

Sulfur concentration and isotope zoning in apatite crystals: implications and applications

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Apatite is a common igneous accessory mineral with a high saturation temperature which can crystallize over a significant portion of magmatic compositional space. Compatibility of sulfate ions in apatite crystal structure allows for up to 1500-2000 ppm sulfur. Extreme immobility of sulfate ions in apatite allows for the preservation of S zoning at the sub-micron scale. We demonstrate that mid-crustal plutonic rocks with typical bulk S contents contain apatites with S zoning mappable by electron microprobe and that some grains contain high S cores that contain an early, important record of conditions of crystallization at the inception of apatite saturation. These apatites present the opportunity to interrogate a stage of magmatic processes that form the fundamental characteristics of arc magmas and that are under-constrained by accessory mineral studies. Analysis of S isotopic composition revealed significant core-rim variation which directly records the isotopic composition of the sulfate component of magmas. This variation is driven by temperature and a range of factors all related to fO_2 of the magma, a petrologically critical but poorly constrained parameter. This method is independent of partition coefficients or absolute magmatic S concentration.

CL and electron probe surveys identified high S concentration cores in ~10% of grains from a granitoids from the Cretaceous Cadiz Valley Batholith in the Mojave. Ratios of ³²S and ³⁴S were determined by SIMS in core-rim transects. Absolute isotopic ratios were determined for a sampling of fragments of a single Durango apatite crystal (UCLA-DA1) by gas source mass spectrometry at 0.324‰ $\delta^{34}S_{CDT}$. Fragments were then used as a standard to correct for in-run SIMS instrumental mass fractionation. High S concentrations and ionization efficiency of S allow for precisions of 0.3 – 0.5‰. High-S concentration apatite cores are on average ~1.5‰ higher in $\delta^{34}S$ than rims and the lowest rim values and highest core values can vary by as much as 4‰. High S concentration and high $\delta^{34}S$ in cores suggest oxidizing environments in magmas in the earliest stages of apatite crystallization, followed by reduction and/or temperature drop along with crystallization, consistent with ascent-driven degassing. Sulfide fractionation is not recorded by, therefore must have preceded, apatite crystallization.