

Variable Redox States of Sulfur in Fertile Arc Magmas

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Porphyry copper systems formed in magmatic arcs represent the largest concentrations of copper and the most massive anomalies of sulfur worldwide. The ore-forming magmas are widely thought to be moderately oxidized with high concentrations of sulfur as sulfate and only minor sulfur as sulfide. However, early saturation of silicate melt with a metal-sulfide phase, followed by the resorption and remobilization of metals and sulfur during degassing-induced oxidation of the magmas, has been posited to be essential for the formation of porphyry copper systems. It remains unclear what the optimal sulfur redox state in the silicate melt is for the formation of porphyry copper systems. Here, we addressed this issue by quantitatively measuring the relative abundances of sulfide and sulfate in sulfur-bearing primary apatite grains hosted in zircon, amphibole, and biotite from arc-like, intermediate-composition rocks associated with porphyry and skarn copper-gold deposits in the Middle-Lower Yangtze River metallogenic belt of Eastern China. The $S_{6+}/\Sigma S$ ratios of the sulfur-bearing apatite grains span a nearly full range, from 0.12 to 0.97, which is independent of the crystallization temperature and pressure of the host minerals at mid- to upper-crustal levels. This is consistent with saturation of silicate melts with either sulfate or sulfide in the ore-fluid-source magma. The results demonstrate that porphyry copper systems can form from intermediate-felsic magmas over a broad range of $S_{6+}/\Sigma S$ ratios and oxygen fugacities (fO_2), possibly throughout Earth history, including the Proterozoic and Archean.