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An experimental study of bromine behaviour in water-saturated silicic melts

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Abstract—To assess the effect of the melt composition on bromine concentrations in magmas, we have investigated bromide solubility for water-saturated, iron-free silicic melts with variable Na+K/Al and Si/Al molar ratios (albite, haplogranite, rhyolite, and pantellerite). The experiments were performed in rapid quench cold-seal autoclaves over a range of pressure (1, 1.5, and 2 kbar) and temperature (900, 1000, and 1080 °C) with run durations from 5 to 7 days. A series of natural volcanic glasses and melt inclusions hosted in magmatic minerals were analysed together with the synthetic glasses by PIXE (proton-induced X-ray emission). The Br concentrations range from 5360 to 7850 ppm for albite, from 2800 to 3900 ppm for haplogranite, from 4300 to 5900 ppm for rhyolite, and from 9745 to 11,250 ppm for pantellerite. Br concentrations are negatively correlated with pressure in H₂O-saturated silicic melts and vary with (Na+K)/Al molar ratio with a minimum value at the ratio close to unity. Br behaves similarly to chlorine for all of these melt compositions. The bromide solubility is similar in albitic and rhyolitic melts, which implies that $D^{f/m}$ is nearly the same for both compositions and is applicable for natural rhyolites as suggested in our previous study (Bureau et al., 2000). This means that the volcanic Br contribution to the atmosphere may be significant. In natural obsidian samples and MI hosted in quartz, olivine, and leucite, the Br concentration varies from < 3 to 28 ppm, with the highest concentrations in pantelleritic melts. We attribute the low Br concentrations of natural melts to a low initial abundance of this halogen in the Earth mantle. However, because Br behaves as an incompatible element before water exsolution, our results imply that magmas could contain much more dissolved Br before eruption and water degassing than the few ppm usually measured in volcanic rocks. Br behaviour during magma crystallisation is controlled by its partitioning into the H₂O-rich fluid phase when this occurs. In addition, its potential high solubility in silicate melts makes it a very sensitive chemical tracer of magma contamination by seawater and Br-rich material. This infers that the investigation of Br behaviour in subduction-zone samples may help for a better understanding of volatiles cycling between the Earth reservoirs. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

Halogens are minor volatiles in the Earth mantle and crust, but they have significant and specific influences on magmatic and degassing processes. Chlorine and fluorine behaviours are now well constrained from several experimental studies (for review, see Carroll and Webster, 1994; Jambon, 1994). Bromine behaviour in magmas is much less known because Br concentrations in magmatic, mantle, or meteoritic samples are extremely low (Yoshida et al., 1971; Dreibus et al., 1979; Schilling et al., 1980; Carroll and Webster, 1994; Jambon et al., 1995). However, Br plays a significant role in geologic processes. For example, volcanic emission of Br may affect the atmosphere (Coffey, 1996). In a previous study, we determined the partition coefficients of Cl, Br, and I between aqueous fluids (f) and albitic melts (m) as $D^{f/m}_x = (X)_{\text{fluid}}/(X)_{\text{melt}}$, where (X) is the concentration of element X in the fluid or in the melt phase (Bureau et al., 2000). We have shown that the halogen partitioning into the aqueous fluid strongly increases with the ionic radius of the element from $D^{f/m} = 8.5 \pm 0.2$ for Cl, to 17.5 ± 0.6 for Br, and 104 ± 7 for I. As Br partitions into an H₂O-rich vapor phase more than Cl, Br is probably injected into stratosphere during large volcanic eruptions of H₂O-rich silicic magmas and presumably plays a key role in the strato-

spheric ozone depletion cycles. In this study, we investigated bromide solubility in various water-saturated silicic melts covering a range of magmas corresponding to various geodynamic environments. Our aim is to understand the effect of the melt composition on Br concentrations in magmas and Br behaviour during volcanic degassing and to better constrain the geochemical cycle of this heavy halogen element. In a first step, we determined the maximum Br concentrations for synthetic iron-free silicic melts with variable Na+K/Al and Si/Al molar ratios at saturation conditions with respect to NaBr and water. In a second step we compared our experimental results with natural samples: volcanic glasses and melt inclusions from different settings.

2. STARTING MATERIALS AND EXPERIMENTAL METHOD

Four iron-free compositions were chosen to represent the silicic melts commonly found in nature, including albite, haplogranite, rhyolite, and pantellerite. The starting glasses were prepared from powders of high-purity oxides and carbonates. These mixtures were decarbonated by slow heating from room temperature to 1200 °C in a platinum crucible within a 10-h period and melted at 1600 °C for 1 h before being quenched as glasses in distilled water and crushed to powders. Experimental conditions were chosen based on the numerous studies performed on Cl partitioning and solubility, assuming that Cl and Br behave more or less similarly. About 10 mg of powder were sealed in Pt capsules together with 3 mg of NaBr-saturated H₂O solution (7 mol.kg⁻¹) corresponding to saturating conditions for the melt with respect to water and molten NaBr (hydrosaline liquid) during the run.

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The experiments were performed at the Bayerisches Geoinstitut Bayreuth (Germany) in rapid-quench, cold-seal TZM vessels over a range of pressure (1, 1.5, and 2 kbar) and temperature (900, 1000, and 1080 °C) with run durations from 5 to 7 days. Because we found no data on Br diffusion in melts, the duration was based both on previous experimental studies of Cl solubility and on our earlier data on Br (Bureau et al., 2000). In this earlier work, we performed two kind of experiments: (1) experiments at 900 °C, 2 kbar, 7 days with the same initial glass charges (10 mg) of albite composition and (2) reference glasses synthesis in rapid-quench, cold-seal TZM autoclaves at 1100 °C, 1 kbar over 3 days. All of our samples were homogeneous with respect to Br concentration. According to these results, we estimate that a run duration of 5 to 7 days is sufficient to attain equilibrium at those pressure and temperature conditions. At the end of an experiment, the sample was isobarically quenched to room temperature within 1 to 2 s by dropping the capsule into the cold zone of the vessel. Capsules were checked for leaks before and after the experiments.

3. ANALYTICAL TECHNIQUES

Because the run products are hydrous glasses containing numerous fluid inclusions, microbeam techniques were necessary to analyse the glass phase to avoid any contamination from the fluid inclusions. Major elements from the natural and synthetic glasses and melt inclusions were analysed by electron microscopy using a Cameca SX50 (Cameca, Université Paris VI). Operating conditions were chosen to be "soft" to avoid any Na loss during the analyses (15 nA, 15 kV, 30- μ m beam size, 10-s counting time per element). Minor elements in natural samples, such as Cl, were measured using "harder" operating conditions: 30 nA, 15 kV, 30- μ m beam size, 100-s counting time. Water concentrations were determined by FTIR spectroscopy. Infrared spectra were taken for doubly polished chips of glasses using a Nicolet Magna 550 Fourier-transform spectrometer coupled to an IR-Plan microscope with a spot analysis of 40- μ m diameter. Water concentrations were calculated from the spectra following the procedures described in Silver and Stolper (1985), Newman et al. (1986), and Nowak and Behrens (1995), depending on the composition of the glasses. The Br concentration of glasses and glassy inclusions were measured by micro-PIXE (proton induced X-ray emission) using the Laboratoire Pierre Süe nuclear microprobe (CEA-CNRS, Saclay, France) at 2.5-MeV incident proton energy (Br $K\alpha$ and $K\beta$ X-rays). The integrated charge (Q) varied between 1 and 3 μ C as a function of the sample concentrations, with 700 to 800 pA as beam current and 30 \times 30 to 5 \times 5 μ m² area analysed using a scanning mode (spot size 2 \times 2 μ m²), depending on the size of the samples (density of fluid inclusions in large pieces of synthetic glasses, small glassy inclusions trapped in crystals). An aluminium filter of 200- μ m thickness was placed in front of the Si(Li) X-ray detector, and the X-rays were detected at an angle of 45° and a distance from the target of 5.5 cm. The data were treated with GUPIX software (Maxwell et al., 1989), as previously described in Bureau et al. (2000). The homogeneity of the synthetic glasses was checked by performing 10 to 15 analyses per sample at different locations.

4. EXPERIMENTAL RESULTS

4.1. Significance of Br Concentrations in Synthetic Glasses

The Br concentrations of the resulting hydrous synthetic glasses range from 5360 to 7850 ppm for albitic glasses, from 2800 to 3900 ppm for haplogranitic glasses, from 4300 to 5900 ppm for rhyolitic glasses, and from 9745 to 11,250 ppm for pantelleritic glasses (Table 1). These hydrous synthetic glasses are homogeneous with respect to Br, water, and major elements for all of the samples. This evidences that equilibrium was reached during the run between the possible phases presence: silicate melt (M), aqueous vapour (V), and molten NaBr (hydrosaline liquid, L). The question is to know which phases that were coexisting at run conditions: M + V, M + V + L (invariant point), or M + L. As discussed by Webster et al.

(1999), for Cl-bearing systems, since Cl solubility and partitioning have been extensively investigated over the last 30 yr, we dispose of a large dataset on experimental conditions. Assuming that both halogens behave more or less similarly, this knowledge of the Cl-bearing systems was exploited for the preparation of Br experiments and to discuss Br concentrations in terms of solubility. Depending on the phase present at the P-T conditions, Br will be saturated with respect to the silicate melt: M + L or M + V + L; or not saturated: M + V (Webster et al., 1999). This means that the maximum Br concentration dissolved in silicate melts is reached when the melt coexists with L or with L + V; bromide solubility is discussed as a function of P, T, and melt composition. Conversely, when silicate melt is in equilibrium with V only, partitioning between the two phases present is discussed.

The concentration of the starting solution has been chosen to maximize the NaBr dissolved in the fluid (72.03 wt.%); the initial mass ratio melt/fluid was close to 3. The calculated final NaBr concentrations of the residual fluid phase are presented in Table 1. Concentrations range from 67.6 to 70.9 wt.%, that evidence that the aqueous phase is always extremely rich or saturated with respect to NaBr at a nearly constant concentration, as suggested by the numerous NaBr crystals trapped in fluid inclusions present in the resulting glasses (Fig. 1). This excludes the possibility of the M + V equilibrium and implies that the melt was saturated with respect to NaBr. However, it does not allow us to distinguish between the two last cases: M + L or M + V + L (Webster et al., 1999). For Cl-bearing systems, Chou (1987) suggests that at 2 kbar, the vapour plus hydrosaline liquid are stable if the weighted average NaCl-equivalent concentration of the volatile phases is roughly 20 to 60 wt.%. But Bodnar et al. (1985) proposed that the phases V + L may not be stable unless the temperature exceeds 1050 to 1100 °C with similar NaCl-equivalent concentrations at 2 kbar. This suggests that we may have not reached the conditions of maximum NaBr concentration in the melt for the runs performed at 900 °C, 2 Kb. Therefore, these last concentrations should be considered as minimum bromide solubility values.

Finally, except in the case of experiments performed at 900 °C, 2 Kb total pressure, we consider that we were at conditions corresponding to the attainment of bromide solubility in the melt. As the Na concentrations of the melt are not changed with respect to the starting composition, in the following discussion, the Br concentration of the glasses will be regarded as bromide solubility in water-saturated melts. Based on the fair number of data presented here and also on the comparison with the well-known solubility of Cl in melts, the following sections address a first evaluation of the main outlines of Br solubility in melts with respect to the main parameters of the experiments (pressure, temperature, bulk composition).

4.2. General Comments

For the four investigated melts (albite, haplogranite, rhyolite, and pantellerite), Br concentrations are strongly dependent on composition. Br concentration in iron-free pantelleritic melts is higher or equal to 1 wt.%; this is nearly three times higher than in iron-free haplogranitic melts. This would suggest that Br concentrations may approach 1 wt.% in natural per-alkaline

Table 1. Experimental conditions and compositions of the synthetic glasses from the four types: albite, haplogranite, rhyolite and pantelerite.

Sample	N ⁽¹⁾	P kbar	T °C	Glass Br ppm ⁽²⁾	H ₂ O ³ wt.%	Na ₂ O wt.%	SiO ₂ wt.%	Al ₂ O ₃ wt.%	K ₂ O wt.%	CaO wt.%	Total ⁽⁴⁾	XBr ⁽⁵⁾ × 10 ⁻²	Fluid NaBr wt.% ⁽⁶⁾
ALBITE													
s70	10	1	900	6366	nd	11.19	64.48	18.30			93.97	0.55	nd
s89-1	5	2	900	5357	5.0	10.80	63.53	18.18			92.51	0.47	70.04
s89-2	5	2	900	5357	nd	11.32	63.30	18.52			93.14	0.47	nd
s89-3	5	2	900	5357	nd	10.73	63.55	18.01			92.29	0.47	nd
s78	10	2	1000	6357	5.1	10.90	63.77	18.08			92.75	0.56	68.97
s71	10	1.7	1080	7853	5.0	11.43	63.40	18.52			93.35	0.69	nd
EtC ⁽⁷⁾		1	1080	2500	3.4	11.49	66.18	17.75			95.42	0.21	nd
HAPLO													
s96	10	1.5	900	3582	4.2	5.85	73.01	12.54	2.98		94.38	0.31	70.71
s82	9	1	900	3899	3.6	6.50	72.97	12.66	3.16		95.29	0.33	70.71
s81-1	8	2	900	3033	4.8	5.68	72.00	12.24	2.91		92.83	0.26	70.95
s81-2	7	2	900	3108	4.8	5.85	72.00	12.32	2.90		93.07	0.27	70.92
s79	15	1	1000	3114	3.6	6.10	73.70	12.44	2.97		95.21	0.26	70.93
s75-1	8	2	1000	3021	3.6	5.91	71.81	12.19	2.75		92.66	0.26	71.14
s75-2	7	2	1000	2804	nd	5.94	72.22	12.19	2.72		93.07	0.24	71.21
RHYO													
s76	7	2	1000	4581	5.2	5.06	70.20	13.55	2.38	1.70	92.89	0.40	70.33
s84-1	6	1	900	5887	3.6	5.45	71.69	13.88	2.48	1.62	95.12	0.50	69.92
s84-2	6	1	900	5887	nd	5.59	71.10	13.86	2.51	1.66	94.72	0.50	nd
s83	10	2	900	4304	4.7	5.26	70.48	13.57	2.38	1.69	93.38	0.37	70.43
s95-1	5	1.5	900	5409	4.3	5.39	71.21	13.94	2.46	1.71	94.71	0.46	70.00
s95-2	5	1.5	900	5409	4.3	5.42	71.02	13.89	2.51	1.70	94.54	0.46	70.00
PANT													
s93	10	2	1000	11150	4.3	9.33	65.30	11.72	4.75		91.10	0.99	67.74
s94-1	5	1.5	900	10905	3.5	9.90	66.18	11.98	4.90		92.96	0.94	67.62
s94-2	4	1.5	900	11049	3.5	9.85	66.35	11.94	4.78		92.92	0.96	67.56
s90	6	2	900	9745	4.4	9.47	65.48	11.85	4.72		91.52	0.86	67.90
s91-1	5	1	1000	11147	nd	10.15	67.15	12.13	4.85		94.28	0.95	nd
s91-2	7	1	1000	11251	3.0	10.06	67.06	12.12	4.89		94.13	0.96	67.53
s92-2	7	1	900	10476	3.0	10.01	66.68	11.97	4.78		93.44	0.90	67.84
s92-1	5	1	900	10346	3.0	10.06	66.51	11.97	4.83		93.37	0.89	67.89

⁽¹⁾ Number of analyses performed with electron microprobe for major elements. Standard deviations are 0.2, 0.3, 0.15, 0.1, 0.1 for Na₂O, SiO₂, Al₂O₃, K₂O, and CaO, respectively.

⁽²⁾ Analyses by PIXE. Standard error is $\pm 10\%$; see details in text and Bureau et al. (2000).

⁽³⁾ FTIR analyses. Standard error is ± 0.2 wt.%.

⁽⁴⁾ Total for major elements without water.

⁽⁵⁾ Calculated molar fraction of Br in the melt.

⁽⁶⁾ Calculated NaBr concentration of the final fluid phase after equilibrium, taking into account the water dissolved in the glass.

⁽⁷⁾ Standard Br, I, Cl-bearing albitic glass (Bureau et al., 2000). nd, not determined.

melts. One could also expect a high ability for Br to enter in highly depolymerised melt networks such as basalts.

The concentrations of Br in synthetic albitic glasses are similar to those in rhyolitic glasses for the same pressure and temperature conditions (Table 1). The partition coefficient $D_{Br}^{f/m}$ was determined to be of 17.5 ± 0.6 for the same albitic melt composition at 2 kbar, 900 °C (Bureau et al., 2000). As the similar Br concentrations were obtained by the experiments with the same starting solutions, this partition coefficient would probably be applicable to the rhyolitic melts. Because rhyolitic melts are at the origin of most of the cataclysmic eruptions, the Br contribution to the atmosphere can be evaluated using the same $D^{f/m}$ of 17.5 ± 0.6 .

4.3. Bromide vs. Chloride Solubility

In this section we compare Br solubility with Cl solubility, but we also make some qualitative comparison with Cl-partitioning data, because our experiments were performed at satu-

ration with respect to water. Investigating an element partitioning between a melt and an aqueous phase implies that the resulting melt will be saturated with respect to water. The limitation of Cl concentration in the melt will be a function of the Cl concentration (NaCl, KCl . . .) in the aqueous phase; Cl and Br speciation in the melt will be a function of its chemical composition.

The temperature of the experiments seems to have small effect on the Br concentrations in melts, as the glasses synthesised at 1000 °C are slightly enriched in Br compared to the glasses synthesised 900 °C. This is similar to Cl behaviour in hydrous felsic melts, where Cl slightly decreases with decreasing temperature (Malinin et al., 1989). Br concentration is negatively correlated with H₂O concentration (Fig. 2). Although it is difficult to distinguish a dependence of the data with pressure, this may be due to a possible negative pressure dependence, as H₂O solubility increases with it. We suggest that Br may compete with OH⁻ to enter the network with OH⁻

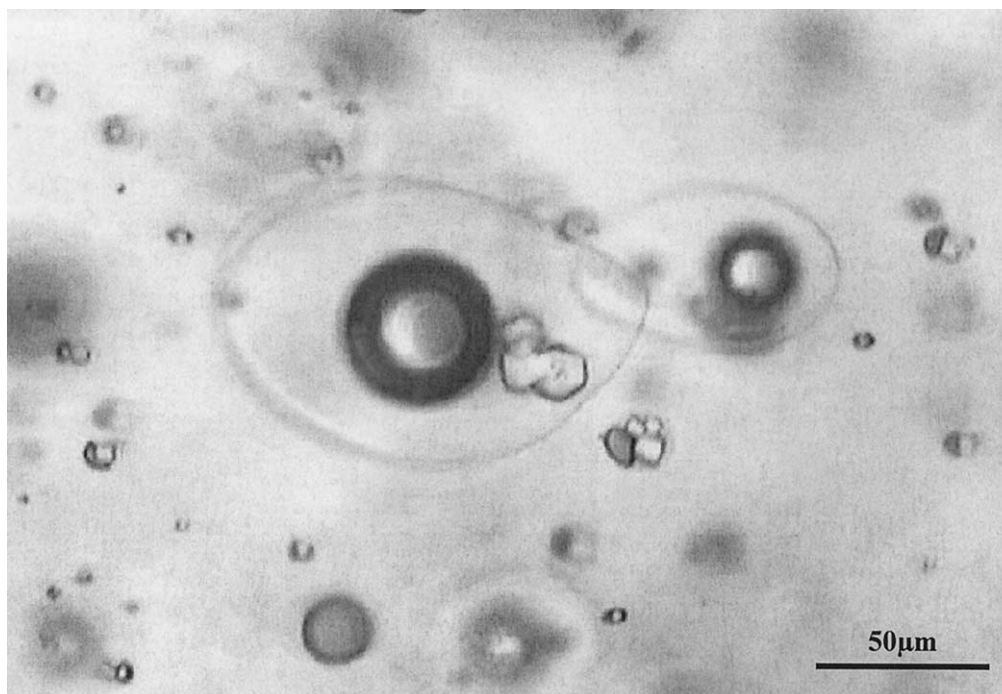


Fig. 1. Picture of the sample s82 (haplogranite). The glass is full of fluid inclusions that have daughter crystals of NaBr. This shows the saturation conditions of the melt at pressure and temperature with respect to molten NaBr and water.

winning at higher pressures. Also, Br concentration in the melt achieves a minimal value for (Na+K)/Al molar ratio close to unity (Fig. 3a). A similar effect of the molar ratio Na+K to Al was previously discussed for Cl concentrations in melts (Malinin et al., 1989; Webster, 1991, 1992; Métrich and Rutherford, 1992). Comparing the results for haplogranite and albite that have the same molar ratio (Na+K)/Al, we observe that the Br concentration in the melt increases with sodium and potassium (Fig. 3b). This seems to be also the case for Br behaviour in the four compositions investigated in this study (Fig. 3a). Similarly to Cl, we observe the smallest concentration for a ratio close to unity, and a higher concentration for peraluminous (rhyolite) and peralkaline (pantellerite) melts with the maximum in the melt for the peralkaline melts. Br may preferentially pair with sodium and/or potassium in sodic melts similar to Cl behaviour with respect to both elements (Webster, 1992). However, Br solubility is about half in albite than in pantellerite, whereas Na content is higher in albite (Fig. 3b). This effect may be due to the silica content; the maximum Br concentrations are observed for the lower silica concentration melts (Fig. 4). Highly depolymerised pantellerite melts with low SiO₂ dissolve much higher Br contents than polymerised haplogranite melts containing ~74 wt.% SiO₂, whereas both have similar Si/Al ratios. The fact that the maximum Br concentration pairs with the lowest silica concentration is also in good accordance with Cl behaviour in melts. Mechanisms of Br dissolution in melts seems to combine the following processes: competition with OH⁻ groups and/or coordination of Br⁻ with Na⁺, K⁺, etc. This last process would require another monovalent cation to enter elsewhere in the melt (which is unlikely as no significant change in the composition is observed) or for OH⁻ (or 1/2 O₂⁻) to drop out of the melt.

Although it is difficult to compare our synthetic compositions with the data obtained for water solubility in silicate melts in the literature, we have observed a slightly lower water content for the Br-bearing melts compared to more or less equivalent Br-free compositions. For albite at 1000 °C, 2 kbar, Br is 6357 ppm, H₂O is 5.1 wt.% instead of 6.1 wt.% (after Silver and Stolper, 1985; Burnham, 1994). For rhyolite at 900 °C, 1 kbar, Br is 5887 ppm, H₂O is 3.6 wt.% instead of 3.66, 3.85, and 3.74 wt.% (after Silver and Stolper, 1985; Burnham, 1994; Newman and Lowenstern, 2002, respectively). For haplogranite at 900 °C, 1 kbar Br is 3899 ppm, H₂O is 3.6 wt.% instead of 4.55 wt.% for sample HPG1 (after Holtz et al., 1995). This favours the hypothesis of competition between the Br⁻ and OH⁻ groups to occupy the same sites in the melt network as the dominant process.

In conclusion, the Br concentration in melts ranges within the same order of magnitude as the concentration of Cl for equivalent hydrous-melt compositions and P-T conditions, either for the studies of Cl solubility (Métrich and Rutherford, 1992; Webster, 1997) or even in the studies of Cl partitioning (Shinohara et al., 1989; Kravchuk and Keppler, 1994). This suggests that Br probably occupies the same sites as Cl in the melt network.

4.4. Halogen's Effect on Br Behaviour for Water-Saturated Melts

A comparison between the synthetic samples and the reference glass EtC provides information about Br behaviour in the presence of Cl and I. This albitic glass was synthesised under saturating conditions with respect to Br, Cl, I, and H₂O; the final concentrations are 3096 ppm Cl, 2486 ppm Br, 962 ppm

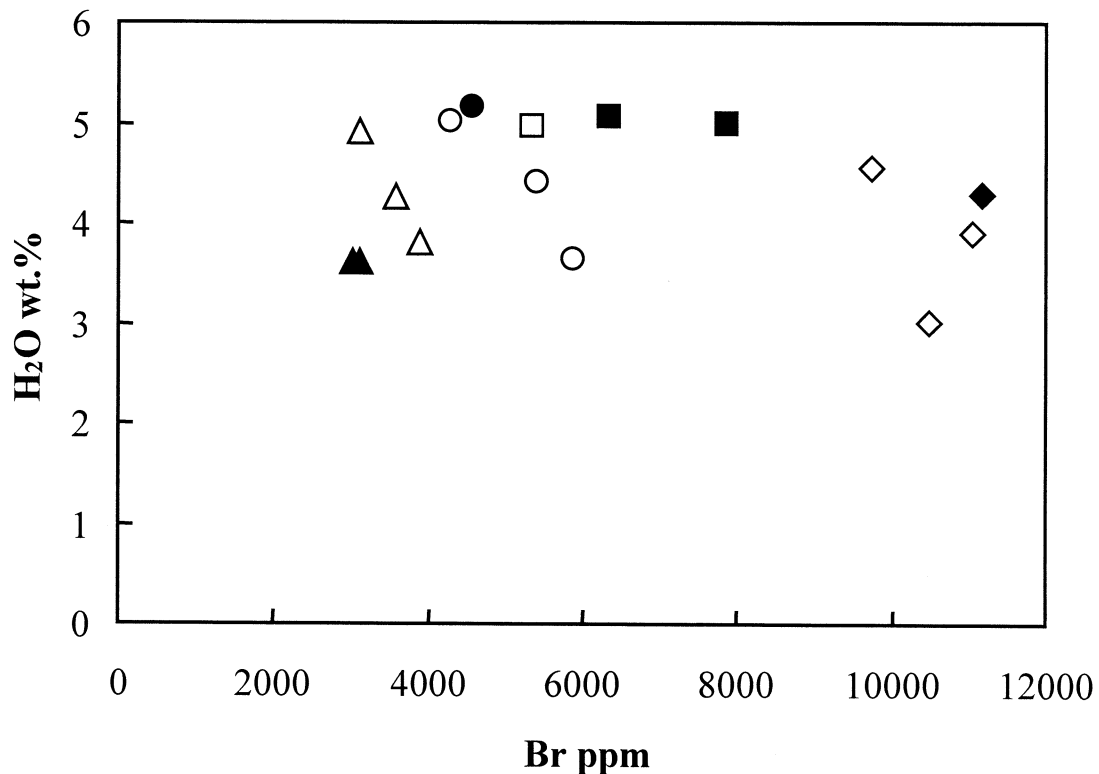


Fig. 2. Total Br concentration of the resulting glasses in ppm vs. total water content. Experiments performed at 900 °C are represented by open symbols and those at 1000 and 1080 °C are represented by closed symbols. Triangles: haplogranite. Circles: rhyolite. Squares: albite. Closed diamonds: pantellerite. For all of the samples, a negative relation is observed between the water content and Br concentrations. Also, the temperature seems to show a small effect; an increasing temperature implies a higher Br concentration in the melt.

I, and 3.4 wt.% H₂O (Bureau et al., 2000), whereas the Br concentrations of the equivalent albitic melts range from 5357 ppm (900 °C, 2 kbar) to 7850 ppm (1080 °C, 1.7 kbar) without the presence of other halogens (Table 1). The sum of the halogen contents from sample ETC (6544 ppm) falls within this range of Br contents. This suggests that a competition may have occurred between Cl, Br, and I to enter and to occupy the sites available in the melt network, because Br concentration is much lower in the melt in the presence of both Cl and I. Also, Cl is much more concentrated than Br and I, which is in good accordance with their respective partitioning behaviours. Cl has more affinities than Br and I for the albitic melt at 2 kbar, 900 °C: $D_{Cl}^{f/m} < D_{Br}^{f/m} < D_{I}^{f/m}$ (Bureau et al., 2000). Taking into account fluorine partitioning behaviour ($D_{F}^{f/m} < D_{Cl}^{f/m}$) (Webster, 1990; Carroll and Webster, 1994), fluorine would be favoured to enter the melt with respect to the other halogens. However, mechanisms involving fluorine may be more complex, as it was demonstrated that when F is enriched in peraluminous melts, Cl solubility is much higher than for a F-deficient melt; this is explained by the ability of F to disrupt the structure of silicate liquids, making additional ions available for complexing with Cl⁻ (Webster, 1997).

5. NATURAL SAMPLES

We have analysed the natural Br concentrations of a selection of well-known volcanic samples with respect to major

elements, water, and Cl concentrations; short descriptions of the samples are given in Table 2. These are volcanic glasses and/or melt inclusions trapped in crystals recovering typical subduction-related magmatic series except pantellerites from Pantelleria Island, typical from intraplate acid volcanism. They are rhyolites from Mount Pinatubo (Philippines) and from Guadeloupe Island, potassium-rich basalts (shoshonites) from Stromboli Island (Italy), potassium-rich basalts and phonolites from Vésuvius, (Italy), and trachytes from Phlegrean Fields (Italy). Br concentrations range from 28 ppm to less than our detection limit of 3 ppm (Table 2). We observed that the Br concentrations from the synthetic glasses are extremely high compared to the chemically equivalent natural samples (see Yoshida et al., 1971; Schilling et al., 1980; Jambon et al., 1995; Villemant and Boudon, 1999). Whereas we studied iron-free melt compositions, some observations based on the study of the synthetic samples seem to be also valid for the natural melts. This is not surprising for rhyolitic melts, as FeO is usually < 2 wt.%, but it seems to be true as well for pantelleritic melts (FeO 7.9 wt.%), as the highest Br concentrations in natural glasses are those of the pantelleritic compositions whose (Na+K)/Al molar ratio is 2 (see Table 2). Therefore, we believe that in the case of silicic melts, the data obtained on iron-free compositions may be applicable to natural systems. The Cl concentrations of the melt inclusions and the glasses of pantellerite are nearly the same, suggesting that no strong degassing event

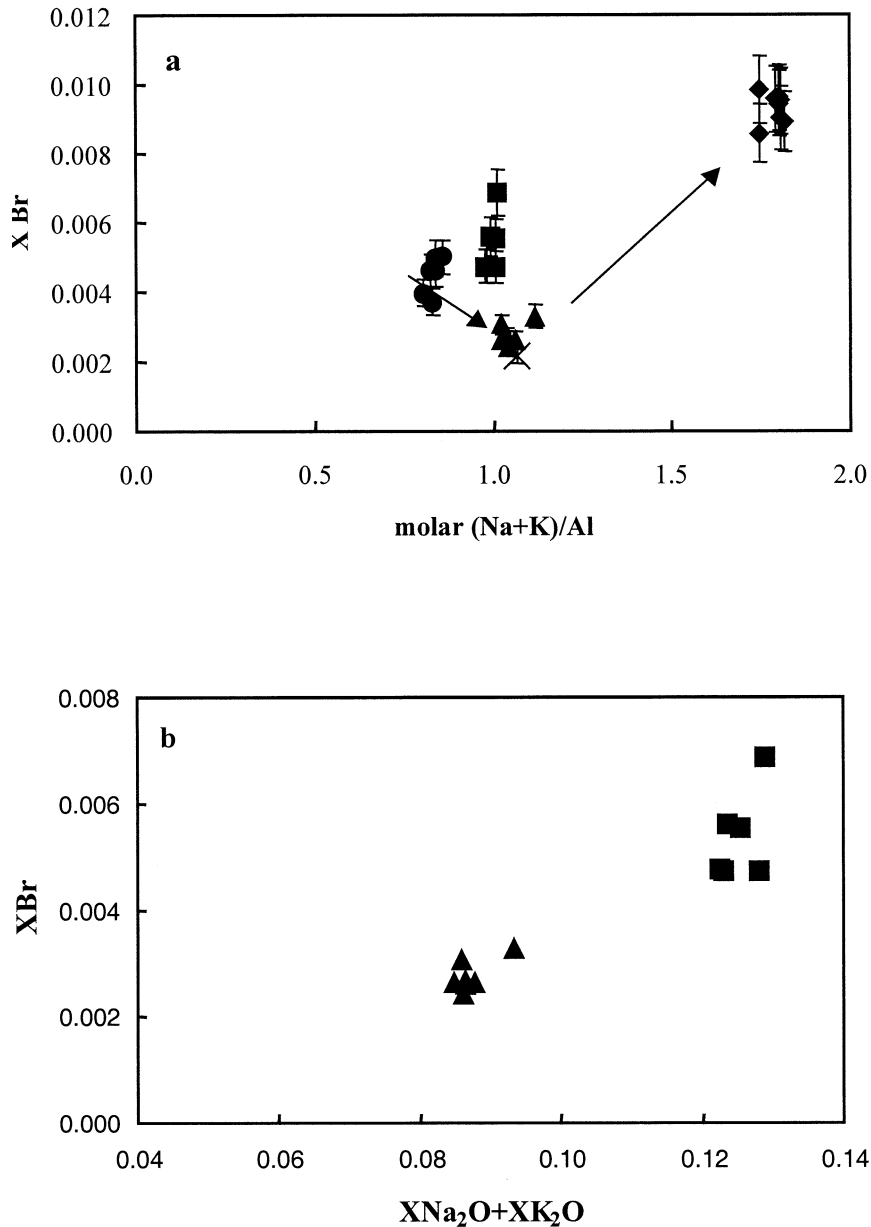


Fig. 3. (a) Molar fraction of Br vs. the molar ratio (Na+K)/Al. (b) Molar fraction of Br vs. molar fraction of Na₂O+K₂O for samples with Na+K/Al = 1. Closed triangles: haplogranite. Closed circles: rhyolite. Closed squares: albite. Cross: albite containing I and Cl. Closed diamonds: pantellerite.

occurred during the Pantelleria eruption as suggested by Lowenstern (1994). This is supported by the fact that the Br concentrations are also very similar to the melt inclusions and to the glass.

6. GEOCHEMICAL IMPLICATIONS

Comparisons between the maximum Br concentrations dissolved in the synthetic glasses at saturation with respect to water and natural hydrous silicic melts show a difference of two or three orders of magnitude. Br, like Cl, is expected to behave as an incompatible element in melts (highly hygromagphile element that stays in the melt instead of entering in

minerals network). This implies that magmas are never saturated with respect to bromides in nature. The Br concentrations of natural volcanic glasses and melt inclusions are close to the Br concentrations of meteorites (Dreibus et al., 1979) and reflect the low initial abundance of this element in the Earth. The ratio Cl/Br (wt. ratio) may be a good indicator of fractionation of Cl with respect to Br in a magma. Br is 200 to 400 times less abundant than Cl in Earth materials. In the Cl chondrites, the mean ratio is 230 (Dreibus et al., 1979), which is supposed to be closed to the primitive mantle. It is more or less constant in the crust at a value of 273 (Newsom, 1995). For the N- and E-MORBs, it is constant at $\sim 400 \pm 100$ (Jambon,

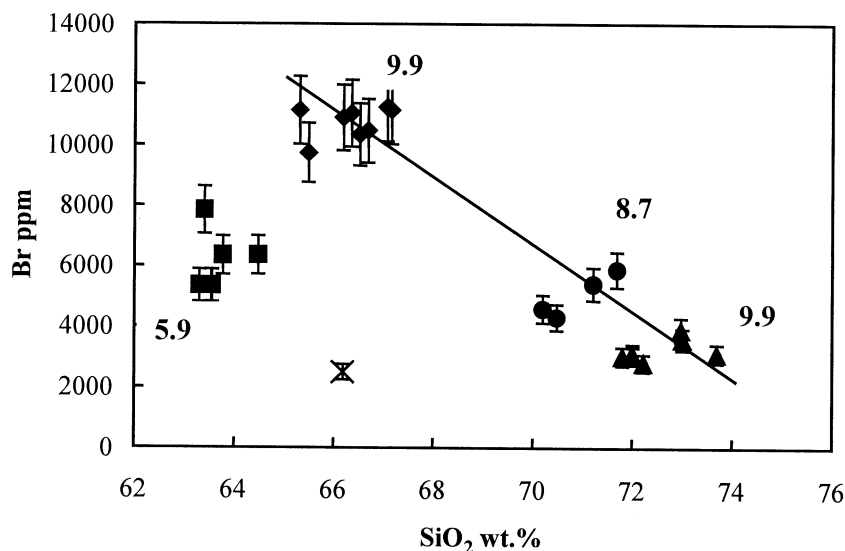


Fig. 4. Total Br concentration in ppm vs. total SiO₂ concentration in wt.% of the glasses; same symbols as in Fig. 3. Numbers are Si/Al molar ratios. For melt compositions having similar Si/Al molar ratios, the maximum Br content is observed for the lowest SiO₂ content.

1994). This ratio is higher in the mid-ocean ridge basalts, likely because MORBs are more degassed. In the present study, the Cl/Br ratio is at 321 to 375 in the moderately degassed melts (pantelleria, Table 2). Guadeloupe Island samples exhibit a ratio of 324, which is in accordance with a partially degassed magma (melt inclusions still contain ~5 wt.% water). Accordingly, assuming an equivalent Cl/Br ratio for Guadeloupe samples, the rhyolitic melt inclusions trapped in quartz from Mount

Pinatubo (H₂O 5.5 wt.%) should contain ≤ 3 ppm Br, which is the detection limit.

In the case of Mount Vesuvius (melt inclusion trapped in Leucite from the 1944 eruption; see Marianelli et al., 1999), which is known to have experienced a significant water degassing process (0.9 wt.% water, Table 2), the ratio is much higher than 300, which is interpreted as the result of a strong fractionation process of Br with respect to Cl during water exsolution.

Table 2. Compositions of natural volcanic glasses and melt inclusions.

Location [±] name	Comp.	Host	SiO ₂ wt.%	TiO ₂ wt.%	Al ₂ O ₃ wt.%	FeO wt.%	MgO wt.%	CaO wt.%	Na ₂ O wt.%	K ₂ O wt.%	P ₂ O ₅ wt.%	H ₂ O wt.%	Total	Cl ppm	Brppm	Cl/Br
Phlegrean Fields Italy CFA47	Trach. g.		61.51	0.46	18.42	2.8	0.42	1.84	5.39	8.01		nd	98.85	4980	12.5 ± 2.5	398
Pantelleria	Pant. 6 mi	Qz	68.9	0.34	7.4	7.3	0.05	0.33	6.4	4.2	nd	2.7	97.62	8980	28 ± 2.5	321
Pantelleria	Pant. g		71.2	0.35	7.7	7.9	0.04	0.33	6.7	4.3	0.03	0	98.55	9105	24 ± 3	379
Guadeloupe GG7W	Rhy. 6 mi	Qz	72.4	0.07	11.3	1.6	0.15	1.48	3.95	2.06	nd	5	98.06	3080	9.5 ± 1.5	324
Vesuvius ⁽¹⁾ Italy, 1944 Vs96- 49	Phon. mi	Le	47.46	1.08	18.04	9.37	3.09	7.36	3.79	5.58	1.22	0.9	97.99	4400	<DL	>>300
Vesuvius 1944 Vs92-8	HK-B. 4 mi	Ol	46.51	1.16	15.45	7.97	5.21	11.18	1.47	5.74	1.07	2.5	98.26	5180	<DL	>>300
Pinatubo Phillipines	Rhy. mi	Qz	73.6	0.13	11.9	0.7	0.18	1.03	3.79	2.83	nd	5.5	99.66	1080	<DL	>300
Stromboli Vancori deposits	Shos. mi	Ol	47.34	1.04	16.94	8.41	5.85	10.81	2.36	1.74	0.54	3.2	99.65	1630	<DL	>300

g: glass. mi: melt inclusion, average of n melt inclusions. Comp. for compositions. Trach is trachyte. Pant is pantellerite. Rhy is rhyolite. HK-B is high potassium basal. Shos is shoshonite. Ol is olivine. Qz is quartz. Le is leucite. nd not determined. <DL below detection limit, from 3 to 5 ppm. Cl contents are ±5%. Cl/Br is a weight ratio.

⁽¹⁾ After Marianelli et al. (1999).

This interpretation agrees with the experimental observation that Br has much more affinities for the aqueous phase than for the melt and agrees also with the proposition that Br may be released in the atmosphere or in the stratosphere in significant amounts by volcanoes (Bureau et al., 2000).

Considering now the samples that have not experienced a significant degassing process with respect to water from Vesuvius (melt inclusions trapped in olivine; see Marianelli et al., 1999) and from Stromboli (Vancori deposits; see Métrich et al., 2001), the Cl/Br ratio is also > 300 . In this case, it cannot be attributed to a fractionation of Br with respect to Cl during water degassing. The mechanism at the origin of this fractionation with respect to the water-degassed magmas is still an open question. However, we could suggest either a preferential Cl enrichment due to Cl recycling from subduction material with respect to Br. Because of the high partitioning of Br into the H₂O-rich fluid phase (Bureau et al., 2000), Cl and Br recycling processes are not similar during dehydration of subducted crust. Br may be more rapidly recycled than Cl toward the surface during the dehydration of the crust beneath subduction zones.

Before water exsolution, Br may be used as an efficient geochemical tracer of magma history. Br may be more reliable than Cl to characterise fractionation processes such as magmatic differentiation, as Cl is known to be moderately incompatible in melts. Cl enters in large amounts in a few magmatic minerals such as apatite. But we do not really know Br's ability to enter into minerals. The potential high solubility of Br in silicate melts makes it a very sensitive chemical tracer of magma contamination by external seawater that is extremely enriched in Br or Br-rich materials such as sediments. Similarly, systematic studies of Br in subduction materials may reveal the recycling of Br from the subducted sediments and seawater-rich subducted slab to the arc magmas. This would put new constraints on volatiles cycling on Earth.

7. CONCLUSION

In this study, we have shown that Br can enter in large amounts in a melt on the order of magnitude of wt.%, whereas much lower Br concentrations, from a few ppb to a few ppm, are observed in natural volcanic products. We have shown that Br behaviour strongly depends on the melt composition, following the same "solubility" rules in hydrous silicic melts as Cl. We have demonstrated that the partition coefficient determined for albitic melts in our previous study is applicable for natural rhyolites. We have presented the first data on Br content in silicic melts (melt inclusions). From a geochemical point of view, we suggest that (1) the low concentration of Br observed in natural melts compared to the synthetic samples (hydrous-silicic melts) is probably related to the low abundance of Br in the Earth mantle because of a low initial abundance of Br; (2) because of its incompatible behaviour in melts and its high affinity for water, Br may be a good tracer of magmatic processes such as differentiation, crystallisation and degassing; and (3) the systematic study of Br in subduction-related magmatic samples may put new constraints on Br and other volatile species (water, Cl) recycling in subduction settings.

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