Atmospheric CFCs and geogenic HCFCs in gas discharges from Mt. Etna and Vulcano Island (Italy)

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Significant concentrations of light hydrocarbons mainly pertaining to the alkane alkene and aromatic groups typically characterize fluids discharged from volcanic hydrothermal systems.
Halogenated species are of great interest due to their strong environmental impact and health effects since they play a key role as primary agents of tropospheric ozone depletion.
The recent increase of halocarbon concentrations in air especially that of chlorofluorocarbons (CFCs) is commonly ascribed to anthropogenic activities. Halocarbons are naturally produced from biogenic activity in soils from biomass combustion and from oceans and are reported to occur in volcanic plumes and gas emissions related to hydrothermal reservoirs. Although volcanic halocarbons were interpreted as related to an atmospheric source although recent studies reported geochemical evidence supporting the idea of a geogenic origin for halocarbons.
In the present study CFCs and HCFCs geochemistry in fumarolic gases discharged from Mt. Etna and Vulcano Island (Southern Italy) was investigated in order to elucidate the possible sources and processes controlling the emission of these organic species in a volcanic environments.
Halocarbon concentrations in gas discharges from these two volcanic systems were compared to those expected when the fraction of air present in our gas samples calculated on the basis of their Ar concentrations is considered. Such a detailed evaluation of halocarbon contribution due to background air values was carried out to assess if these gas compounds might have been generated in volcanic fluids from a geogenic source to check the efficiency of genetic
processes such as halogenation of methane and alkenes at hydrothermal conditions.
Our calculations evidence that the concentrations of most hydrogenated halocarbons in gases from both Etna and Vulcano are up to three orders of magnitude higher than those expected considering air as their unique source implying that these compounds have a geogenic origin.
Abundances of CFCs appear to be consistent with background air suggesting that processes of complete halogenation of organic compounds in natural environments are not efficient.