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The Organic Chemistry of Volcanic Gases

at Vulcano (Aeolian Islands, Italy)

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Abstract

In order to assess the source strength, composition and formation of trace organic constituents in volcanic gas emissions, we collected a total of 48 samples of sorbent-trapped volcanic gases, sublimates, condensates from active vents of the La Fossa crater on the island of Vulcano (Aeolian Islands, Italy) as well as ambient and industrial air, during three sampling campaigns in the years 1999, 2000 and 2001. Previously, trace organic gas analyses from volcanic sources have been limited by analytical problems such as the strong sulfur, halogen acid and water matrix that is deleterious to sensitive trace organic analysis by GC-MS. We developed a novel analytical and sampling approach that allows reliable, sensitive and quantitative analysis by *Short-Path Thermal Desorption-Solid Phase Microextraction-Cryotrapping-Gas Chromatography/Mass Spectrometry* (SPTD-SPME-CF-GC-MS.

In a total of 158 GC-MS analyses we detected and selectively quantified well over 100 compounds in each sample. We found alkanes, alkenes, arenes, phenols, aldehydes, carboxylic acids, esters, ketones, nitriles, furans, PAH's and their halogenated, methylated and sulfonated derivatives, as well as various heterocyclic compounds including thiophenes. Most compounds are present at concentrations well above laboratory, ambient air, adsorbent and field blank levels. For some analytes (e.g., CFC-11, CH_2Cl_2, CH_3Br), concentrations are up to several orders of magnitude greater than even mid-latitudinal industrial urban air maxima. Air or laboratory contamination is negligible or absent on the basis of inert gas and noble gas isotopic measurements.

The organic compounds are interpreted as the product of inorganic, abiogenic gas-phase radical reactions. On the basis of isomer abundances, *n*-alkane distributions and the substitution pattern the compounds are considered to have been formed by high temperature (e.g., 900 °C) alkyl free radical reactions and halide electrophilic substitution on arenes, alkanes and alkenes.

Model global volcanic halocarbon fluxes from our own and published compositional data on a number of halocarbons have been obtained by scaling to published volcanic CO_2 fluxes. This yields global halocarbon fluxes in the range from $1.0\text{x } 10^{-9}$ Tg y^{-1} ($CClF_3$) to $1.2 \text{ x } 10^{-4}$ Tg y^{-1} (CH_3Cl). Methyl bromide (CH_3Br) and methyl iodide (CH_3I) are estimated to have a volcanic model source strength of up to 1.3 x 10^{-6} Tg y^{-1}, however, it is noted that other brominated compounds were identified. The significance of organic emissions from quiescent volcanic degassing as opposed to explosive eruptions to stratospheric chemistry is that the negligible aqueous solubility of most emitted organic compounds does not lead to a quantitative tropospheric washout effect as postulated for explosive volcanic HCl and HF emissions.

Simple modeling suggests that episodic, catastrophically large, explosive events such as flood basalt eruptions do not impact the short-term ozone chemistry to the same magnitude as today's anthropogenic emissions but may modify the natural atmospheric reactive balance over much longer (geological) time spans. In addition, the apparent abiogenic organic chemistry of volcanic gases may give insights into the possible hydrothermal origin of early life on Earth, as indicated by the presence of simple amino acids, nitriles, and alkanoic acids.

In order to clarify the source of these compounds we have sampled soil gas emissions of organic compounds and determined CO_2 fluxes along a profile spanning from the vegetated base of the active La Fossa cone (Vulcano Island, Italy) over the unvegetated volcanic flank, the crater rim and base, into fumarolic areas.

The results indicate that a) the majority of volatile organic compounds in the soil gas show significant increases in concentration towards the crater and fumaroles, b) emissions of the halocarbon CFC-11 (CCl_3F) correlate well with soil CO_2 fluxes measured on site ($R^2=0.91 \pm 0.02$) and both increase towards the crater and fumaroles, and c) diffusive emissions therefore contribute significantly to the volcanic halocarbon source strength. Other ozone depleting substances were found in concentrations significantly above those found in field and system blanks, including CH_3Br, CH_3Cl, CH_3I, C_2H_5Br, and chlorinated benzenes. Abundances range from upper pptv to ppmv (e.g. CFC-11: max. 1200 pptv diffusive, 3700 pptv fumarolic/dry gas, dry air: 268 pptv). On the basis of these results, the natural volcanic source strength of halocarbon emissions to the atmosphere requires re-evaluation and correction to higher values.