

Synchronous sulfur and chlorine isotope ratio measurement in apatite via SIMS

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The mineral apatite is nearly ubiquitous in terrestrial igneous systems and is common in Lunar and other extraterrestrial materials. Apatite is refractory and also can be dated via the U-Pb or Pb-Pb system. Finally, apatite is a reservoir for many important volatile phases, including OH, Cl, F, S and in some cases C. Terrestrial apatites record significant S isotopic fractionations (Economos et al., 2017; Hammerli et al., 2021), while Lunar apatites record Cl isotopic fractionations of up to 80‰ (e.g. Boyce et al., 2015). In this contribution, we will first demonstrate that cathodoluminescence imaging via scanning electron microscopy allows an effective characterization of apatite grains and then present a methodology for synchronous measurement of S and Cl isotope ratios by secondary ionization mass spectrometry (SIMS). The analytical protocol requires multi-collection capabilities with a mix of faraday cup (FC) and electron multiplier (EM) detectors. The detector configuration includes measurement of masses 32 (FC), 34 (EM), 35 (FC) and 37 (FC). Analytical errors are dependent on concentrations, but can be as low as 0.4‰ for $\delta^{34}\text{S}$ and 0.2‰ for $\delta^{37}\text{Cl}$ (1σ). This synchronous measurement of S and Cl allows for the quantification of S concentration in the analytical volume, which has thus far proved challenging due to the complex, fine-scale zoning of S concentration in apatite crystals. This calculation is accomplished through the construction of a calibration curve using several apatite standards of known S and Cl concentrations. Several examples of the utilization of this method will be highlighted, including measurements in detrital apatites, which show systematic S isotopic variation over time, but no Cl isotopic variation outside of analytical error. Potential applications include exploring degassing of Lunar and other extremely volume-limited extraterrestrial samples, interplay between magmatic and brine processes in the formation of hydrothermal ores, and characterizing redox variations that facilitate the accumulation of large eruptible volumes of sulfur in arc volcanoes.