Stratospheric input of heavy halogens (Br, I) from large explosive volcanic eruptions: Information from melt inclusions

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Large explosive volcanic eruptions inject gases, aerosols and ash into the stratosphere, thus influencing stratospheric chemistry and the Earth´s radiation budget. Halogens responsible for catalytic ozone depletion following large eruptions comprise chlorine (Cl), and the heavy halogens bromine (Br) and iodine (I) occurring in trace amounts in volcanic plumes. Due to the higher catalytic potential for ozone destruction of Br and I compared to Cl, even trace amounts of these elements in volcanic emissions are relevant for stratospheric chemistry. We have analysed halogens in volcanic glasses and in glass inclusions in phenocrysts using electron microprobe and synchrotron-XRF microprobe methods. Halogens from bulk glass samples were extracted using pyrohydrolysis, and analysed by ICP-MS.

Eruptions investigated include Baitoushan, China /North Korea (ca. 969 AD), Mt. Hudson, Chile (1991), and several dacitic Quaternary eruptions from Nicaragua. Chlorine concentrations in glass inclusions are typically 2000 to 4000 ppm, which is on average about 50% higher than the concentrations in the matrix glasses. Br concentrations in glass inclusions are typically in the range of 2 to 20 ppm. This gives an average Cl/Br ratios of about 300:1. Using the petrologic method, involving the concentration differences of halogens between the glass inclusion and those retained in the matrix glass, the average Cl/Br ratio of the volcanic emissions were about 200:1. Typical I concentrations of Nicaraguan glass inclusions range between 1 and 3 ppm. The resulting Cl/ I ratio of eruptive emissions is about 1100:1. Depending on eruption size, each large event injected between several kt and several hundred kt Br and I into the atmosphere. As a first approach to estimate global Br and I fluxes from subduction zones, although affected by several sources of uncertainty, we combine these halogen ratios of 200:1 and 1100:1 for Cl/Br and Cl/I, respectively, with the global eruptive Cl flux of 1.5 x 10^8 kg m^{-1} Ma^{-1} (Wallace 2005, JVGR) , leading to fluxes of 7.5 x 10^5 kg m^{-1} Ma^{-1} for Br and 1.4 x 10^5 kg m^{-1} Ma^{-1} for I.

XAFS study of the structural behaviour of monazite

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Natural monazite that have undergone radiation damage over billion years, appear to be good analogues to understand the behavior of such matrix under storage and weathering conditions.

To investigate the structural behavior of monazite, several natural samples were collected from different location around the world. The samples were characterized using SEM, XRD and electron microprobe.

Analysis of the EXAFS data collected at the L_{III} edge of Th incorporated in monazite structure show an average interatomic distance Th-O equal to that of Ce-O (2.50(2) Å) in crystalline monazite. Therefore, no expansion or contraction of the local structure around Th substituting REE in monazite was observed.

In addition, EXAFS spectra at P-K edge show an average of ~4.5 atoms in the coordination shell in metamict monazites. This over-estimation of the coordination number in metamict monazites is explained by the presence of certain P atoms 3-, 5- and/or 6-fold coordinated: This is due, undoubtedly, to the effects of the radiation damage on the structure of monazite. Moreover, the average interatomic distance of the coordination shell was found to be (~1,61(2) Å) longer than the one in crystalline monazites (~1,56(2) Å). This is explained by the large number of atoms first neighbours and the large distortion of the polyhedron of coordination.