Reactive Halogen Chemistry in Volcanic Plumes

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A decade ago the discovery of reactive bromine in a volcanic plume was published for the first time. Since then many measurements and modeling have been undertaken to understand the radical chemistry in volcanic plumes, in particular, the interaction between volcanic gas species, released under strongly reduced conditions, and the oxidizing atmosphere.

Technical advances have lead to more continuous data acquisition with enhanced frequency, in particular, with relatively easy to use remote sensing techniques, e.g. DOAS and FTIR. In open conduit volcanoes, acquired data sets provide new possibilities to investigate volcanic volatile compositions with a good temporal resolution partly even during explosive eruptions.

Many halogen containing molecules are non-inert gas molecules; therefore, care has to be taken in volcanological interpretations. It is, for instance, of great importance to link the measurements of halogen oxides (which are often easy to measure) and gaseous hydrogen halides to the total emission flux of the halogen species in order to estimate the pristine composition of gases exsolved from magmas. In particular, it is important to better understand the effects of meteorological conditions on the formation and measurements of halogen oxides, but as well the influences on measurements of hydrogen halides which are often considered as stable. Only with this knowledge we can relate changes of the measured gas ratios to the volcanic fluids emitted by the underlying magma and can interpret the data as signals, which describe the evolution of magmatic bodies inside the Earth.

A summary of the current knowledge and the most important improvements made during the last decade will be presented, focusing on bromine and chlorine and to a minor extend on iodine. We will present an overview of measurement data including new unpublished results from in-situ and remote sensing measurements. The formation process of BrO, ClO and OClO in volcanic plumes will be discussed showing measurements from close proximity to the crater up to a distance of several km or tens of km away from the emission point at several volcanic sites (among others: Etna, Nyiragongo, Masaya, Popocateptl, Gorely). The variation on the order of a factor of 3 in bromine monoxide to sulfur dioxide ratios will be shown to depend on plume age, and meteorological influences as long as we exclude measurements at crater rims. Beside these variations there are changes of the ratios of a factor up to 8 most probably caused by changes in volcanic activity. Also, improvements and uncertainties of the determination of total halogen contents due in-situ sampling (alkaline trap sampling) will be mentioned and discussed.