

Porphyry copper genesis and zircon geochemistry

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Both ion microprobe (SHRIMP-RG) and laser ablation-ICP-MS methods provide U/Pb age and trace element compositional “fingerprinting” for zircon. SHRIMP methods provide higher mass resolution and sensitivity appropriate tracking magmatic processes (Ti-in-zircon geothermometry, Sc and Nb contents, and Ce and Eu anomalies), whereas LA-ICP-MS (Lu et al., 2016) provides high through-put that can potentially be applied to prospecting via studies of granitoid or detrital zircons.

SHRIMP data indicate that arc magmatic rocks are characterized by zircon with relatively high U/Th >0.6 , high Sc/Yb >1 , and relatively low Ti (<20 ppm) compared to MORB and plume settings (Grimes et al., 2015). Our database of zircon geochemical compositions from a variety of plutons in the Americas includes both pre-ore and post-ore granitoids and mineralizing Cu±Au±Mo porphyries in a single district. Zircons from non-mineralized intrusions, similar to other arc magmatic rocks, have a wide range of Ti-in-zircon temperatures, and evolve from high to low temperature with increased Hf content, decreased REE and Y contents, decreased Th/U ratio, and increased negative europium anomaly (Eu_N/Eu_N^*). Commonly, ore-related porphyries differ by having low Ti-in-zircon temperature estimates (750 to 650°C) and $Eu_N/Eu_N^* >0.4$. As Ti-in-zircon temperature decreases, Eu_N/Eu_N^* is constant or increases, REE and Y contents decrease by a factor of *ca.* 10, and the middle REE/heavy REE ratio decreases. Large positive Ce anomalies (Ce_N/Ce_N^*) are sometimes observed (Ballard et al., 2002), but remain difficult to measure accurately.

Zircon compositional diversity in arc granitoids largely reflects initial melt composition and evolution via crystallization, but in many cases U- and Th-rich growth zones document contamination by crustal melts. At temperatures of $\leq 1,000^\circ$ to 760°C , melt cooling accompanied by crystallization of either hornblende or apatite causes a decrease in the middle/heavy REE (Gd/Yb) ratio of zircon, and can be distinguished on Ce/Sm versus Gd/Yb plots via small versus large increases of Ce/Sm, respectively (Lee et al., 2017). Evolution to low temperature produces a large negative europium anomaly ($Eu_N/Eu_N^* < 0.3$) attributed to crystallization of Eu^{2+} -rich plagioclase from relatively water-poor melts, which commonly do not produce ores.

Mineralizing granitoid melts likely separated from lower- to middle-crustal source regions at low crystal content, high water content, and low temperature (850-800°C), and lack high temperature zircon (Lu et al., 2015; Dilles et al., 2015). The small negative Eu_N/Eu_N^* anomaly attests to high water content and suppression of plagioclase crystallization (e.g., high Sr/Y of whole rock). At temperatures $<760^\circ\text{C}$, these oxidized and water-rich arc magmas crystallized titanite, which strongly incorporates REE and Y ($D_{\text{REE}} \text{ XI/m} = 200\text{-}1000$; Colombini et al., 2011), and decreases the REE content of melt and zircon. Consequently, zircon crystallizes with low Gd/Yb (<0.2). The distinctive increase of zircon Eu_N/Eu_N^* in mineralized porphyries during crystallization at near solidus temperatures of 750-650°C is a complex process; oxidation of melt (Eu^{2+} to Eu^{3+}) via degassing of SO_2 -rich ore fluids (Dilles et al., 2015) and titanite crystallization both cause an

increase in Eu_N/Eu_N^* , whereas crystallization of observed Na-plagioclase causes a decrease. Trace elements of zircon are fertile for future research and minerals exploration.