

Tracking the evolution of a submarine arc-hosted hydrothermal system through the deportment of phosphorous and rare-earth elements

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The seafloor structure of an arc-hosted hydrothermal system was drilled by IODP Expedition 376 at Brothers volcano. Recovered cores contain accessory phosphates that offer clues to its evolution. Caldera wall (Hole U1530A) alteration mineral assemblages indicate an older, inactive, low-pH, magmatically influenced hydrothermal system (≥ 225 m below seafloor [mbsf]) that is partially overprinted by a seawater-dominated, medium-pH, higher temperature hydrothermal system forming a near-seafloor stockwork zone [1]. Additionally, a younger cone (Hole U1528D) hosts an active, low-pH, magmatic fluid-driven hydrothermal system akin to the deeper caldera wall seafloor section.

The composition of phosphate minerals changes from magmatic to hydrothermal mineral formation stages. The sole primary (magmatic) phosphate contained in fresh volcanic rocks (Holes U1529B, U1531E) is euhedral fluor-chlorapatite found in the matrix or as inclusions in clinopyroxene and plagioclase phenocrysts. Secondary (metasomatic) phosphate mineralization, however, is represented by a variety of different phases. Interstitial anhydrous fluorapatite is associated with late-stage seawater-derived alteration minerals. This secondary apatite often exists along with disseminated, relic florencite [$\text{LREEAl}_3(\text{PO}_4)_2(\text{OH})_6$] crystals. The latter can also be found in vugs that occasionally resemble the shape of apatite crystals. Within the stockwork zone (≤ 20 mbsf), magnesium metasomatism has led to formation of Mg-enriched fluor-chlorapatite and fluorine-rich Mg-hydroxyphosphates. At the volcanic cone, magmatic apatite has been replaced by a compositionally complex paragenesis of euhedral aluminum-phosphate-sulfate (APS) minerals. APS crystals show oscillatory zoning manifested by alternating LREE-phosphorous-enriched and -depleted growth shells. Sulfur enrichment occurs at the expense of phosphorous depletion.

This suggests that hydrothermal apatite formation was prevented by the initially magmatically influenced fluid circulation due to highly acidic conditions that solely favored APS minerals as the only P-bearing precipitates. Among these, LREE-bearing, P-rich APS phases may have formed during low-S and/or high-P pulses with decreased chloride activity, as lower chlorine contents coincide with enrichment of REE in compositionally zoned APS crystals. Their seawater-driven alteration may have formed a significant phosphorous source to

enable the precipitation of late-stage hydrothermal apatite. The latter even shows rare minute ($< 2 \mu\text{m}$) inclusions of REE-phosphates monazite (LREE) and xenotime (HREE) likely resulting from dissolution-precipitation reactions.

[1] de Ronde et al. (2019), *Geology* 47, 762–766.