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Volatile variations in magmas related to porphyry Cu-Au deposits: Insights from amphibole geochemistry at Duolong, central Tibet

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Ore-forming fluid exsolution in a shallow magma chamber is a critical step in the formation of porphyry Cu±Mo±Au deposits, but direct evidence for this step is rarely found. Here, Cl abundance, major-trace element content and H isotope analysis of amphiboles in diorite and barren granodiorite porphyry samples from the Duolong porphyry-epithermal Cu-Au district are presented, in order to reveal processes associated with fluid exsolution and magma evolution. The low-Al Mg-hornblende in diorite formed at ~ 750-860 °C and ~ 80-200 MPa. These amphibole show slightly convex upward REE patterns with distinctly negative Eu anomalies and negative anomalies in Pb, Sr, Eu, Zr, Hf, and Ti on primitive mantle-normalized diagrams, suggesting that they crystallized from the same arc magma after plagioclase and magnetite crystallization. Large variations of estimated melt H_2O content (~ 6 to 3 wt%) and Cl content in amphiboles (0.09-0.38 wt%), as well as low δD values (-103 to -113‰) likely indicate that the magmas underwent large scale fluid exsolution, contributing to the formation of Duolong Cu-Au mineralization. Additionally, amphiboles from the barren granodiorite porphyry show two distinct populations, distinguished by their Al content. Low-Al amphiboles (Mg-hornblende) were formed at ~ 790-870 °C and ~ 100-230 MPa, whereas high-Al amphiboles (tschermakite) were formed at 880-970 °C and 210-400 MPa. Some high-Al amphiboles have slightly convex REE patterns with no negative Eu anomalies, a depletion in Nb, Zr, and Hf, and positive Sr, Ba, and Pb anomalies, likely consistent with amphibole crystallization from more mafic basaltic-andesitic melts. Low-Al amphiboles show different compositional trends compared to the diorite, suggesting that they crystallized from different magmas. Combined with mafic magma replenishment indicated by the positive correlation between Al^{IV} and Mg# values in high-Al amphiboles, the low-Al amphiboles likely crystallized from the new hybrid magmas with mafic to intermediate magma compositions. Meanwhile, small variations in Cl content (0.08-0.24 wt%) in low-Al amphiboles were controlled by Mg# rather than fluid exsolution. Thus, the low δD values (-102 to -122‰) were likely inherited from dioritic magmas that underwent fluid exsolution. Importantly, Cl compositional variation and H isotope signatures in amphibole have potential application as a powerful tool to identify ore-forming and barren intrusions within porphyry Cu±Mo±Au deposits.