

## NATURAL HALOCARBONS IN VOLCANIC GASES

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In spite of numerous studies on volcanic and hydrothermal gas emissions, very few have focused on the organic chemistry of these discharges. The release of SO<sub>2</sub> and CO<sub>2</sub> has been the predominant subject in analytical and theoretical studies. Following these results, a common understanding of the impact of volcanic aerosols on global warming, stratospheric chemistry and atmospheric cycles now has been established widely across fields such as atmospheric and environmental sciences, geochemistry and geophysics.

Volcanic eruptions rapidly penetrate the otherwise relatively undisturbed tropopause, allowing immediate quantitative injection of contaminants into the stratosphere, including labile short-lived compounds which normally never reach such altitudes. The significance of the emission of organic compounds from major eruptions and quiescent volcanic degassing has so far been neglected in environmental and atmospheric impact studies. Two major reasons for this omission have been the difficult sampling conditions and the complex analytical problems due to severe adverse matrix effects (e.g. water, sulfur, and acids) during chromatographic separation of trace organic compounds, and their identification by gas chromatography–mass spectrometry (GC–MS).

In an ongoing study of the organic and halocarbon discharges from volcanic systems, a large range of compounds have been detected significantly above atmospheric background concentrations, using novel analytical techniques. The analytical developments are (1) separation of gases from condensates during sampling, and (2) the application of solid phase microextraction (SPME) prior to high resolution GC–MS analyses. The use of SPME has markedly reduced a high sulfur background which previously prevented detection of trace organic compounds, and reduced introduction of water and inorganic acids which are deleterious to high resolution GC–MS. The majority of the organic compounds have not been previously reported from volcanic emissions. Our results from different sites in the Mediterranean (Italy, Greece), Kamchatka and New Zealand provide quantitative data on compounds including short chain alkanes, alkenes, arenes, and their halogenated (F, Cl, Br and I) and sulfonated derivatives (e.g., HCFC's, CFC's, perfluorocarbons).

For some compounds (e.g., CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>), concentrations are several orders of magnitude greater than present-day atmospheric backgrounds, and above midlatitudinal industrial urban air maxima. Among the detected and quantified compounds are furans, phenanthrene; chlorinated, fluorinated and brominated mixed polyhaloalkanes, such as trichlorofluoromethane (CFC–11), methyl bromide, 2,2–difluoropropane (HFC–272), dichloromethane (R–30), chlorobenzene, and thiophene. As a result of the increased sensitivity of our new method, measured halocarbon concentrations in volcanic gas emissions have to be corrected to values higher than previously estimated. Based on the large range of isomers detected, we deduce these compounds to have been synthesized by gas–phase reactions in an ascending gas column together with subsequent abiogenic alkylation, halogenation, and sulfidation, reactions. Although the roles of surface catalysis by mineral surfaces at high temperatures are still poorly known, the organic distributions observed are interpreted as high temperature (e.g. 900°C) alkyl free radical reactions, and halide electrophilic substitution on arenes.