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

MARION LOUVEL1,2,*,‡, ANITA CADOUX3,†, RICHARD A. BROOKER2, OLIVIER PROUX4, and JEAN-LOUIS HAZEMANN5

1Institute for Mineralogy, WWU Muenster, DE48149, Germany
2School of Earth Sciences, Bristol University, BS81RJ, Bristol, U.K.
3GEOPS, Université Paris Sud, CNRS, Université Paris-Saclay, 91405 Orsay, France
4Observatoire des Sciences de l’Univers Grenoble (OSUG), UMS 832 CNRS, Universite Grenoble Alpes, F-38041 Grenoble, France
5Institut Néel, UPR 2940 CNRS, Universite Grenoble Alpes, F-38000 Grenoble, France

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 (Ca2+) 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% SiO2) 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

INTRODUCTION

Despite their minor concentrations compared to H2O and CO2, halogens (F, Cl, Br, and I) are critical elements in the evolution of magmatic and volcanic systems, for instance affecting magma rheology and enabling the scavenging and hydrothermal concentration of metals in the crust (Dolejš and Zajacz 2018; Webster et al. 2018 and references therein). Their release through volcanic degassing has also been demonstrated to affect atmospheric chemistry with the rapid transformation of HBr to reactive BrO during explosive eruptions triggering ozone depletion at local (within volcanic plume; Bobrowski et al. 2003; Roberts et al. 2009) to global scales (if the plume reaches the stratosphere; Cadoux et al. 2015; Klobas et al. 2017; Kutterolf et al. 2013). Recent improvements in the analytical characterization and detection limits for F, Cl, Br, and I in solid, liquid, or gaseous samples (i.e., Cadoux et al. 2017; Lubcke et al. 2014; Roberts et al. 2017; Seo et al. 2011) have also opened new opportunities to use halogen concentrations and elemental ratios (F/Cl, Cl/Br, or BrO/SO2) from volcanic fumaroles, undegassed melt inclusions, or degassed lavas as tracers of magma storage conditions, magmatic/hydrothermal activity, or eruption dynamics (Balcone-Boissard et al. 2010; Dinger et al. 2018; Lubcke et al. 2014; Seo and Zajacz 2016). Yet, the effect of decompression on Br/S fractionation or the role of mineral sinks such as apatites and sodalites in the volcanic cycling of halogens remain poorly constrained and thus limits the interpretation of these samples.

The accurate interpretation of the information carried in melt inclusions or degassing patterns at different volcanic centers requires the development of comprehensive geochemical models that describe the behavior of different volatiles during fluid exsolution and especially how they partition between magma (melt + crystals) and bubbles or brines (Burgisser et