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New insights on Br speciation in volcanic glasses and structural controls on halogen degassing

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Abstract

The volcanic degassing of halogens, and especially of the heavier Br and I, received increased attention over the last 20 years due to their significant effect on atmospheric chemistry, notably the depletion of stratospheric ozone. While the effect of melt composition on halogen diffusion, solubility, or fluid-melt partitioning in crustal magma chambers has been thoroughly studied, structural controls on halogen incorporation in silicate melts remain poorly known, with only few studies available in simplified borosilicate or haplogranite compositions.

Here, we demonstrate that high-energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS) with a crystal analyzer spectrometer (CAS) is well-suited for the study of Br speciation in natural volcanic glasses which can contain lower Br concentrations than their laboratory analogs. Especially, HERFD-XAS results in sharper and better-resolved XANES and EXAFS features than previously reported and enables detection limits for EXAFS analysis down to 100 ppm when previous studies required Br concentrations above the 1000 ppm level. XANES and EXAFS analyses suggest important structural differences between synthetic haplogranitic glass, where Br is surrounded by Na and next-nearest oxygen neighbors, and natural volcanic glasses of basaltic to rhyodacitic compositions, where Br is incorporated in at least three distinct sites, surrounded by Na, K, or Ca. Similar environments, involving both alkali and alkaline earth metals have already been reported for Cl in Ca-bearing aluminosilicate glass and our study thus underlines that the association of Br with divalent cations (Ca^{2+}) has been underestimated in the past due to the use of simplified laboratory analogs. Overall, similarities in Cl and Br structural environments over a large array of compositions (46–67 wt% SiO_2) suggest that melt composition alone may not have a significant effect on halogen degassing and further support the coupled degassing of Cl and Br in volcanic systems.

Keywords: Halogens, bromine, magmas, volcanic glasses, speciation, HERFD-XAS; Halogens in Planetary Systems