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Emission of molecular chlorine from Earth’s volcanoes: a case of catalytic oxidation

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Up to 25 mg/m3 (10 ppmv) of molecular chlorine Cl2 together with 450 mg/m3 (270 ppmv) of HCl have been measured in August 2008 in gases escaping from New Tolbachik scoria cones, Kamchatka. This is the first natural point source of Cl2 in troposphere. The cones (55 [U+F0B0] 41’ N, 160 [U+F0B0] 14’E, 1200m asl) were formed during major Tolbachik Fissure eruption of basaltic lava in 1975. Thirty-three years after eruption, numerous discharges of hot gas (100-430 [U+F0B0] C) are scattered throughout craters’ rim. Gas releases through small holes and fissures in altered rocks. This gas has a composition unusual for volcano discharges. Actually, this is hot air (>98%) with admixture of water vapor (1-2%) and acid species including CO2 0.07-0.09 %, HCl 150-350 ppmv, Cl2 5-10 ppmv, some SO2, HF etc. To determine Cl2, HCl and SO2, we used colorimetric gas detector tubes. Also, we filled evacuated bottles with dry gas to measure N2, O2, Ar and CO2 by gas chromatography.

To ensure the possibility of such gas composition, we made thermochemical calculations (HSC 6.1). As a starting point, we used measured composition of gas. The model predicts equimolar amounts of Cl2 and HCl at 200 [U+F0B0] C. Equilibrium mixing ratio of NO2 is 3 orders of magnitude lower Cl2; other possible oxidizing species (ClOX, NO, HNO3) are in minor amounts. Therefore we concluded that Cl2 was the only oxidizing species to be measured by our detector tubes. Also, model has shown that little amount of SO2 can coexist with Cl2 in dilute mixture with air at 200-400 [U+F0B0] C.

We account high concentrations of Cl2 in Tolbachik gases for catalytic oxidation of HCl inside the cones: 4HCl + O2 = Cl2 + 2H2O. Ambient air seeps into highly porous material of the cone, is being heated inside and mixes with HCl that is slowly released by scoria particles. This is a natural analogue of Deacon process well known in industry. To check this hypothesis, we made a series of experiments. In lab, we filled silica glass tube with basaltic scoria and let pass through it a slow flow of air with admixture of diluted hydrochloric acid. After being roasted at 600 [U+F0B0] C, basaltic scoria acquired strong catalytic properties. Concentration of Cl2 in gas after passing the tube with roasted basalt was 2.5 orders of magnitude higher than in a blanc run (the tube filled with silica granules). The possible catalyst is fine hematite Fe2O3 formed on surface of scoria particles at 600 [U+F0B0] C in oxidizing atmosphere. We also observed formation of different copper chlorides like CuCl2, KCuCl3 at the outlet of the tube. These substances are known to be the most effective catalysts in industrial Deacon process. However, all these chlorides were deposited outside the reactor and seemed to have minor contribution in the catalytic process.

Our lower estimate of total release of Cl2 from Tolbachik cones is 0.5 g/s that corresponds to 15 tons per year. This is a very rough assessment. More precise measurements of gas composition as well discharge rates at Tolbachik cones are required.