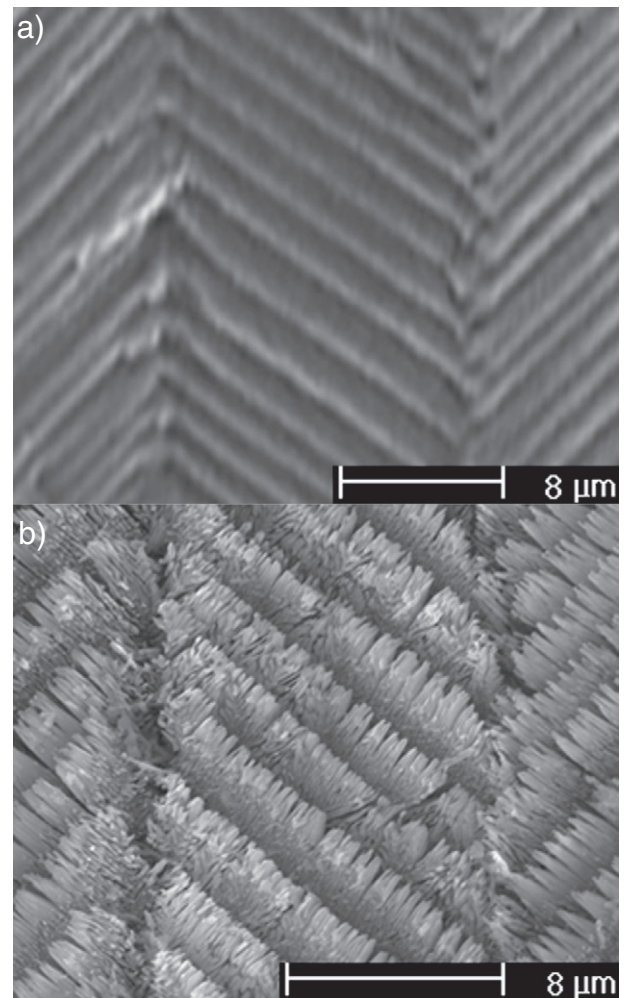
Mineral replacement processes are ubiquitous in the Earth’s crust and most rocks are metasomatised to some extent, although this is not always recognised without a detailed textural study. The extent to which fluid composition, as well as P,T conditions, controls the equilibria in rocks has yet to be fully appreciated.

## 10. Applications of coupled dissolution–precipitation reactions in “geo-inspired” methods of material synthesis and in engineering

### 10.1. Material synthesis

Although the start and end products in an interface-coupled dissolution–precipitation reaction may be the same as those obtained by a solid-state phase transformation (according to the thermodynamics), the reaction rate by the former mechanism may be orders of magnitude faster and very importantly, the mechanism preserves the external solid volume of the system (i.e. pseudomorphs are obtained). These features can be exploited for the synthesis of materials that are often difficult to obtain via traditional methods or materials with unique properties. For example, this method has been successfully used to synthesise compounds with magnetic, semiconducting and superconducting properties and low thermal stability such as the thiospinel mineral violarite ((Ni,Fe)<sub>3</sub>S<sub>4</sub>, Xia et al., 2008) or compounds with photovoltaic applications such as roquesite (CuInS<sub>2</sub>) (Brugger et al., 2010) as well as the synthesis of micro-porous gold (Brugger et al., 2010) and three-dimensional ordered arrays of nanozeolite of uniform size and crystallographic orientation (Xia et al., 2009a Fig. 13).

Interface-coupled dissolution–precipitation has also been exploited to create porous coordination polymer (PCP) crystals by pseudomorphic replacement of a shaped “sacrificial” metal oxide (Reboul et al.,



**Fig. 13.** Hydrothermal pseudomorphic replacement synthesis of three-dimensional ordered arrays of zeolite crystals. Secondary electron micrographs showing the surface morphologies of (a) parent leucite grain and (b) analcime product. Leucite grains contain twin lamellae that are replicated in the analcime. Images courtesy of Fang Xia.

2012). In this case a mesoporous alumina fabricated matrix is replaced by microporous by Al-PCP, by the coupled dissolution of alumina which provides the Al, and precipitation of the Al-PCP from the interfacial solution which contains the organic ligands. This principle is being applied to other metal oxide phases to create designed architectures by pseudomorphic replication. This is the same principle that allows the reproduction of fine details of carbonate biominerals (cuttlebone, coral, etc.) when it is replaced by hydroxyapatite (Kasiopas et al., 2010), a process which has been proposed for the synthesis of porous biocompatible material for bone implants (Heness and Ben-Nissan, 2004).

### 10.2. Preservation of building stone

The coupled dissolution–precipitation strategy also has applications in the protection of stone-based cultural heritage artefacts and building stone. The process of stone decay results in the deterioration of its physical properties, as well as its original petrographic and chemical characteristics. The composition and textural characteristics of carbonate stones (limestones, dolomites and marbles) make them particularly susceptible to deterioration. Field observations have revealed that natural patinas on stone have a protective effect for outdoor sculpture and buildings exposed to acidic environments (Hansen et al., 2003). Oxalates, oleates and phosphates appear naturally in the surface of ornamental and building stone exposed to the environment, forming layers, crusts or patinas that protect the stone substrate (e.g. Del Monte and Sabbioni, 1983; Böke and Gauri, 2003; Sassoni et al., 2011). These layers form most likely by a pseudomorphic, coupled dissolution–precipitation reaction, in which the dissolution of the carbonate substrate is followed by the precipitation of a Ca (or Mg)-bearing phase that nucleates and grows on the carbonate surface (Ruiz-Agudo et al., 2013a). Thus, this natural process could be used in the design of conservation treatments that mimic the natural process of patina formation (Doherty et al., 2007). Such treatments would be based on the in situ replacement of the original stone substrate by a new mineral assemblage that acts as a protective barrier against chemical weathering by acid or saline solutions due to the low solubility of the replacing phases compared to that of the original carbonate minerals.

### 10.3. CO<sub>2</sub> capture and storage by mineral carbonation

The reduction in industrial emissions of CO<sub>2</sub> is one of the major challenges of this century. The capture of CO<sub>2</sub> of anthropogenic origin and its injection into geological formations is considered as the safest and most permanent option for the permanent storage of this greenhouse gas, linked to global warming. Pilot schemes are being carried out worldwide to test such a feasibility, for example, the CarbFix Project in Iceland (Gislason et al., 2010). Mineral carbonation strategies for carbon dioxide capture and storage mimic natural carbonation processes, such as those occurring during in situ hydration and carbonation of mantle peridotite outcrops at low temperature after contact with near-surface groundwater (Kelemen and Matter, 2008; Matter and Kelemen, 2009). Both in situ and ex situ mineral carbonation processes rely on the dissolution of silicate rocks in contact with fluids rich in CO<sub>2</sub> and the subsequent precipitation of carbonate phases. During this coupled dissolution–precipitation process, the CO<sub>2</sub> consumed remains trapped as a stable mineral phase.

Recently, many experimental studies have been devoted to the mineralization of CO<sub>2</sub> (e.g. Giammar et al., 2005; Beárat et al., 2006; Daval et al., 2009a,b; Hövelmann et al., 2011, 2012). A critical aspect tackled by many of these studies is the development of porosity during the coupled dissolution–precipitation process (Daval et al., 2013). Passivation of the surface of the unreacted pristine mineral by the formation of a non-porous layer of product will result in the arrest of the carbon dioxide capture. However, if interconnected porosity is generated within the precipitating product, it will allow the advancement of the

reaction front, making the capture of CO<sub>2</sub> by mineral carbonation efficient. This ultimately depends on factors such as the relative solubilities of the dissolving and the precipitating phases, their molar volume or the growth mechanism of the replacing product (see above). It is therefore essential to know in detail the parameters controlling the process and the development of porosity to optimize the capture process.

## 11. Conclusion

In all of the examples given in this review, the underlying principle is that the dissolution of a mineral by an aqueous solution results in an interfacial fluid film that may become supersaturated with respect to a new mineral phase, and that this phase may nucleate within this interfacial region. The spatial coupling between dissolution and precipitation depends on the rate-determining step in the overall process and factors such as the crystallographic relationships between the parent and product phases, the porosity generation in the product phase and the evolution of the fluid composition at the reaction interface all play a major role. However, the common observation in both nature and experiment that one solid phase can be replaced by another via coupled dissolution–precipitation suggests that this is a universal mechanism of reequilibration during fluid–mineral interaction.

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