The role of melt composition on aqueous fluid vs. silicate melt partitioning of bromine in magmas

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ABSTRACT

Volcanogenic halogens, in particular bromine, potentially play an important role in the ozone depletion of the atmosphere. Understanding bromine behaviour in magmas is therefore crucial to properly evaluate the contribution of volcanic eruptions to atmospheric chemistry and their environmental impact. To date, bromine partitioning between silicate melts and the gas phase is very poorly constrained, with the only relevant experimental studies limited to investigation of synthetic melt with silicic compositions. In this study, fluid/melt partitioning experiments were performed using natural silicate glasses with mafic, intermediate and silicic compositions. For each composition, experiments were run with various Br contents in the initial fluid (H_2O–NaBr), at T–P conditions representative of shallow magmatic reservoirs in volcanic arc contexts (100–200 MPa, 900–1200 °C). The resulting fluid/melt partition coefficients ($D_{Br}^{f/m}$) are: 5.0 ± 0.3 at 1200 °C–100 MPa for the basalt, 9.1 ± 0.6 at 1060 °C–200 MPa for the andesite and 20.2 ± 1.2 at 900 °C–200 MPa for the rhyodacite. Our experiments show that $D_{Br}^{f/m}$ increases with increasing SiO_2 content of the melt (as for chlorine) and suggest that it is also sensitive to melt temperature (increase of $D_{Br}^{f/m}$ with decreasing temperature). We develop a simple model to predict the S–Cl–Br degassing behaviour in mafic systems, which accounts for the variability of S–Cl–Br compositions of volcanic gases from Etna and other mafic systems, and shows that coexisting magmatic gas and melt evolve from S-rich to Cl–Br enriched (relative to S) upon increasing degree of degassing. We also report first Br contents for melt inclusions from Etna, Stromboli, Merapi and Santorini eruptions and calculate the mass of bromine available in the magma reservoir prior to the eruptions under consideration. The discrepancy that we highlight between the mass of Br in the co-existing melt and fluid prior to the Merapi 2010 eruption (433 and 73 tons, respectively) and the lack of observed BrO (from space) hints at the need to investigate further Br speciation in 'ash-rich' volcanic plumes. Overall, our results suggest that the Br yield into the atmosphere of cold and silicic magmas will be much larger than that from hotter and more mafic magmas.

1. Introduction

Volcanic degassing is an important process in sustaining the composition of Earth's atmosphere (e.g., Gaillard and Scaillet, 2014; Mather, 2015). Whilst much progress has been made constraining global volcanic fluxes, uncertainties remain regarding the emissions of the key halogen species, especially the trace Br- and I-bearing species (Pyle and Mather, 2009). However, improvements

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in remote sensing techniques and analytical techniques, and their application to an increasing number of active volcanoes, have provided new data on the concentrations of these minor components in volcanic gases (e.g., Gerlach, 2004; Aiuppa et al., 2005; Aiuppa, 2009; Bobrowski et al., 2015), which in turn can be used to better constrain their global fluxes to the atmosphere (Pyle and Mather, 2009). Bromine has received particular attention over the last decade, owing to its important role in atmospheric chemistry in general (e.g., Oppenheimer et al., 2006; Roberts et al., 2009, 2014) and ozone depletion in the troposphere and stratosphere in particular (von Glasow et al., 2009; Kutterolf et al., 2013; Cadoux et al., 2015). Global compilations show that Br sources (emissions to the atmosphere) and sinks (removal routes from the atmosphere) are not strictly balanced, hinting at a missing natural source of Br (Montzka et al., 2011). The direct detection of HBr and BrO in volcanic plumes (Bobrowski et al., 2003; Aiuppa et al., 2005) suggests that volcanic activity may be one such a source.

The correct evaluation of the contribution of past volcanic eruptions to atmospheric chemistry depends on our ability to evaluate Br behaviour in magmas, in particular its partitioning between silicate melt and gas phases. So far, only a few experimental studies have been performed on this topic, and have investigated Br behaviour in synthetic albite to rhyolite melt compositions (Bureau et al., 2000; Bureau and Métrich, 2003). However, natural silicate melt compositions can depart significantly from such model systems, in particular by having elevated contents of Fe, Mg or Ca, which (as Na) can complex with halogens thereby enhancing their solubility in silicate melts (Cochain et al., 2015). The relationship between halogen solubility and their complexation with cations has been shown for Cl; chlorine solubility in most silicate melts is dominantly controlled by the abundances of Mg $\sim$ Ca > Fe > Na > K > network-forming Al > Li $\sim$ Rb $\sim$ Cs, but Ti, F, and P also have strong influences (e.g., Webster et al., 1999; Webster and De Vivo, 2002). There is thus a need to evaluate the role of melt composition on Br behaviour in magmas, which is the main motivation of the present study. To that end, we have performed fluid/melt partitioning experiments on natural basalt, andesite and rhyodacite compositions under P–T–H_2O–redox storage conditions relevant to shallow arc magmas. Combining our Br partition coefficient for the basaltic composition, with other experimental data on S and Cl behaviour, and volcanic gas compositions from the literature, we develop a simple first-order model to predict the S–Cl–Br degassing behaviour in mafic systems. We also measure Br contents of melt inclusions from Etna, Stromboli, Merapi and Santorini eruptions and estimate the mass of bromine in the pre-eruptive magmas, this allows us to address the atmospheric contribution of open-vent mafic volcanoes versus that of intermediate-silicic volcanoes.

2. Fluid/melt partitioning experiments

2.1. Starting material

The selected starting materials are natural volcanic rocks: a hawaiitic basalt from a 2002 Etna eruption (Lesne et al., 2011a, 2011b; Iacono-Marziano et al., 2012), a calc-alkaline andesite and a rhyodacite from the Santorini Upper Scoria-2 (USC-2) and Minoan eruptions, respectively (Cadoux et al., 2017). The whole rocks were crushed and ground in an agate mortar. About 10 g of the powders were melted twice (and ground in between), to ensure homogenization, in a platinum crucible at 1400 °C–1 atm for 3–4 h in a piezoceramic oven, and quenched in cold water. The resulting dry glasses were ground to powder and constituted the starting

Table 1
Major element composition of the starting dry glasses used for the partitioning experiments.

Volcano: eruption Sample name	Etna: 11/22/2002 ET02PA27[a]		Santorini: USC-2 S09-22[b]		Santorini: Minoan S82-30[c]	
Major oxides (wt%)	$n = 32$	$\pm 1\sigma$	$n = 8$	$\pm 1\sigma$	$n = 22$	$\pm 1\sigma$
SiO$_2$	47.95	0.82	58.88	0.43	71.24	0.26
TiO$_2$	1.67	0.11	1.28	0.05	0.45	0.04
Al$_2$O$_3$	17.32	0.27	16.16	0.17	14.87	0.15
FeO$_{tot}$	10.24	0.13	8.18	0.25	2.85	0.18
MnO	nd	nd	0.20	0.09	0.08	0.05
MgO	5.76	0.28	2.77	0.09	0.73	0.05
CaO	10.93	0.37	6.46	0.12	2.34	0.14
Na$_2$O	3.45	0.16	4.07	0.15	4.24	0.08
K$_2$O	1.99	0.10	1.67	0.06	3.08	0.11
P$_2$O$_5$	0.51	0.12	0.31	0.06	0.13	0.04
Original sum	99.82		96.66		98.40	

Major element analyses performed by electron microprobe.
n: number of analyses, σ: standard deviation of the average of n analyses, nd: not determined.
These dry glasses were also used to synthesize Br standards characterized in Cadoux et al. (2017).
[a] From Iacono-Marziano et al. (2012).
[b] From Cadoux et al. (2017), recalculated to 100%.
[c] From Cadoux et al. (2014, 2017), recalculated to 100%.

material for both (i) bromine standard glasses synthesis (Cadoux et al., 2017) used to calibrate bromine analyses (Section 3) and (ii) partitioning experiments. The compositions of the starting glasses are given in Table 1.

2.2. Experimental procedure

Equilibrium partitioning experiments (neglecting kinetic effects) were performed in an Internally Heated Pressure Vessel equipped with a rapid quench device at the Institut des Sciences de la Terre d'Orléans (ISTO, Orléans, France). The chosen experimental T–P–fO_2 conditions are representative of those in shallow crustal reservoirs in volcanic arc contexts (Martel et al., 1999; Di Carlo et al., 2006; Cadoux et al., 2014; Kahl et al., 2015) and are reported in Table 2: T (± 10 °C) = 900, 1060 and 1200 °C, P (± 2 MPa) = 100 and 200 MPa, and fO_2 estimated around the Ni–NiO (NNO) buffer, on the basis of the partial pressure of H$_2$ imposed in the vessel ($\sim$2 bars; Di Carlo et al., 2006; Cadoux et al., 2014).

We deliberately used a fluid solely composed of H$_2$O and Br. Experiments with simplified fluids are necessary for comparison with future experiments which will include additional volatile species (e.g., CO$_2$, S), and will permit us to assess whether or not the presence of other volatile species can modify Br behaviour.

Capsules were always loaded so that the mass ratio between the aqueous fluid and the glass (silicate) phases was equal to or lower than 0.1 (Table 2), which avoids significant silicate dissolution into fluid during experiments. About 50 to 100 mg of glass powder was loaded into Au or Au–Pd capsules (2.5 mm internal diameter, 20–30 mm in length) together with 3–8 mg of a solution composed of distilled water and dissolved NaBr salt. These amounts of solution (6–10 wt%) ensure the attainment of fluid saturation of the silicate melts at the investigated T–P conditions. Different solutions with Br contents between 0.1 and 14 wt% Br were employed. The runs lasted between 24 and 92 h, depending on the temperature (Table 2). Chlorine partitioning experiments of Alletti et al. (2009) performed at 1200 °C with a basaltic melt showed that 3–4 h were sufficient to attain equilibrium at 1200 °C and $P > 1$ MPa. Considering that Br diffusion coefficient appears to be 2–5 times lower than the other halogens in basaltic melts (at 500 MPa to 1.0 GPa, 1250 to 1450 °C and at anhydrous conditions; Alletti et al., 2007), we chose a 24 h run duration for our experi-