

Natural Halocarbon Compounds in Volcanic Gases

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Very few studies of volcanic and hydrothermal gas emissions have focused on the carbon-based (organic) chemistry of these discharges. The potential impact of cataclysmic events such as large explosive eruptions on the chemistry of the earth's atmosphere is well known. The atmospheric loading of volcanogenic SO₂ and CO₂ into the stratosphere has been documented, modeled and quantified in numerous studies, and their impact on global warming and atmospheric cycles is well established. Volcanic eruptions quickly penetrate the otherwise rather undisturbed tropopause, allowing immediate injection into the stratosphere, even of compounds with a short half-life that otherwise never reach such altitudes. The importance of such organic compounds from major volcanic emissions have so far been neglected in environmental and atmospheric impact studies. In an ongoing study of the organic and halocarbon discharges from volcanic systems, a large range of compounds have been detected well above atmospheric background concentration, using novel instrumental techniques. Our results from different test sites in the Mediterranean, Kamchatka and

New Zealand have led to quantitative information on compounds varying from simple alkanes, alkenes, and arenes to polyhalogenated and sulfonated higher aromatics, HCFC's, CFC's, and methyl halogenides, in some cases at concentrations up to several orders of magnitude higher than present-day atmospheric background. Among these are furans, anthracene, chlorinated, fluorinated and brominated mixed polyhalomethanes, such as trichlorofluoromethane (CFC-11), methylbromide, 2,2-difluoropropane (HFC-272), dichloromethane, chlorobenzene and others. As a result of the increased sensitivity of our method, halocarbon concentrations higher than previously reported have been detected. Based on our findings and the isomers present, we suggest these compounds have formed via gas-phase reactions in an ascending gas column together with subsequent polymerization, and halogenation reactions by high temperature radical chain reactions for the alkanes, as well as electrophilic substitution halogenation for arenes. The role of surface catalysis by mineral phases at high temperatures is poorly known.