Complex mineral zoning patterns caused by ultra-local equilibrium at reaction interfaces

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**ABSTRACT**

Chemically zoned minerals are useful records of temporal variations in ambient conditions and bulk chemical composition of the fluid from which the minerals precipitate. In fluid-buffered systems, zoning of mineral compositions is expected to reflect directly the evolution of fluid composition. Here we show that during rapid fluid-rock reactions, ultra-local equilibrium can form complex mineral zoning patterns, even when the overall system is highly fluid buffered. We reacted cleaved calcite single crystals with aqueous arsenate-phosphate solutions with molar ratios of As(As + P) between 0.01 and 0.15 at 250 °C and water-saturated pressure. We find that complex zoning patterns are solubility controlled, and can be explained by an established method (Kasioptas et al., 2011) which assumes that the solution contains varying proportions of arsenate and phosphate. See the GSA Data Repository\textsuperscript{1} for experimental details.

**INTRODUCTION**

Chemically zoned mineral grains may record a time series of conditions experienced by the rock (e.g., Spear and Selverstone, 1983). The compositions recorded are a function of the prevailing pressure, temperature, effective bulk chemical composition (Gaidies et al., 2008), crystal surface structure (Rakovan and Reeder, 1994, 1996), and kinetics effects (Putnis, 2010), as well as any post-growth modification processes, e.g., volume diffusion and deformation (Florencio and Spear, 1991; Steffen and Selverstone, 2006). There are a number of mechanisms by which relatively simple concentric zoning patterns may form (Pearce and Wheeler, 2010), but many complex zoning patterns are commonly more difficult to explain (Menard and Spear, 1996). In fluid-rich systems, such as those associated with hydrothermal mineralization, complex mineral zoning patterns are commonly interpreted to reflect transient changes in fluid composition or varying degrees of fluid buffering (e.g., Yardley et al., 1991). In this paper we show how interface-coupled dissolution-precipitation reactions in a heavily fluid-buffered system lead to the formation of complex zoning patterns on a microscopic time scale. Continued reaction subsequently modifies these microstructures as the mineral-fluid system approaches equilibrium.

Interface-coupled dissolution-precipitation reactions have been shown to operate in a wide range of mineral systems (Putnis, 2009; Qian et al., 2010, 2011; Ruiz-Agudo et al., 2012; Zhao et al., 2013). In many cases they occur at laboratory time scales under hydrothermal conditions, meaning that they are more efficient than diffusion-controlled reactions at geological conditions. The microstructures developed during dissolution-precipitation reactions are affected not only by fluid composition (Jonas et al., 2013) and mineral solubility (Pollok et al., 2011), but also by factors such as pH (Xia et al., 2009). Existing experimental studies of mineral replacement are mainly focused on replacement reactions involving replacement of one phase by another or alteration of one end member of a solid solution to an intermediate composition. In this study, we reacted calcite with fluid of varying compositions to investigate the extent to which variations in fluid chemistry are reflected by the mineral chemistry. Apatite has the general formula: $A_4(\text{X})_3\text{Y}$, where $A = \text{Ca}, \text{Ba}, \text{Na}, \text{Sr}, \text{Pb}$, rare earth elements (REE); $\text{X} = \text{PO}_4, \text{AsO}_4, \text{CO}_3, \text{SO}_4, \text{VO}_2$; and $\text{Y} = \text{OH}, \text{Cl}, \text{F}$ (Putnis and Fleet, 2002). The wide range of cationic and anionic substitutions in apatite can allow fingerprinting of the parent fluid composition over a wide range of geological conditions (e.g., Binder and Troll, 1989; Zhu and Sverjensky, 1991). While many studies have used magmatic apatite as an indicator of petrogenetic processes (Streek and Dilles, 1998; Piccoli and Candela, 2002), apatite is increasingly being used to study the chemistry of hydrothermal fluids (Bath et al., 2013). Cleverley (2006) found strong elemental zonation in hydrothermal apatite formed in Mount Isa copper deposits in Australia, with S-rich cores (0.5% SO\textsubscript{3}) and As-rich rims (5% As\textsubscript{2}O\textsubscript{5}). However, the applicability of the studies discussed above is reliant on the apatite chemistry reflecting the initial fluid chemistry and remaining unchanged since formation.

**EXPERIMENTAL METHODS AND RESULTS**

**Hydrothermal Experiments**

The experiments to react calcite with aqueous solutions of arsenate and phosphate to form apatite follow an established method (Kasioptas et al., 2011) except that the solution contains varying proportions of arsenate and phosphate. See the GSA Data Repository\textsuperscript{1} for experimental details.

**Results**

Short reaction times (1–5 h) lead to partial conversion of 1–2 mm-sized cleaved calcite crystals, resulting in crystals with calcite cores surrounded by a layer of As-bearing apatite (Figs. 1A and 1B). Full pseudomorphic conversion of 1–2 mm calcite grains to As-bearing hydroxylapatite generally occurs within 48 h (Figs. 1C and 1D). Calcite reacted with pure phosphate solution shows minimal reaction even after 5 d at 250 °C.

**Partially Reacted Samples**

Partially reacted samples have a pure calcite core surrounded by a newly formed As-bearing apatite rim (Figs. 1A and 1B). The apatite crystals grew with their c-axes oriented perpendicular to the reaction front as in the As-absent case (Kasioptas et al., 2011). Partially reacted grains preserve chemical disequilibrium features developed as the reaction progresses.

\*GSA Data Repository item 2014149, experimental and analytical methods, is available online at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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After 5 h, the apatite shell is ~200 μm thick (Fig. 1B). The As concentration generally increases from the original grain boundary to the reaction front, with As-rich and As-poor regions forming tube-like structures in a variety of orientations with respect to the reaction interface (Figs. 1A and 1B). These structures are marked closer to the reaction front and are less distinct closer to the original calcite grain boundary. Elemental microanalyses from sample 2-7 (Fig. 2) show that these tube-like As-rich regions close to the reaction front can have greater than 8× As enrichment with respect to the bulk reactant fluid composition. Although these As-rich rims are near the reaction front, they do not have a direct interface with the calcite. The apatite at the interface with calcite is consistently As poor (Fig. 2).

Summing the composition over 10 μm intervals perpendicular to the reaction front shows the first-order increase in As between the original boundary and the reaction front (Fig. 3). A secondary reaction interface not only reduces the average As content of the apatite but also homogenizes the composition (shown by the reduced compositional range; Fig. 3) and destroys the tubular structure. The homogenized composition approaches the calculated equilibrium value (black dashed line in Fig. 3) calculated from fully reacted samples (see below).

Experiments with longer reaction times (20 h; Fig. 1C) resulted in conversion of all the calcite to As-bearing apatite, but the distribution of As is heterogeneous with a number of regions in the grain displaying As concentrations that are higher than the solution concentration.

**Fully Reacted Samples**

A homogeneous distribution of As formed throughout the apatite grain after 48 h reaction.
time (Fig. 1D). These fully reacted samples were analyzed for As, P, Ca, and Na content (see Table DR1 in the Data Repository). There is a linear correlation between the As content of the apatite product and initial As concentration in the solution with mole ratio of $A_{\text{soln}}/A_{\text{fluid}} = 0.207$ (Fig. 4).

**Coupled Two-Stage Reaction Mechanism**

We propose that the observed element distribution (Figs. 1–3) and bulk chemical analyses (Fig. 4) can be best explained by a two-stage reaction process. First, a reaction between calcite and a mixed AsO$_4$-PO$_4$ solution forms As-bearing apatite with heterogeneous As compositions. Secondly, an equilibration reaction forms a homogenous As-bearing apatite with As composition approaching equilibrium with the bulk fluid.

The heterogeneity of the As concentration in the partially reacted samples (Figs. 1A and 1B) develops during the first stage which involves reaction of the bulk solution with the pure calcite and the development of intragranular porosity. The composition of precipitated apatite is controlled by the composition of the fluid in the thin reaction interface. Deeper inside the crystal, near the advancing reaction front, the micro-porous structure restricts the rate of diffusion and equilibration between the reaction-front fluid and the bulk solution. Arsenic-poor apatite forms first; as the apatite grows, phosphate is preferentially removed from the solution resulting in an elevated As concentration in the fluid near the reaction front. This ultra-local increase in the concentration of As results in the next apatite to form having a much higher As concentration than would be expected from the bulk solution (Fig. 2). The reaction front becomes faceted as the calcite is dissolved. The preexisting lobate reaction front combined with temporal variations in As content of the fluid is preserved as the tube-like structures (Figs. 1 and 2). Near the original calcite-fluid boundary, there is rapid (with respect to the reaction rate) equilibration and/or mixing of the intergranular fluid with the bulk solution, so the AsO$_4$ concentration in the reaction product quickly becomes diluted and returns to a composition close to that of the original reaction fluid.

The primary reaction between calcite and As-P-bearing solution can be written as:

$$10\text{CaCO}_3 + x\text{PO}_4^{2-} + (6-x)\text{AsO}_4^{3-} + 2OH^- = Ca_{x}(PO_4)_{10-x}(AsO_4)_{x}(OH)_2 + 10CO_3^{2-},$$

where $x$ refers to moles PO$_4^{3-}$ in the reaction product.

As the reaction progresses, a second-stage mechanism becomes important. The AsO$_4^{3-}$ co-precipitated in the highly porous apatite is released by dissolution and equilibrated with the bulk solution. Precipitation of new apatite leads to the destruction of the tube-like structures, a decrease of porosity (mole volume of hydroxylapatite is larger than calcium arsenate), and development of a “homogenization front” (Fig. 3) that sweeps behind the original reaction front. Further time allows the completion of this reaction, so that the arsenate/phosphate mole ratio of the final apatite is proportional to that of the initial solution. This reaction is also controlled by relative solubility. Arsenic-rich hydroxylapatite is more soluble than As-poor hydroxyapatite (e.g., Zhang et al., 2011) so treatment of As-bearing apatite with more phosphate-rich solutions leads to complete homogenization of the As (Fig. 1D). The secondary reaction can be simply described as solid solution substitution between phosphate and arsenate:

$$Ca_{10}(PO_4)_{10-x}(AsO_4)_{x}(OH)_2 + yPO_4^{3-} = Ca_{10}(PO_4)_{10} + (AsO_4)_{x} + (OH)_2 + yAsO_4^{3-},$$

where $y$ denotes the moles AsO$_4^{3-}$ being replaced by PO$_4^{3-}$. These two types of reaction (Equations 2 and 3) are not isolated but take place in a coupled fashion. Fundamentally, the two reactions are controlled by the relative solubilities of solid solution and end-member mineral phases.

**Geological Implications**

Earlier studies have invoked the calcite-apatite reaction to explain the formation of marine phosphorite deposits (Ames, 1959) and phosphatic rocks (Birch, 1979). It is likely that hydrothermal fluid flow is also an effective way to formapatite solid solutions by reaction with calcite, and that given sufficient time for achieving equilibrium, the compositions formed are a function of the fluid composition.

More generally, this study shows that during rapid fluid-rock reactions, ultra-local kinetic effects can lead to the development of fluids with locally extreme nonequilibrium compositions and the formation of complex zoning in minerals, even when the overall system is highly fluid buffered. Despite fluid-rock ratios on the order of 2500 by mass, the development of an ultra-lo-locally differentiated solution at the thin reaction interface in our experiments leads to an As enrichment greater than 8 times that of the bulk fluid (Fig. 2). Interpretation of the complex zoning patterns that resulted during the partial reactions in terms of changes in bulk fluid would not only be extremely complex but also erroneous. The heterogeneity caused by fluid differentiation at a reaction interface could also be superimposed upon other sources of compositional heterogeneity such as sectoral or intrasectoral zoning (e.g., Rakovan and Reeder, 1994, 1996; Stowell et al., 2011) or overgrowth of preexisting heterogeneities in minor and trace element abundances (Yang and Rivers, 2001).

The secondary reaction front that leads to homogenous As distribution highlights that equilibration of different chemical components may occur at different rates. This study shows that equilibration of solid solution minerals with a
fluid is a multi-stage process. The relative rates of diffusion to the reaction interface and chemical reactions that take place there are important factors in determining the composition of reaction products.

While the chemically heterogeneous microstructures seen in these experiments are re-equilibrated within 48 h, short-lived hydrothermal events such as those developed during seismic events may have the potential to preserve these textures. Knowledge of the behavior of the mineral solid solution under consideration, especially with respect to solubility equilibria and kinetics, will enable successful interpretation of the compositions and flow rates of hydrothermal fluids in the crust.

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