

Copper and tin isotope fractionation during arc magma differentiation: Insights from New Zealand volcanoes

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Copper (Cu) and Sn isotopes provide critical insights into the Earth's core-mantle processes, but limited data from arc volcanoes restrict their application in hydrothermal systems where material recycling occurs. Particularly for Sn, there is currently no available data for arc magmas. This study investigates Cu and Sn isotopic compositions, along with clinopyroxene-H₂O concentrations, from two New Zealand volcanoes, Whakaari (active, northernmost Taupo Volcanic Zone) and Taranaki (rear-arc volcano, ~200 km west of the Hikurangi Trough). Whakaari samples include lavas, pumices, crater lake, sediments, volcanic ash, and hot spring water, while Taranaki provides pumices. These lava and pumice samples are mainly basaltic andesites and andesites.

Whakaari lavas exhibit pronounced isotopic fractionation in both Cu ($\delta^{65}\text{Cu} = -0.19\text{‰}$ to 0.59‰) and Sn ($\delta^{122/118}\text{Sn} = -0.241\text{‰}$ to 0.361‰), significantly broader than Taranaki's $\delta^{65}\text{Cu}$ (-0.19‰ to 0.20‰) and $\delta^{122/118}\text{Sn}$ (0.124‰ to 0.235‰). The Cu isotopic compositions in Whakaari samples are comparable to some published arc samples from Tonga and Mariana, whilst the Sn isotopic values from Whakaari are also similar to those of highly differentiated granitic samples. The larger variations in Whakaari are primarily due to fractional crystallisation and degassing: sulphide precipitation induces significant Cu isotopic fractionation, while degassing in a shallow magma chamber exerts a stronger influence on Sn isotopes. In contrast, Taranaki's weaker Sn isotope fractionation ($\delta^{122/118}\text{Sn} = 0.124\text{‰}$ to 0.235‰) and narrower Cu range suggest less degassing and earlier Fe-Ti oxide precipitation.

The role of degassing is further supported by two key observations: low magmatic H₂O concentrations in clinopyroxene (2.67 wt.% to 0.29 wt., average 0.83 wt.%) and systematic Sn-isotope concentration variations within Whakaari samples. These findings suggest a deeper reservoir of sulphide beneath Whakaari, potentially indicating an embryonic copper porphyry deposit.