## Hydrothermal fluid chemistry at Brothers submarine arc volcano

## V.K. Stucker<sup>1</sup> and C.E.J. de Ronde<sup>2</sup>

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Analytical Geochemist, GNS Science, Avalon Lower Hutt 5040. Email: V.Stucker@gns.cri.nz

## 2.

Principal Scientist, GNS Science, Avalon Lower Hutt 5040. Email: Cornel.deRonde@gns.cri.nz

Brothers submarine volcano, located along the Kermadec arc north of New Zealand, provides a unique opportunity to study two distinct end-member hydrothermal systems in close proximity. Hydrothermal vent fields at the NW Caldera and Upper Caldera sites are most similar to mid-ocean ridge counterparts in featuring "black smoker" sulfide chimneys and fluid chemistry dominated by water-rock interactions. Two resurgent cones (i.e., Upper and Lower Cones) emerge from the southern part of the caldera. These volcanic edifices are host to separate vent fields that feature "white smokers" rich in elemental sulfur and natroalunite, with evidence for prevalent magmatic degassing. Multiple voyages to Brothers volcano between 2004 and 2018 have allowed us to evaluate both the spatial and temporal changes in the hydrothermal fluid chemistry at these sites.

Hydrothermal systems located on the caldera walls follow the typical zero-Mg and zero-sulfate chemistry common to black-smoker systems rich in sulfide and minerals. Recent observations have shown active phase separation of higher than seawater salinity "brines" and lower than seawater salinity "vapors" occurring at the seafloor. Phase separation plays a major role in the chemistry of the fluid being discharged from the chimneys, with brines dominanting the fluid composition in recent years, including high metal contents (e.g., up to 13 mmol/kg Fe). Fluids from the Cone sites are strongly influenced by magmatic degassing dominated by SO<sub>2</sub>, H<sub>2</sub>S and CO<sub>2</sub>. Unlike "black smoker" water-rock systems, the end-member fluids are not characterized by zero magnesium. In fact, in 2004/2005 fluids from the Upper Cone site had Mg values slightly elevated (53.5 mmol/kg) concentrations, as did the Lower Cone in 2018 (59 mmol/kg), over background seawater (52.8 mmol/kg). Sulfate concentrations are also elevated (up to 150%) above seawater values in these samples due to the disproportionation of SO<sub>2</sub>. The pH of vent fluids from the two cones vary dramatically, from ~2 at the Upper Cone to 4 to 5 at the Lower Cone. Greater concentrations of CO2 occur at the Lower cone site. Gas fractionation, system permeability and gas fluxes are likely responsible for the temporal variations in the fluid chemistry at the different Cone sites.

In summary, fluid analysed from hydrothermal vent sites located on the caldera walls at Brothers are very different in chemical composition to those seen associated with the two resurgent cones. Time series study of both fluid types has provided insight into the chronic nature of discharge at these sites and subseafloor processes at work. We aim to resolve the conundrum of why only the caldera sites are mineralised and start to understand the chemical connection between the Caldera and Cone sites.