*Abstract* – Sorbent-trapped volcanic gases, sublimates and condensates from active vents of the La Fossa crater on the island of Vulcano (Aeolian Islands, Italy) as well as ambient and industrial air were quantitatively analyzed by *Short-Path Thermal Desorption-Solid Phase Microextraction-Cryotrapping-Gas Chromatography/Mass Spectrometry* (SPTD-SPME-CF-GC-MS). Among the well over 100 detected and quantified compounds are 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 found at concentrations well above laboratory, ambient air, adsorbent and field blank levels. For some analytes (e.g., CFC-11, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Br), concentrations are up to several orders of magnitude greater than even midlatitudinal 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<sub>2</sub> fluxes. This yields global halocarbon fluxes in the range from  $1.0 \times 10^{-9}$  Tg y<sup>-1</sup> (CClF<sub>3</sub>) to  $1.2 \times 10^{-4}$ Tg y<sup>-1</sup> (CH<sub>3</sub>Cl). Methyl bromide (CH<sub>3</sub>Br) and methyl iodide (CH<sub>3</sub>I) are estimated to have a volcanic model source strength of up to  $1.3 \times 10^{-6}$  Tg y<sup>-1</sup>, 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 and quiescent fumarolic 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.