



## Volcanic Plume Chemistry: Models, Observations and Impacts

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Volcanic plumes are highly chemically reactive; both in the hot, near-vent plume, and also at ambient temperatures in the downwind plume, as the volcanic gases and aerosol disperse into the background atmosphere.

In particular, DOAS (Differential Optical Absorption Spectroscopy) observations have identified BrO (Bromine Monoxide) in several volcanic plumes degassing into the troposphere. These observations are explained by rapid in-plume autocatalytic BrO-chemistry that occurs whilst the plume disperses, enabling oxidants such as ozone from background air to mix with the acid gases and aerosol. Computer modelling tools have recently been developed to interpret the observed BrO and predict that substantial ozone depletion occurs downwind. Alongside these modelling developments, advances in in-situ and remote sensing techniques have also improved our observational understanding of volcanic plumes.

We present simulations using the model, PlumeChem, that predict the spatial distribution of gases in volcanic plumes, including formation of reactive halogens BrO, ClO and OCIO that are enhanced nearer the plume edges, and depletion of ozone within the plume core. The simulations also show that in-plume chemistry rapidly converts NO<sub>x</sub> into nitric acid, providing a mechanism to explain observed elevated in-plume HNO<sub>3</sub>. This highlights the importance of coupled BrO-NO<sub>x</sub> chemistry, both for BrO-formation and as a production mechanism for HNO<sub>3</sub> in BrO-influenced regions of the atmosphere.

Studies of coupled halogen-H<sub>2</sub>S-chemistry are consistent with in-situ Alphasense electrochemical sensor observations of H<sub>2</sub>S at a range of volcanoes, and only predict H<sub>2</sub>S-depletion if Cl is additionally elevated. Initial studies regarding the transformations of mercury within volcanic plumes suggest that significant in-plume conversion of Hg<sup>0</sup> to Hg<sup>2+</sup> can occur in the downwind plume. Such Hg<sup>2+</sup> may impact downwind ecology through enhanced Hg-deposition, and causing enhanced biological uptake of mercury.

Excitingly, we can now begin to compare the model simulations to very recently reported in-situ aircraft and balloon measurements in downwind volcanic plumes, which found e.g. ozone depletion at Redoubt, ozone depletion and elevated HNO<sub>3</sub> at Erebus and sulfate-H<sub>2</sub>O interactions at Kilauea. Satellite observations of volcanic BrO, and DOAS observations of BrO under varying plume conditions have also recently been reported. Such comparisons may highlight additional chemistry (e.g. HO<sub>2</sub>NO<sub>2</sub> at Erebus), identify further underlying processes (e.g. the role of plume dispersion and gas fluxes in controlling plume chemistry), guide future field-observation strategies, and support and improve the model simulations that aim to understand volcanic emissions, plume chemistry, and predict the environmental impacts of volcanic plumes.