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Coupled dissolution and precipitation at mineral–fluid interfaces

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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_2-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.

Contents

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

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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}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 direct 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 ($Ca_{0.5}Mg_{0.5}CO_3$) 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 Ca^{2+} ion compared with 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 $<-441>$ 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.