

## Making andesites in a lower crustal hot zone: Preconditioning the lithosphere of Taupo Volcanic Zone

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Hauhungatahi Volcano is a dissected cone, 12 km west of Ruapehu Volcano. Recent <sup>40</sup>Ar/<sup>39</sup>Ar step-heating dating experiments on a range of samples have yielded a preferred age between 860 – 900 ka, considerably older than andesites from Ruapehu massif, where the oldest rocks are ~230 ka.

Here we compare Hauhungatahi andesites to those of the younger Ruapehu edifice and develop a petrogenetic model in the context of time and geochemistry. Hauhungatahi rocks have a distinctive phenocryst assemblage relative to the younger andesites of Ruapehu, with a generally higher ratio of clinopyroxene ( $\pm$  olivine) to plagioclase. Accordingly, they are low in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Zr, Rb, and Ba but high in MgO, (>9% wt) Ni (> 100 ppm), Cr (>400 ppm) and Sr (>400 ppm) relative to most Ruapehu andesites. Hauhungatahi andesites are LREE enriched ((Ce/Sm)<sub>n</sub> ~ 2), with slight positive Eu-anomalies and flat HREE (Dy – Lu between 7 – 10 x chondrite). In contrast Ruapehu andesites also show LREE enrichment relative to HREE, but with slight negative-Eu anomalies and Dy – Lu > 10 x chondrite. Radiogenic isotopes (Sr, Nd and Pb) from Hauhungatahi show subtle distinctions from the Ruapehu data with lower <sup>87</sup>Sr/<sup>86</sup>Sr at a given <sup>143</sup>Nd/<sup>144</sup>Nd.

We interpret these distinctions as resulting from the early stages of arc development in the crustal setting of TVZ, reflecting the interaction between mafic andesite and wehrlite cumulates in a hot zone at the crust – mantle interface.

## Biogeochemical processes in flooded underground mine workings of Butte, Montana, USA

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Once one of the USA's most important mining districts, the city of Butte, Montana is now more renowned for its environmental damage. Notable features include the highly acidic (pH 2.5) and metal-rich Berkeley Pit Lake, over 15,000 km of flooded underground mine workings, and a polluted alluvial aquifer that is located at the headwaters of the largest EPA Superfund site in the US.

The flooded underground mine workings of Butte have a wide range in water chemistry that is largely controlled by the district-wide zonation in primary ore mineralogy, as well as a number of equilibrium and non-equilibrium processes. Mine water in the Cu-rich "Central Zone", which includes the Berkeley Pit Lake and nearby Kelley Shaft, has a high acidity and very high concentrations of Fe, Zn, and other metals. Kelley Mine water is surprisingly devoid of dissolved Cu, possibly due to formation of secondary chalcocite on pyrite in the flooded mine workings. In contrast, mine shafts in outer areas that were mainly mined for Ag, Mn, and Zn contain water that is pH-neutral, strongly reduced, H<sub>2</sub>S-rich, and metal-poor. Geochemical modeling suggests that most of the mine shafts are near equilibrium with one or more carbonate minerals, including siderite, rhodochrosite, smithsonite, and calcite. All of the shaft waters are anoxic, with Eh controlled by Fe<sup>2+</sup>/Fe<sup>3+</sup>/HFO or H<sub>2</sub>S/SO<sub>4</sub><sup>2-</sup>/mackinawite.

Stable isotopes of water show that the Berkeley Pit Lake is significantly evaporated, whereas all of the mine shafts plot near average recharge water on the local meteoric water line. Large variations in the S and O isotopic compositions of dissolved sulfate are explained by a combination of three processes, operating to different extents and/or different rates: 1) oxidation of pyrite and other sulfide minerals; 2) dissolution of hydrothermal CaSO<sub>4</sub>; and 3) bacterial sulfate reduction (BSR). The S-isotopic composition of dissolved H<sub>2</sub>S ranges from -35 to +5 ‰, with the more positive values in waters that have had the greatest extent of BSR. The isotopic composition of dissolved inorganic carbon in many of the mine waters is consistent with equilibration with rhodochrosite. However, lighter  $\delta^{13}\text{C}$  values in the H<sub>2</sub>S-rich shafts suggest a biological component, most likely derived from oxidation of organic carbon during BSR.