

Sulfur-in-apatite as an indicator for the redox variability of porphyry systems and potential for metal mobility

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Sulfur is the fundamental elemental anomaly in arc-related porphyry-type ore deposits, which are important sources of Cu, Au, Ag, and Mo. A growing body of data suggests that S oxidation state (e.g., S²⁻, S⁴⁺, S⁶⁺) plays an essential role in controlling ore metal mobilization and enrichment. For instance, previous studies observed an effect of oxygen fugacity and, thus S oxidation state, on the melt solubilities and the fluid-melt partitioning of certain ore metals. The oxidation state of S is intrinsically linked to oxygen fugacity (fO_2), and it has been hypothesized that co-variation of S oxidation states and fO_2 may be responsible for the globally observed, several orders-of-magnitude variability in ore metal ratios (e.g., Cu/Au) among porphyry deposits, and even IOCG deposits. Apatite—commonly $Ca_{10}(PO_4)_6(F,Cl,OH)_2$ —is commonly an accessory phase in magmatic and hydrothermal systems, and incorporates redox sensitive elements such as S. Hence, S-in-apatite may serve as a powerful geochemical tool that will allow us to test the hypothesis that variation in oxygen and sulfur fugacity are a master control on ore metal variability (e.g., Cu/Au ratios) in porphyry deposits. In this study, we investigate biotite-hosted apatite grains in samples from the Carmen de Andacollo Cu-porphyry deposit (Chile), which is inferred to have crystallized at $fO_2 = FMQ + 0.4 (\pm 1.17)$. X-ray absorption near-edge structure (XANES) spectroscopy at the S *K*-edge was used to quantify the oxidation state of S in apatite, which can elucidate potential redox variability during the evolution of the porphyry system. The results indicate intra-crystalline zonation of S-in-apatite with respect to the integrated S⁶⁺/ΣS peak area ratios, where the S⁶⁺/ΣS ranges from 0.68 to 0.95. Using an experimentally derived calibration that relates the S⁶⁺/ΣS peak area ratio to fO_2 (FMQ), the fO_2 as recorded by S-in-apatite, ranges from ~FMQ +0.4 to +1.2, and is consistent with the fO_2 range proposed within the literature. Two testable hypotheses include: [a] magmatic apatites crystallized from a silicate melt(s) buffered at distinctly different redox conditions, which records redox evolution of the system (e.g., relatively reduced = ~FMQ +0.4; and relatively oxidized = ~FMQ +1.2); [b] primary apatite that was hydrothermally altered by S-bearing reducing/oxidized fluid(s) that are derived from lower levels within the plumbing system, resulting in redox overprinting, and therefore modifying the S⁶⁺/ΣS peak area ratios.