

## Reconstructing volatile evolution in melts using zircon-hosted apatite inclusions: Implications for the use of apatite as a fertility indicator

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### ABSTRACT

Porphyry Cu deposits are genetically associated with oxidized, hydrous, and volatile-rich (e.g., Cl, S) magmas. Magmatic volatiles play a crucial role in the fertility of magmas associated with porphyry Cu mineralization. A continuous, volatile record from volatile undersaturation to fluid saturation in the magma reservoir is significant for understanding the genesis of porphyry Cu deposits. Apatite serves as a reliable recorder of the magmatic-hydrothermal history in porphyry Cu systems, with its volatile evolution providing an effective method for identifying the occurrence of volatile saturation. In this study, we measure the compositions of apatites occurring as inclusions in various minerals, including zircons, in both fresh and altered pre-mineralization monzogranite and inter-mineralization monzogranite porphyry from the Zhunuo porphyry Cu deposit in the Gangdese belt, southern Tibet. Cathodoluminescence and composition reveal significant differences between unaltered and hydrothermally altered apatites. Primary magmatic apatites exhibit homogeneous yellow to brown luminescence, whereas hydrothermally altered apatites display a wide range of distinctive luminescence colors (e.g., dull yellow-green, green, and gray). Furthermore, primary magmatic apatites show a significantly higher Mn/Fe ratio ( $>1.5$ ) and rare earth element (REE) plus Y contents ( $>4500$  ppm) compared to hydrothermally altered apatites (Mn/Fe  $< 1.5$ , REE+Y  $< 4500$  ppm). Zircon-hosted apatite inclusions demonstrate decreasing  $X_{\text{Cl}}/X_{\text{OH}}$  ratios ( $\sim 1.0\text{--}0.2$ ) with increasing  $X_{\text{F}}/X_{\text{OH}}$  ( $2\text{--}11$ ) and  $X_{\text{F}}/X_{\text{Cl}}$  ( $4\text{--}48$ ) ratios, indicating volatile exsolution during or prior to zircon crystallization in the magma chamber. Phenocryst-hosted apatite inclusions and ground-mass apatite crystals have comparable volatile compositions, characterized by higher  $X_{\text{F}}/X_{\text{OH}}$  ( $5\text{--}25$ ) and  $X_{\text{F}}/X_{\text{Cl}}$  ( $15\text{--}75$ ) but lower  $X_{\text{Cl}}/X_{\text{OH}}$  (mostly  $< 0.3$ ) compared to zircon-hosted apatites. We infer that the phenocryst-hosted apatite inclusions may have formed during/after fluid exsolution or may not escape re-equilibration with the residual melt due to the less robust nature of their silicate hosts. The calculated melt Cl contents, derived from low- $X_{\text{F}}/X_{\text{Cl}}$  zircon-hosted apatites in the monzogranite porphyry are  $0.17 \pm 0.06$  wt%, overlapping with those of the monzogranite ( $0.12 \pm 0.04$  wt%). The relatively high Cl contents of primary ore-forming magmas likely facilitate the effective extraction of Cu from the melt into the hydrothermal fluid. Our study highlights that apatite-in-zircon is more valuable than non-zircon-hosted apatite grains for reconstructing melt volatile evolution and could be a better Cu-fertility indicator for porphyry Cu mineralization than other forms of apatite.

**Keywords:** Apatite inclusions, zircon, volatiles, fluid exsolution, porphyry Cu deposit, cathodoluminescence