Geophysical Research Abstracts
Vol. 16, EGU2014-10771, 2014
EGU General Assembly 2014

New insight into halogen release from experimental studies on BrO/Br ratios in volcanic plumes

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Since the discovery of BrO in a volcanic plume (Bobrowski et al. 2003) many measurements have been performed as well as modelling 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. Besides the goal in atmospheric chemistry to better determine the impact of volcanic emission (e.g. reactive bromine) on the local (and maybe global) scale, volcanologists also have an interest to understand if the BrO/SO_2 ratios can be used as a monitoring parameter giving further insides in dynamic processes of volcanoes. However, one of the arguments which potentially makes volcanological interpretations difficult is the reactivity of BrO. Therefore it is, of great importance to link the measurements of BrO and gaseous hydrogen bromide to the total emission flux of bromine in order to estimate the pristine gas composition released from magmas.

In particular, trace gas composition of the surrounding atmosphere, the volcanic gas composition and meteorological parameters can all potentially effect the formation of BrO and might have to be considered. Some of these factors potentially also influence near source (crater rim) in-situ measurement. We need to answer the question: Can we correlate BrO measurements to the total bromine outgassing? Only with this knowledge we can relate changes of the measured gas ratios (BrO/SO_2) to the volcanic fluids emitted by the underlying magma and can interpret data as signals from depth, which provide insight on the degassing of magmatic bodies inside the Earth.

Some studies indicate that the BrO/SO_2 ratio is close to a temporarily equilibrium already after only few minutes of the gas emission from the vent (e.g. Bobrowski and Giuffrida, 2012). This equilibrium seems to be relatively independent from meteorological parameters except for extreme conditions.

We here present an empirical approach to answer the above question by discussing BrO formation studies from five different volcanoes, Stromboli and Etna (Italy), Masaya (Nicaragua), Gorely (Russia) and Nyiragongo (DR Congo). These volcanoes represent a broad variation in their geological settings, surrounding environment and climate. They cover subduction related systems and rift volcanism and encompass climate zones from the subarctic to the tropics.

For the BrO studies Multi-Axis-Differential Optical Absorption Spectroscopy (MAX-DOAS) measurements have been carried out. Active alkaline traps were applied to determine bromine emissions at the crater rim. All measurements have been taken simultaneously or within a maximum time distance of a few hours. From these measurements we determined that a range of about 5% to 30% of the total bromine is transformed into BrO. We show and discuss how the varying BrO-Br partition is related partly to the geological settings, the various meteorological conditions and explore further possible influences. We will shortly discuss the current limitations of the commonly used measurement techniques itself and introduce possible future improvements.