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

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Chemical compositions of zoned minerals record a time-series of conditions experienced by the rock. They are a function of the prevailing pressure, temperature and effective bulk chemical composition as well as any post-growth modification processes e.g. volume diffusion and deformation. In fluid-buffered systems, zoned mineral compositions should be 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 calcite single crystals with arsenate-phosphate solutions with molar ratios of As/(As+P) between 0.011 – 0.145 at 250°C and water-saturated pressure with fluid-rock mass ratios in excess of 2500%. Porous, fine-grained apatite polycrystals with varying arsenic contents replaced the calcite by an interface-coupled dissolution reprecipitation mechanism. During the first few hours of the reaction, complex zoning patterns of arsenic content within the apatite formed. The scale of the arsenic variations corresponds with the scale of corrugations of the reaction interface. The variations in arsenic content of the apatite result from spatially and temporally varying increases in the arsenic content of the reaction interface fluid. Since phosphate diffusion cannot keep pace with the reaction rate arsenic becomes enriched in the reaction interface fluid as phosphate is preferentially used in the reaction. The most arsenic rich parts of the apatite crystal show an 8-fold enrichment in arsenic with respect to the bulk fluid composition but only at an ultra-local scale. Once the calcite is completely consumed, the porous crystal equilibrates with the bulk fluid over a few days because the grain size is much finer and diffusion can keep pace with the equilibration reaction. This study highlights the complexity that can arise from ultra-local fluid composition variations due to rapid fluid-rock interaction in a short-lived fluid flow event, such as that can occur during a seismic cycle. Subsequent interpretation of the complex zoning patterns to reflect the evolution of bulk fluid would not only be extremely complex but also erroneous.