

Tracking Ore Fluid Chemistry from Chemical Zonation of Minerals: Elemental Distribution and Oxidation State of Arsenic in Synthesized and Natural Hydrothermal Apatite

Weihua Liu,^{1*} Mark Pearce,¹ Chris Ryan,¹ Barbara Etschmann,² Joël Brugger,² and David Paterson³

¹CSIRO Mineral Resources Flagship, Clayton, Vic 3168, Australia

²Monash University, Clayton, Vic 3168, Australia

³Australian Synchrotron, Clayton, Vic 3168, Australia

E-mail, weihua.liu@csiro.au

Chemical zoning in mineral grains developed by fluid-rock interactions allows for the assessment of fluid composition and interaction conditions in ancient geological systems. The microstructures and chemical speciation developed during these reactions have the potential to yield a great deal of information if they are interpreted correctly.

Apatite has the general formula $A_5(X)_3Y$, where $A = Ca, Ba, Na, Sr, Pb, REE$, $X = PO_4, AsO_4, CO_3, SO_3, VO_3$, and $Y = OH, Cl, F$. The wide range of cationic and anionic substitutions into apatite should allow fingerprinting of the parent fluid composition over a wide range of geological conditions. In particular, Cleverley found strong elemental zonation in hydrothermal apatite formed in Mt Isa Cu deposits in Australia, with S-rich cores (0.5% SO_3) and As-rich rims (5% As_2O_5). Tracing the origin of the observed zonation and interpreting it in terms of fluid-rock interaction is fundamental to understanding how metals are transported and deposited.

In order to explore the chemical processes of mineral replacement reactions under hydrothermal conditions and, in particular, to test the hypothesis that the observed chemical zonation in apatite can track the chemical evolution of hydrothermal ore fluids from which apatite was precipitated, we have conducted a series of hydrothermal mineral replacement experiments to establish a relationship between apatite composition and fluid chemistry.

In the first series of experiments we have reacted calcite crystals with As(V)-bearing phosphate solutions at 250°C. These results showed that complex zoning patterns and solid solution between apatite and arsenate apatite formed within hours. These zoning patterns were destroyed within days during secondary reactions, reflecting rapid fluid-rock reactions. Ultra-local equilibrium can form complex mineral zoning patterns, even when the overall system is highly fluid buffered. We then reacted calcite with mixed As(III)/As(IV)-bearing solutions with varying oxidation ratios. X-ray Near-Edge Spectroscopy (XANES) measurements showed that the bulk oxidation state of As in the As-bearing apatite correlates to the As oxidation state in the parent fluid. Micro-mapping of the As oxidation state using the XANES imaging method (XFM beamline, Australian Synchrotron) reveals complex distribution of As(V)/As(III) ratios, with As(V) tending to be in the center of the apatite grains, and As(III) on the edge and along fractures. XANES measurements on natural samples (Ernest Henry IOCG deposits, Australia; As-anomalous amphibolite-facies gneiss from Binntal, Switzerland) revealed only As(V).

These results show that apatite is sensitive to the local fluid composition during crystallization, and that some of the complexity in As zoning in apatite may be due to fluctuations in As(V)/As(III) ratios in the fluid. However, the oxidation ratios recorded are controlled more strongly by crystal structure than by equilibrium between apatite and the fluid, and the mineral may not be able to preserve the original oxidation ratios in the fluid.