



Bromine speciation in hydrous silicate melts at high pressure



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ABSTRACT

Br speciation in hydrous silicate melts at high pressure has been investigated up to 7.6 GPa using X-ray absorption spectroscopy (XAS) at the Br K-edge in a Paris–Edinburgh press. Br in silicate melts is surrounded by an average of 6 Na cations, a number slightly increasing with pressure (5.8 to 6.6), with a Br–Na distance increasing from 3.49 to 3.72 Å. Two oxygens, either from a water, an –OH molecule or from the tetrahedral silicate network, with an average Br–O distance of 1.80 Å, form the closest coordination shell around Br ions. The persistence of an alkali shell around Br, in a structure similar to crystalline NaBr, throughout the pressure range investigated shows that Br can be retained in the melt structure at relatively high pressure and supports the idea of its deep recycling. Finally, our results confirm that Br could be efficiently degassed with water at low pressures and that Br may also have been efficiently degassed along with water during the early stages of an oxidized magma ocean.

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1. Introduction

The halogens (fluorine, chlorine, bromine and to a lesser extent iodine) influence the properties of silicate melts and play an important role in a range of magmatic and hydrothermal processes, from the evolution of magmatic systems to the transport of metals in fluids and the environmental impact of atmospheric emissions during degassing processes (e.g., Chevychelov et al., 2008; Aiuppa et al., 2009; Edmonds et al., 2009; Pyle and Mather, 2009; Baasner et al., 2013). In order to predict the physical and chemical properties of silicate melts, the fluids that they exsolve, and the glasses that they form, a detailed knowledge of the solubility and speciation of halogens in silicate melts at relevant conditions of pressure and temperature is essential. Most previous experimental studies have focussed on the determination of their solubility, partitioning behavior or diffusion at pressures relevant for degassing processes ($P < 0.3$ GPa) (Webster, 1992; Bureau et al., 2000; Signorelli and Carroll, 2002; Bureau and Métrich, 2003; Alletti et al., 2007; Baker and Balcone-Boissard, 2009). In a more recent investigation conducted at pressures of up to 1.7 GPa, Bureau et al. (2010) suggested that the Br cycle in subduction zones is divided in two parts:

one superficial cycle, with Br being returned to the atmosphere via volcanism, and another deeper cycle, with Br being recycled back to the mantle via silicate melts. This raises the question of the Br local environment in high-pressure silicate melts as a function of pressure, which is currently virtually unknown. Knowledge of the local structure is particularly important for activity-composition models, which are used to calculate the effects of mixing on the thermodynamic properties of a system. Experimental measurements are therefore needed to constrain the local structure around the halogens in order to further quantify their chemical behavior (solubility, partitioning behavior and diffusion) in the subducting slab, mantle wedge and Earth's mantle. In addition, such measurements will ultimately help to model halogen mobilization, transport and degassing in subduction zones or during the degassing of the magma ocean.

In this context, X-ray absorption spectroscopy (XAS), and more particularly extended X-ray absorption fine structure (EXAFS) spectroscopy can play an important role as it is extremely sensitive to the short-range structure around selected atomic sites in both solid and liquid phases. Indeed, in situ XAS measurements have previously been performed in hydrothermal diamond-anvil cells (HDAC) or autoclaves to characterize the speciation of diverse elements in geologically relevant environments at pressures of up to 2.4 GPa (Testemale et al., 2009; Louvel, 2011; Louvel et al., 2013; Mayanovic et al., 2013). The preliminary in situ XAS work of Louvel (2011) in HDAC on Br speciation in aqueous

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fluids, hydrous haplogranitic and sodium disilicate melts at up to 2.2 GPa has shown that water molecules in the coordination shell of Br in the fluids are gradually replaced by Na ions as the amount of dissolved alkali silicates in the fluid increases. In the present work, we investigated the Br speciation in a hydrous alkali silicic melt at high pressure using XAS at the Br K-edge and a Paris–Edinburgh press. Here, the use of the Paris–Edinburgh press has enabled us to record high-quality data with stable experimental conditions at higher pressures and temperatures relevant to subduction zones and the upper mantle. We therefore focussed our study on the speciation of Br in a hydrous silicic melt up to 7.6 GPa and 1400 °C. XAS (EXAFS and XANES) analysis were conducted on the parent Br bearing glass at ambient conditions, on the melt at 2.1, 3.4 and 7.6 GPa at 1400 ± 70 °C, and on the resulting high-pressure quenched glasses. Six crystalline standards (CaBr₂, FeBr₂, NaBr, KBr, KBrO₃, NaBrO₃) were measured to facilitate the modeling of the possible Br valences and chemical environments that may be present in the investigated melts and glasses.

2. Materials and methods

2.1. Generation of high-pressure high-temperature conditions

For the in situ measurements, high pressure–high temperature (high *P*–*T*) conditions of up to 7.6 GPa and 1400 °C were generated using a Paris–Edinburgh press. We used a modified cell assembly calibrated by Van Kan Parker et al. (2010), consisting of a 7/2.4 mm boron epoxy gasket, a graphite heater and an hBN pressure transmitting medium. We used nano-polycrystalline diamond (NPD) capsules synthesized at Geodynamics Research Center, Ehime University, Matsuyama, Japan (Irifune et al., 2003) instead of single crystal diamond or polycrystalline diamond capsules in order to eliminate the serious interference of the diamond Bragg peaks in the EXAFS spectra. Pt–Rh5% lids were also inserted on either side of the nano-polycrystalline diamond capsule to prevent the loss of volatiles. The NPD cylinder (1.5 mm in height and 0.75 mm inner diameter) and Pt–Rh5% lids were enclosed between two hBN caps on both ends acting as *P*-transmitting media. High *T* was achieved by resistive heating through the graphite heater. A Pt foil was inserted between the diamond capsule and the graphite heater as a pressure marker. Pressure transmission to the sample inside the rigid nano-polycrystalline diamond capsule is fully achieved for temperature above 1000 °C (Van Kan Parker et al., 2010). Experiments were conducted by cold compression of the sample to a given pressure, followed by gradual heating to 1400 °C at constant oil pressure. The temperature was determined from previous calibration measurements of the cell-assembly (Van Kan Parker et al., 2010) and the pressure was derived from the cell volume of Pt. Estimated error bars are ± 0.25 GPa on *P*, and ± 70 °C on *T*. Before recording the EXAFS spectra, the molten state of the sample was assessed by the disappearance of crystalline Bragg peaks in the diffraction patterns recorded on a MAR detector. X-ray radiographic images of the sample were systematically recorded before and after collection of XAS data to check for homogeneity/heterogeneity of the sample and the lack of crystallization.

2.2. Samples and characterization of materials

Silicic andesite samples from recent eruptions of Mt. Pelée (Martel et al., 1998) were first melted at 1450 °C under atmospheric conditions for one hour before quenching to a glass in distilled water. The glass was ground in an agate mortar under ethanol and re-melted to ensure chemical homogeneity. It was then doped with 4 wt.% NaBr and 4 wt.% H₂O in a internally heated pressure vessel pressurized with an Ar–H₂ gas mixture, holding for forty-two hours at 1250 °C and 0.2 GPa thus ensuring the presence of iron in its reduced form, Fe²⁺, in the parent glass. The composition of the parent glass and the quenched products recovered from the 2.1 and 3.4 GPa runs, as specified in Table 1, were determined with a CAMECA SX100 electron microprobe at the EMMAC

Table 1

Chemical composition^a (wt.%) of the starting material and of the recovered glass samples.

	Parent glass	Quenched glass	
		2.1 GPa	3.4 GPa
SiO ₂	73.27 ₍₇₀₎	71.29 ₍₅₈₎	71.50 ₍₇₂₎
TiO ₂	0.30 ₍₁₎	0.29 ₍₇₎	0.28 ₍₁₎
Al ₂ O ₃	12.20 ₍₃₀₎	11.93 ₍₂₅₎	13.23 ₍₃₃₎
FeO ^b	0.83 ₍₁₆₎	0.04 ₍₁₂₎	0.02 ₍₁₀₎
MgO	0.41 ₍₄₎	0.40 ₍₁₉₎	0.41 ₍₅₎
MnO	0.08 ₍₁₎	0.09 ₍₂₎	0.04 ₍₁₎
CaO	2.29 ₍₁₄₎	2.19 ₍₁₃₎	2.26 ₍₁₄₎
Na ₂ O	4.19 ₍₂₁₎	4.79 ₍₂₉₎	4.85 ₍₂₃₎
K ₂ O	1.60 ₍₁₃₎	1.62 ₍₁₈₎	1.73 ₍₁₄₎
P ₂ O ₅	0.01 ₍₁₎	0.01 ₍₁₎	0.01 ₍₁₎
Cl	0.01 ₍₁₎	0.01 ₍₂₎	0.01 ₍₁₎
Br ^{c/d}	2.20 ₍₂₂₎ /2.28 ₍₁₃₎	2.27 ₍₃₁₎ /2.21 ₍₁₅₎	2.27 ₍₂₂₎ /1.97 ₍₁₂₎
H ₂ O ^{e/f}	3.50 ₍₅₀₎ /3.72 ₍₃₆₎	4.20 ₍₅₀₎ /–	3.80 ₍₅₀₎ /4.41 ₍₄₃₎

^a Average of 10 analyses given with the standard deviation (number in brackets) in terms of the least unit cited.

^b Total iron reported as FeO.

^c Determined by PIXE analysis.

^d Determined by electron microprobe analyses.

^e Determined by Raman spectroscopy.

^f Determined by ERDA analysis.

center (The Edinburgh Materials and Micro-Analysis Centre), University of Edinburgh. It was not possible to retrieve and analyze the quenched sample from the 7.6 GPa run as a blowout occurred before quenching. The microprobe analyses were performed under “soft” operating conditions, in order to avoid any loss of Na and volatiles, with a 15 kV accelerating voltage, a defocused beam of 10 μm and a current of 15 nA. We note that the parent glass and the run products have similar chemical compositions, given the analytical uncertainties, with the exception of the lack of iron in the run products, a result of the reaction between the Fe²⁺ present in the parent glass with the Pt–Rh5% lids of the Paris–Edinburgh cell assemblies. The electron microprobe analysis of Br is hindered by the high ionization potential for the K-lines of Br, resulting in low count rates and the overlapping of the L-lines of Br and the K-lines of Al. The Br concentration of the parent glass and glasses quenched from high pressure was instead determined by Proton-induced X-ray emission (PIXE) analyses performed using a nuclear microprobe (LEEL, CEA/DSM/IRAMIS/SIS2M, CEA Saclay, France) (Khodja et al., 2001), using $3 \times 3 \mu\text{m}^2$ incident beam of protons at 3.2 and 2.5 MeV. Br was detected based on the Kα and Kβ X-rays (11.92 and 13.29 keV respectively). The details of the procedure are described in (Bureau et al., 2010). The PIXE analysis yielded a Br concentration of 2.20 ± 0.13 wt.% for the starting glass, which is identical to the Br concentration determined by electron microprobe analysis within analytical uncertainties (see Table 1). The glasses quenched from high pressure were also studied by Scanning Electron Microscopy (SEM) with a Zeiss Ultra 55 field emission scanning electron microscope (SEM) with a working distance of 3 ± 0.2 mm and an acceleration voltage of 15 keV at the Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), Sorbonne Universités, Paris, France (Fig. 1a). A few sanidine crystals are noticeable in the vicinity of the capsule's walls, but these do not hinder the EXAFS analysis as the EXAFS spectra are representative of the sample in the center of the capsule. The water content of the samples was determined by Raman spectroscopy measurements (Losq et al., 2012) and by Elastic Recoil Detection Analysis (ERDA) (Bureau et al., 2009). Raman spectra were acquired at the IMPMC using the 1500 grooves/mm grating of the spectrometer and a 514 nm wavelength laser and are shown on Fig. 1b. ERDA measurements were carried out using a nuclear microprobe (LEEL, CEA/DSM/IRAMIS/SIS2M, CEA Saclay, France) producing a 3 MeV ⁴He⁺ micro-beam with a final incident beam size of approximately $16 \times 4 \mu\text{m}^2$ (horizontal \times vertical).

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