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Magmatic volatile controls on Cu and Mo mineralization in collisional porphyry systems

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Porphyry Cu–Mo divergence is commonly attributed to differences in redox state, water content, and volatile budgets, yet the quantitative role of halogens during magma differentiation in collisional settings remains unclear. Here we compare collisional porphyry Cu and porphyry Mo systems from the Gangdese belt (southern Tibet) and the southern margin of the North China Craton, and reconstruct melt volatile evolution by integrating apatite halogen chemistry with thermodynamic forward modeling. Bulk-rock and zircon data indicate that Cu-forming magmas were more hydrous than Mo-forming magmas, whereas both were moderately oxidized. Both magma types were derived from initially water-rich sources (H_2O > 4 wt%) and reached fluid exsolution only at very high dissolved water contents (>7.8 wt%), but they followed contrasting halogen trajectories prior to fluid saturation.Cu-related magmas were initially enriched in both Cl (0.20–0.35 wt.%) and F (0.40–0.55 wt.%), but evolved toward significant F depletion (bulk crystal-melt partition coefficient, $D^{c/m}_F \approx 1.8$) due to early and extensive amphibole fractionation. In contrast, Mo-related magmas had lower initial F (0.2–0.3 wt.%) and comparable Cl (0.2–0.35 wt.%), but became progressively enriched in both halogens ($D^{c/m}_F \approx 0.7$; $D^{c/m}_{Cl} \approx 0.4$) during prolonged crystallization that lacked significant amphibole separation. We propose that this halogen dichotomy provides a first-order control on metallogenic divergence in collisional porphyry systems: sustained F build-up lowers melt viscosity and promotes long-lived differentiation and Mo enrichment, whereas Cl-rich, more hydrous magmas more efficiently generate metal-transporting fluids conducive to Cu-focused mineralization. Ultimately, the divergent initial volatile budgets inherited from distinct sources, coupled with contrasting amphibole fractionation pathways, dictate the magmatic F–Cl evolution and the ensuing Cu vs. Mo mineralization (Fig. 1).

