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HALVIRE: HALogen activation in Volcanic plumes In Reaction chamber Experiments

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Volcanic gas emissions are of importance for atmospheric chemistry on a local and with a varying extent on a global scale. The discovery of reactive halogen chemistry in volcanic plumes brought new insights into the significance of volcanic halogen emissions. The investigation of reactive halogen species (e.g. BrO, OClO, IO, I_2) made great progress recently, numerous field studies were conducted, but revealed many uncertainties concerning the responsible mechanism and influencing environmental parameters (e.g. plume gas and aerosol composition, relative humidity, potential role of NO_X emissions). Understanding the influence of these parameters on halogen activation (i.e. conversion from hydrogen halides to reactive halogen species (RHS)) in volcanic plumes is essential for an interpretation of the results e.g. 1) in terms of drawing conclusions about magmatic processes, eruption forecasting based on BrO/SO_2 ratios, or 2) in terms of their atmospheric impact (for instance ozone destruction, oxidation of mercury or reduced methane life time).

Experiments are currently undertaken to investigate a simplified volcanic plume (SiO_2 and sulfuric acid aerosols with H_2O, CO_2, SO_2, HCl, HBr as trace gas components) under controlled conditions in a Teflon smog chamber at the University of Bayreuth. The 3.5 m^3 smog chamber is equipped with a solar simulator and comprehensive instrumentation: Hydroxyl radicals, atomic Cl and Br are determined by the radical clock technique, RHS (BrO, ClO, OClO) are measured by a White multi-reflection cell and multi-channel cavity enhanced-DOAS (Differential Optical Absorption Spectroscopy), and other halogen species (Br_2, Cl_2, HOBr and BrCl) by FAPA-MS (Flowing Atmospheric-Pressure Afterglow Mass Spectrometry) and offline sampling techniques (gas diffusion denuders and alkaline traps). SO_2, CO_2, NO_X and O_3 are monitored by standard in-situ gas analyzers and particle size distributions are determined by SMPS (Scanning Mobility Particle Sizer Spectrometer).

The combination of these techniques gives the possibility to explore the role of the heterogeneous reactions in halogen activation, representing a current lack of understanding in volcanic research. In particular, the influence of (1) NO_X and O_3, (2) initial HCl/HBr ratio, (3) relative humidity, and (4) the particle composition (towards more complex real volcanic “ash”) on the reactive halogen chemistry (including the bromine explosion mechanism) will be investigated within the project. The first experimental phase has been started in January 2018. We will present the set-up and preliminary results of those first experiments. The observations will be later evaluated and placed into a larger context to better understand natural processes. Here, the CAABA/MECCA model will support the interpretation.