

## The microstructure and trace metal geochemistry of pyrite from porphyry Cu deposits

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Porphyry copper deposits (PCDs) are currently the world's largest source of copper and molybdenum, and are also among the largest reservoirs of gold in the upper crust. Despite the fact that pyrite is a ubiquitous mineral phase in these deposits, the major and trace element chemistry of pyrite from PCDs remains poorly understood.

Here we report the first comprehensive trace element database of pyrite from the Dexing deposit, China's largest porphyry Cu deposit, determined using a combination of electron microprobe analysis (EMPA) and secondary-ion mass spectrometry (SIMS). Results show that the concentrations of precious metals (e.g., Au, Ag), metalloids/chalcogens (e.g., As, Sb, Se, Te), and base/heavy metals (e.g., Cu, Co, Ni, Zn, Hg) in pyrite from a PCD are more significant than previously thought (e.g. ~6 wt.% Cu, ~3 wt.% As, ~0.25 wt.% Au, and ~0.2 wt.% Ni).

EMPA-WDS elemental mapping and SIMS depth profiling reveal that some of these metals occur exclusively in solid solution in the pyrite structure (e.g., As, Ni) or are present in solid solution and also in micro- to nano-sized inclusions (e.g. Cu and Au). The mineralogical occurrences are associated with complex textural and chemical features such as oscillatory growth zoning and sector zoning with variable porosity, where Cu-rich, As-(precious metals)-poor zones alternate with As-(precious metals rich)-rich, Cu-poor zones, and with barren pyrite zones.

These observations point toward a decoupled behavior of Cu and As in this porphyry system, strongly suggesting that selective partitioning of metals into pyrite is most likely the result of changes in fluid composition, probably caused by fluid mixing and repeated and intermittent pulses of Cu and As-bearing fluids of magmatic/ hydrothermal origin. Despite the fact that more studies are needed to increase our knowledge about metal partitioning in sulfides during the hydrothermal stages of PCDs formation, the observations and data presented here support an important role of pyrite as a record of fluid variations, and as a host of precious and base metals, metalloids/chalcogens and potentially PGEs.

## The disparate crystal records of the Youngest Toba Tuff, Indonesia

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The 74 ka Youngest Toba Tuff (YTT) is the product of a giant eruption (>2800 km<sup>3</sup>) from the Toba Caldera Complex of Sumatra, Indonesia. The YTT sample suite spans the compositional range of 63-75 wt.% SiO<sub>2</sub>, with most >68.8 wt.% SiO<sub>2</sub>. The narrower compositional range of quartz-hosted melt inclusions suggests that YTT compositional heterogeneity may reflect a spectrum of crystal-liquid mixtures [1]. Quartz from high silica rhyolites are relatively unzoned whereas those from low silica rhyolites have Ti, and therefore temperature, reversals late in their crystallization history. Limited diffusional relaxation across these bands suggests rim crystallization within a few ka of eruption [2]. In contrast, allanite from a high silica rhyolite grew extensively over >35 ka and are not reversely zoned at the rims [3]. <sup>238</sup>U-<sup>230</sup>Th-<sup>206</sup>Pb zircon crystallization dates range to even older ages but mainly predate eruption by <400 ka. Despite the strong crustal signature of the YTT (<sup>87</sup>Sr/<sup>86</sup>Sr ~ 0.714), bonafide xenocrysts are relatively rare. Growth on individual zircon grains occurred over a protracted time interval (>100-500 ka), and was likely episodic. Zircon ages in high silicic rhyolites may span a more limited range. Zircon from individual rocks exhibit a significant Th/U compositional range and evidently crystallized from a plumbing system with a wider range in thermochemical conditions than those characterized by YTT matrix glasses. Cores nucleated over at least a 300 ka interval, often from relatively unevolved magmas. Zircon rims grew from host melts and yield ages that range from ~80 ka to ~115 ka. Compositional reversals are recorded by rims in zircon from low silica rhyolite but not high silica rhyolite. Considered collectively, ages and age ranges obtained from YTT phases decrease in the order zircon > allanite > quartz, a sequence that parallels that for attainment of phase saturation conditions. Minerals stable in more diverse magmatic compositions apparently persisted longer. Crystals were apparently remobilized intermittently by magmatic rejuvenation rather than being incorporated by foundering of roof rocks at the time of eruption. Domains that ultimately erupt as low silica rhyolites were remobilized beginning 40 ka before eruption – based on the zircon/allanite ages – with the most recent reheating occurring within a few thousands years of eruption [2].

[1] Chesner and Luhr (2010), *JVGR*; [2] Matthews *et al.*, (2012) *J Pet*; [3] Vazquez and Reid (2004) *Science*