

Rapid communication

The mechanism of reequilibration of solids in the presence of a fluid phase

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Abstract

The preservation of morphology (pseudomorphism) and crystal structure during the transformation of one solid phase to another is regularly used as a criterion for a solid-state mechanism, even when there is a fluid phase present. However, a coupled dissolution–reprecipitation mechanism also preserves the morphology and transfers crystallographic information from parent to product by epitaxial nucleation. The generation of porosity in the product phase is a necessary condition for such a mechanism as it allows fluid to maintain contact with a reaction interface which moves through the parent phase from the original surface. We propose that interface-coupled dissolution–reprecipitation is a general mechanism for reequilibration of solids in the presence of a fluid phase. © 2007 Elsevier Inc. All rights reserved.

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1. Introduction

Understanding the mechanisms of phase transformations from one solid phase to another is of considerable fundamental importance as well as industrial application in chemistry. Most phases can exist in different structural states (polymorphs) only one of which will be thermodynamically stable for a given range of physical and chemical conditions. Polymorphic phase transformations are driven by changes in these physicochemical conditions, but their kinetics are determined by the available mechanisms. The mechanisms of solid–solid phase transformations by a purely solid state route have long been investigated in metallic, ceramic and mineralogical systems [1–3]. Descriptions of phase transformations as displacive, martensitic and reconstructive are well understood, as are the factors which determine the microstructural development associated with each mechanism. A key feature of the microstructure of solid–state phase transformations is the crystallographic relationship between the parent and

product phases, defined by structural similarities, interfacial strain and elastic anisotropy.

However, if a solvent is present, a second mechanism is also available for solid–solid phase changes. In the chemical literature, a landmark paper by Cardew and Davey [4], defined the term *solvent-mediated phase transformations* in which the metastable phase is dissolved and a more stable phase then nucleates and grows *independently* from solution. The use of the word *independently* is important in the present context as it has had a lasting influence on the chemical literature on solvent mediated phase transformations.

Although the original Cardew and Davey paper mainly focussed on iso-chemical phase transformations, the general question of how one solid phase reequilibrates to form another in the presence of a solvent is applicable in the cases where chemical components from this solution are incorporated in the new solid phase. The mechanism of changes in chemical composition as well as structure need to be considered. Typical examples include cation and anion exchange in which the parent structure is only slightly modified, to cases of complete structural and chemical reorganization (e.g. the replacement of CaCO₃ by

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$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the presence of an aqueous solution containing SO_4 ions).

The fact that ion-exchange mechanisms take place without changes in the morphology of the parent crystal has led to the assumption that ions diffuse between the solution and the crystal framework by a solid-state exchange process, especially when the crystalline phase has negligible solubility in the solution. Crystallographic relationships between parent and product phase have generally been used as a criterion for a solid-state mechanism.

Recently, novel hydrothermal synthesis routes for alkali-metal molybdenum bronzes (K_xMoO_3) have been described in which the parent precursor phase, hydrogen molybdenum bronze (H_xMoO_3), is heated in aqueous alkali solutions [5–9]. The retention of crystal size and morphology during the reaction led to the proposal of a solid-state transformation mechanism, and in later papers, to the definition of structure-inheriting solid state reactions (SISSRs) under hydrothermal conditions [8,9].

Here we highlight some recent results on the mechanism of solid reequilibration in the presence of a fluid phase, and to propose a unified approach to the mechanism of “solvent-mediated phase transformations” and “structure-inheriting solid-state reactions”.

2. The mechanism of interface-coupled dissolution–precipitation reactions

Whenever a solid is in contact with an aqueous solution, dissolution of even a few monolayers of the parent surface may result in a fluid boundary layer which is supersaturated with respect to a more stable solid phase. Nucleation of the product phase on the parent surface will depend on nucleation kinetics, but will be enhanced if the degree of epitaxy between the two solids is high, i.e. if the structures of parent and product are similar. The epitaxial precipitation of the product on the surface of the parent enhances the dissolution rate of the parent, which in turn increases the growth rate of the product [10,11]. Such an autocatalytic reaction leads to a feedback mechanism between dissolution and precipitation such that their rates become equal. The epitaxial nucleation transfers the crystallographic information from parent to product.

Continuation of the transformation reaction depends on keeping open fluid transport pathways to the reaction interface between parent and product solids. In other words, porosity must be generated in the product phase. The generation of porosity depends on two factors: the relative molar volumes of the two solid phases, and more importantly, on the relative solubilities of the two phases in the fluid. If the original crystal dimensions are preserved by the initial dissolution and epitaxial nucleation, and the product has a smaller molar volume than the parent, then some porosity must result. Secondly, from basic thermodynamics, the solubility of the more stable phase will be lower than that of a metastable phase. Thus more solid will

be dissolved than reprecipitated, again resulting in a porosity if the original crystal dimensions are preserved. The combination of molar volume change and relative solubility may result in an overall volume deficit relative to the original crystal volume, and this manifests itself as a porosity, which is the volume within the product phase occupied by the fluid phase. As shown in an example below, a volume deficit reaction does not necessarily require a decrease in the molar volume associated with the phase transformation.

If the combined effect of solid molar volume change, and relative solubility does not result in a volume deficit, and hence no porosity in the product phase, the reaction cannot proceed by this mechanism beyond a few layers, and the parent phase is effectively armoured from further interaction with the fluid.

In volume deficit reactions a pseudomorphic replacement reaction (preserving original crystal morphology) can take place at a reaction interface which moves from the original crystal surface through the parent. The parent dissolves in the fluid at the interface and immediately reprecipitates as the product. In polymorphic transformations there is no change in chemical composition, whereas in ion-exchange reactions the ions are exchanged at the coupled dissolution–precipitation reaction interface.

This overall scenario allows for a whole spectrum of pseudomorphic, interface-coupled dissolution–precipitation replacement reactions, in which the microstructural evolution will depend on the degree of crystallographic misfit between parent and product, analogous to solid-state reaction mechanisms. At one end of the spectrum, a parent single crystal may be replaced by a single crystal of the product phase. As the structural similarity between the solid phases decreases, the product may be polycrystalline, or even multi-phase if the original interaction between fluid and metastable solid results in a boundary layer of fluid which is supersaturated with respect to more than one phase.

This general mechanism of phase transformation by interface-coupled dissolution–precipitation has been verified for a wide range of materials [12]. The examples which follow illustrate the various key aspects of the mechanism.

2.1. The replacement of a single crystal of KBr by a single porous crystal of KCl by reaction with a saturated KCl solution at room temperature [13,14]

When a single crystal of KBr is immersed in a saturated KCl solution at room temperature, an immediate replacement reaction begins from the original crystal surface with the dissolution of KBr and the reprecipitation of $\text{K}(\text{Br},\text{Cl})$ solid solution (Fig. 1a). With excess fluid available for reaction, the end result is a single crystal of almost pure KCl, with the same dimensions and crystallographic orientation as the original KBr. The product KCl is porous reflecting both the decrease in molar volume of the solid and the solubility of the product relative to the parent

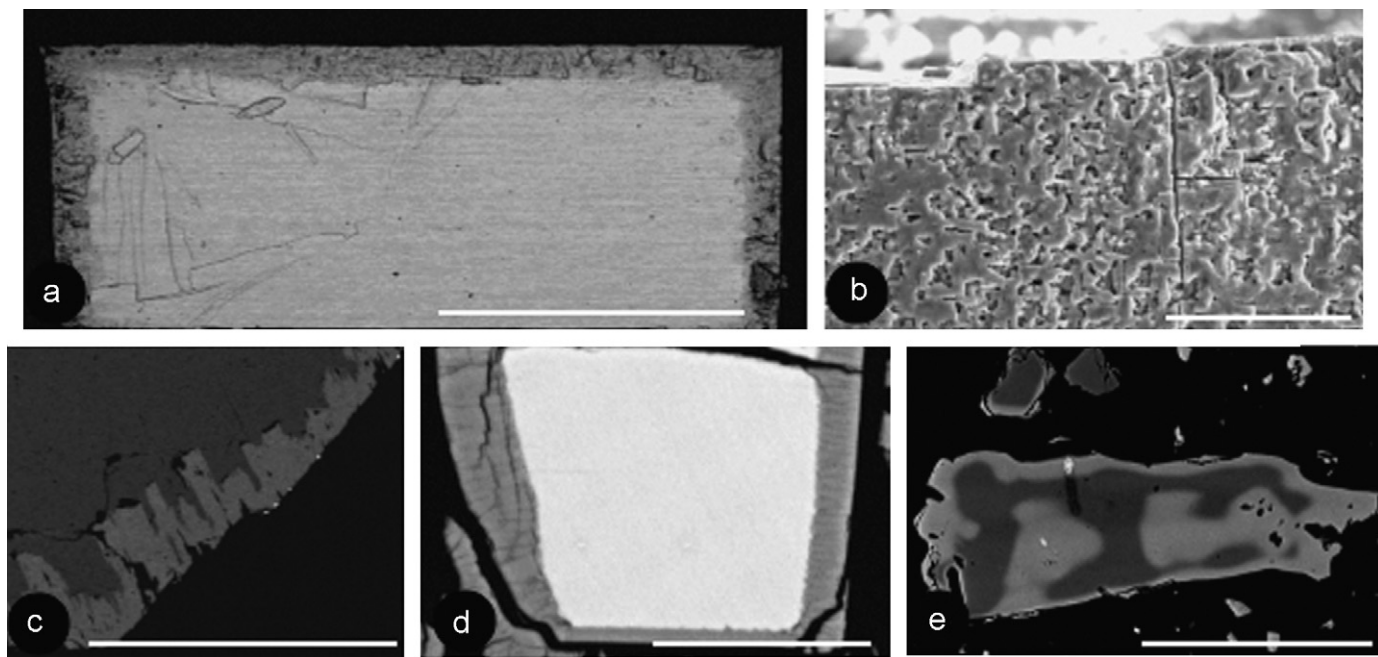


Fig. 1. (a) Back-scattered scanning electron (BSE) micrograph of a cross section through a KBr crystal (lighter core) partially replaced by K(Br,Cl) after 1 min reaction time. Scale bar: 1 mm. (b) Scanning electron micrograph of the external surface of the reacted crystal in (a) showing porosity. Scale bar: 100 μm . (c) BSE image of cross section of partially reacted $\text{NaAlSi}_3\text{O}_8$ crystal (upper left) with a lighter rim of KAlSi_3O_8 . Scale bar: 1 mm. (d) BSE image of partially reacted KAlSi_2O_6 (lighter core) with a darker rim of $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$. Scale bar: 50 μm . (e) BSE image of pyrochlore (dark core) with a lighter rim of pyrochlore depleted in Ca and Na. Scale bar: 100 μm .

(Fig. 1b). The rate of migration of the reaction interface through the parent crystal is consistent with a diffusion-controlled mechanism with a value of $D \sim 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, typical of self-diffusion coefficients in an aqueous solution (and ~ 10 orders of magnitude larger than solid-state diffusion coefficients in alkali halides [13]. When the KCl fluid is enriched in ^{40}K as a tracer, mass spectrometry confirms that the ^{40}K is incorporated in the product KCl, confirming a dissolution–reprecipitation mechanism where all constituents are exchanged at the reaction interface. Real time phase-shift interferometry [14] shows that the dissolution and reprecipitation is confined to a fluid boundary layer at the reaction interface.

2.2. The ion-exchange of $\text{NaAlSi}_3\text{O}_8$ by KAlSi_3O_8 in a KCl solution under hydrothermal conditions [15]

When sodium feldspar (albite) is equilibrated in the presence of a 2 M KCl solution in a hydrothermal apparatus at 600 $^\circ\text{C}$ and 200 MPa the reaction is pseudomorphic (Fig. 1c), resulting in the formation of KAlSi_3O_8 with a sharp reaction interface migrating through the crystal. The crystallographic orientation of the parent feldspar is preserved across the reaction interface. Using ^{18}O as a tracer in the aqueous solution (95% enrichment of ^{18}O) and subsequent detection of the ^{18}O by the shift of the Raman spectral peaks and by direct imaging using time-of-flight secondary ion mass spectrometry (TOF-SIMS) confirms that the oxygen in the silicate framework is also replaced by oxygen from the solution [15,16]. The rate of

the reaction also is not consistent with solid-state diffusion, and all the results indicate that this ‘ion-exchange’ process is achieved by an interface-coupled dissolution–reprecipitation process.

2.3. The replacement of leucite KAlSi_2O_6 by analcime $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ [17]

The replacement of KAlSi_2O_6 by $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ in 3.5% NaCl solution at 150 $^\circ\text{C}$ also proceeds by a dissolution–reprecipitation mechanism (Fig. 1d), although these are zeolitic minerals in which the channels within the silicate framework are sufficiently large such that a simple ion exchange mechanism might be expected. The reaction is pseudomorphic and porosity is generated in the analcime despite the fact that its molar volume is 10% higher than that of leucite. The sharp reaction interface, as well as the fact that ^{18}O in the aqueous solution is incorporated in the analcime silicate framework further confirms that a dissolution–reprecipitation, rather than a solid-state diffusion mechanism is involved.

2.4. The ‘leaching’ of Ca and Na from natural pyrochlore $(\text{Ca}_{1.23}\text{Na}_{0.75})(\text{Ta}_{1.78})\text{O}_{6.28}\text{F}_{0.57}$ [18–20]

The apparently selective removal of some components from a solid by reaction with a fluid is often referred to as ‘leaching’, a term which also carries with it the implication of a solid-state diffusion mechanism. As an example that ‘leaching’ also involves a dissolution–reprecipitation

mechanism, a natural pyrochlore sample was treated in a solution containing 1 M HCl and 1 M CaCl₂ at 175 °C. The selective removal of Ca and Na from the pyrochlore is paralleled by the incorporation of ¹⁸O in the structure at the reaction interface (Fig. 1e) which has also been shown to be sharp at the sub-micron scale. The crystallographic structure is also preserved across the interface [19].

3. Discussion

The four examples above are a selection to illustrate that it is possible to preserve crystallographic relations during a dissolution–reprecipitation reaction, and that the key factors controlling such a mechanism are (i) coupled dissolution and nucleation within a fluid boundary layer at the parent solid surface, and (ii) generation of porosity which enables fluid and mass transport to and from the reaction interface. Isotope tracers can be used to determine the extent to which ions from the solution are incorporated into the product solid.

Other published examples share many of the features of an interface-coupled dissolution–reprecipitation mechanism: the replacement of chlorapatite by hydroxyapatite under hydrothermal conditions [21], reequilibration of yttrium-bearing fluorapatite in acidic solutions [22], the pseudomorphic replacement of SrSO₄ by SrF₂ [23], the conversion of SrSO₄ to SrCO₃ [24], as well as anion exchange in chain coordination polymers [25,26]. Some of these reactions, e.g. chlorapatite to hydroxyapatite, only involve a small structural change, while in others e.g. SrSO₄ to SrCO₃, the crystal structure is completely different. Nevertheless, the reactions are pseudomorphic.

The examples given span from transformations in highly soluble salts to sparingly soluble silicates and polymers. Because the reactions take place at the parent–product interface, the *relative* solubility of the two solids is more important than their absolute solubility as only a small amount of material needs to be in solution at the interface at any one time. The overall kinetics of interface-coupled dissolution–reprecipitation reactions may be controlled by the rate of mass transfer through the fluid phase when solubilities of parent and product are high, or by the rates of dissolution and precipitation in cases of low solubility solids.

Interface-coupled dissolution–reprecipitation is a special case of a solvent-mediated phase transformation in which nucleation of the product takes place at the surface of the parent which defines the initial step of a pseudomorphic replacement. The degree of epitaxy defines the crystallographic relations between the parent and product and allows for a spectrum of microstructures, in which the distribution of the fluid phase within the porous product plays a fundamental role.

This mechanism has wide-ranging implications of relevance to any solid–fluid interaction which involves the pseudomorphic replacement of one solid phase by another.

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