

Lower Oxygen Fugacity and Divergent Redox Trajectories in Porphyry Mo Versus Cu Systems: Evidence From Apatite Sulfur K-edge μ -XANES

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Porphyry Cu deposits are widely associated with moderately to highly oxidized arc magmas, yet the redox conditions governing porphyry Mo fertility remain poorly constrained. To address this, we determined the oxygen fugacity (fO_2) of causative magmas for three porphyry Mo deposits and coeval barren intrusions along the northern margin of the North China Craton by using in situ micro-X-ray absorption near-edge structure (μ -XANES) spectroscopy at the S K-edge to measure the relative abundances of S²⁻, S⁴⁺, and S⁶⁺ in apatite inclusions trapped within zircon and apatite in groundmass. Integrated S⁶⁺/ Σ S peak area ratios were used with the experimentally calibrated sulfur-in-apatite oxybarometer to calculate fO_2 at the time of crystallization for both populations of apatite. This methodology constrains fO_2 of causative magmas before degassing, avoiding overprinting effects of late-stage hydrothermal alteration and re-equilibration with residual melts, and after degassing. The three porphyry Mo deposits Caosiyao (~1.76 Mt Mo), Dasuji (~0.40 Mt Mo), and Quanzigou (~0.05 Mt Mo) formed in an extensional setting, and the substantial difference in their Mo endowment provides an ideal framework for comparative redox analysis. The apatite oxybarometer data reveal that fO_2 shows no correlation with Mo endowment or tonnage across the three deposits and that the fO_2 of the porphyry-Mo causative magmas systems is systematically lower than coeval barren intrusions and causative magmas for Cu-dominant porphyry deposits worldwide. Notably, the results show that the fO_2 of the porphyry-Mo causative magmas decreased during degassing, whereas the fO_2 of the barren intrusions increased during degassing as is commonly reported for porphyry-Cu systems. These findings indicate a fundamental difference in the redox conditions and evolution during formation of Mo-dominant versus Cu-dominant porphyry systems. This reframes the role of fO_2 in assessing magmatic fertility for Mo-dominant ore systems.