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Volcanic emissions of molecular chlorine

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Volcanoes emit significant amounts of hydrogen chloride into the atmosphere, while other chlorine species in volcanic plumes are usually negligible. When eruption ceases, the cooling volcanic cone can work as a giant chemical reactor to convert residual HCl into
molecular chlorine (Cl2). Up to 60 ppmv (180 mg/m3) of Cl2 together with 30-77 ppmv HCl were measured in gas emissions from the Tolbachik scoria cones, Kamchatka, which are still hot after the 1975-1976 eruption. Other gas components were atmospheric air (94-99 vol%),
water vapor (1-6 vol%) and acid species (HF, CO_2, total less than 0.1 vol%). Two different processes can account for the existence of Cl2 in the Tolbachik emissions. The catalytic oxidation of volcanic HCl by air oxygen is probably the main source of Cl2. Fine crystals of
Fe and Cu oxides and chlorides on the altered basalt surface serve as a catalyst. The oxidative decomposition of the Na, K and Mg chloroferrates, formed as a result of acid leaching on the
cones, can also create high concentrations of molecular chlorine in volcanic gases. Both processes are cases of complex gas-water-rock interaction and have a unique interest because they have been described in nature for the first time.The estimated total discharge of Cl2 from the Tolbachik cones is ca. 12-16 t/yr.