

Halogen Chemistry in Volcanic Plumes (Invited)

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Volcanoes release vast amounts of gases and particles in the atmosphere. Volcanic halogens (HF, HCl, HBr, HI) are co-emitted alongside SO₂, and observations show rapid formation of BrO and OCIO in the plume as it disperses into the troposphere. The development of 1D and Box models (e.g. *PlumeChem*) that simulate volcanic plume halogen chemistry aims to characterise how volcanic reactive halogens form and quantify their atmospheric impacts.

Following recent advances, these models can broadly reproduce the observed downwind BrO/SO₂ ratios using “bromine-explosion” chemistry schemes, provided they use a “high-temperature initialisation” to inject radicals (OH, Cl, Br and possibly NO_x) which “kick-start” the low-temperature chemistry cycles that convert HBr into reactive bromine (initially as Br₂). The modelled rise in BrO/SO₂ and subsequent plateau/decline as the plume disperses downwind reflects cycling between reactive bromine, particularly Br-BrO, and BrO-HOBr-BrONO₂. BrCl is produced when aerosol becomes HBr-depleted. Recent model simulations suggest this mechanism for reactive chlorine formation can broadly account for OCIO/SO₂ reported at Mt Etna.

Predicted impacts of volcanic reactive halogen chemistry include the formation of HNO₃ from NO_x and depletion of ozone. This concurs with HNO₃ widely reported in volcanic plumes (although the source of NO_x remains under question), as well as observations of ozone depletion reported in plumes from several volcanoes (Mt Redoubt, Mt Etna, Eyjafjallajökull). The plume chemistry can transform mercury into more easily deposited and potentially toxic forms, for which observations are limited. Recent incorporation of volcanic halogen chemistry in a 3D regional model of degassing from Ambrym (Vanuatu) also predicts how halogen chemistry causes depletion of OH to lengthen the SO₂ lifetime, and highlights the potential for halogen transport from the troposphere to the stratosphere.

However, the model parameter-space is vast and only partially constrained by available observations. Reactions on aerosol are a key driver of the chemistry and are affected by uncertainties in both the HOBr reactive uptake coefficient and the aerosol surface area. Recent work has explored the reactive uptake of HOBr on sulfate-rich aerosol, whilst field-measurements at Mt Etna have aimed to quantify the size-resolved primary aerosol emission, towards improving model representations of this highly non-linear volcanic plume halogen chemistry.