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1 An in-situ experimental HP/HT study on bromine release from a  
2 natural basalt

3

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23

24 ABSTRACT

25 We present the first in-situ partitioning data for bromine between a natural basaltic melt  
26 and a coexisting fluid. For this study hydrothermal diamond anvil cell experiments at  
27 pressures up to 1.7 GPa were conducted. We combined laser heating to melt the basalt  
28 glass with external heating to lower the temperature gradient in the cell and to initiate  
29 circulation for the aqueous fluid. Bromine concentrations were measured in-situ with X-  
30 ray fluorescence in the basaltic melts, glasses, and in the fluid. From the results we  
31 calculated partition coefficients of  $D^{\text{Br}}_{\text{fluid/melt}} = 1.19$  to  $3.92$  in the range of 0.4 to 1 GPa  
32 for aqueous fluids. Experiments with neon as the surrounding fluid ( $D^{\text{Br}}_{\text{fluid/melt}} = 0.38 \pm$   
33  $0.01$  at 1.1 GPa) suggest that Br-release from a basalt into volatiles that have no  
34 bonding affinity with Br is weak. This should be the case for dry intra-plate volcanic  
35 eruptions. From the experimentally gained partition coefficients and from global Br  
36 concentration values in melt inclusions of arc magmas, we calculated an annual global  
37 Br flux of  $23.5 - 72.9 \times 10^9$  g/y.

38

39 KEYWORDS

40 bromine, fluid/melt partitioning, volcanic degassing, SXRF, hydrothermal diamond anvil

41 cell

42

## 43 1. INTRODUCTION

44 Halogens are very reactive chemicals and play a significant role as volatile elements in  
45 geodynamic processes. In crustal hydrothermal fluids (e.g., brines and molten salts),  
46 halogens are major agents for the metal transport and thus play a critical role in ore-  
47 forming processes (Aiuppa et al., 2009). Halogens are also important constituents of  
48 volcanic fumaroles and volcanic ejecta. Once released to the atmosphere halogens  
49 have an environmental impact and can e.g., contribute to ozone destruction (e.g.,  
50 Daniel et al., 1999; Gerlach et al., 2004).

51 The heavy halogen bromine (Br) has a low abundance on Earth, but it is highly reactive  
52 and an important chemical agent in the atmosphere (Fehn, 2012). Besides plankton and  
53 burning biomass, volcanoes have been recognized as a significant (Gerlach et al.,  
54 2004) if not the controlling, (Pyle and Mather, 2009) contributor to the actual  
55 atmospheric Br content. Especially arc volcanoes release large amounts of Br gas  
56 compounds: The first detection of volcanic BrO has been recorded by Bobrowski et al.  
57 (2003) from the Soufrière Hills volcano (Montserrat). Since then, Br gas compounds  
58 have been reported in several case studies e.g., from Mt. Etna (Aiuppa et al., 2005;  
59 Pyle and Mather, 2009; Bobrowski and Giuffrida, 2012; Roberts et al. 2018) or Mt.  
60 Masaya (Witt et al, 2008).

61 Based on models from Etna's degassing measurements Br is estimated to be rather  
62 less abundant in basalts compared to e.g., chlorine (Cl) or sulfur (Bobrowski and  
63 Giuffrida, 2012). The Br concentrations range from  $\mu\text{g/g}$  to  $\text{ng/g}$  in volcanic rocks and in  
64 mantle rocks (Newsom, 1995). Yet, Br fluxes from arc volcanoes are estimated to be in  
65 the range of  $5\text{-}15 \times 10^9$  g/y HBr per year (Aiuppa et al., 2005; Pyle and Mather, 2009,

66 Webster et al., 2018, Cadoux et al., 2022). HBr is the dominant species of Br emitted  
67 from volcanoes (Roberts et al., 2018). Once in the stratosphere, Br is notably involved  
68 in the destruction of ozone as it reacts to form BrO and eventually BrO<sub>x</sub> (Bobrowski et  
69 al., 2003). These conversions are significant: 1 ng/g of BrO can destroy about 10 ng/g  
70 of ozone per minute (Bobrowski et al., 2003). This is about 60 times more efficient  
71 (Sinnhuber et al., 2009) than the ozone destruction by Cl in this respect (Daniel et al.,  
72 1999; Gerlach et al., 2004; Gutmann et al., 2018 for review).

73 However, the deep cycling of Br, its behavior in magmas, and the transfer to the Earth's  
74 surface is poorly understood. There is scant data, but Br solubility has been shown to  
75 be very high in silica-rich systems (Bureau and Métrich, 2003; Bureau et al., 2010).  
76 Depending on the Br content in degassing magmas the annual volcanological Br flux to  
77 the atmosphere could be strongly underestimated, and therefore, the impact of Br on  
78 ozone destruction in the Earth's stratosphere as well.

79 So far, there are only a few experimental studies about Br partitioning between a silicate  
80 melt and a fluid. The pioneering study was conducted by Bureau et al. (2000) with an  
81 albitic melt composition at 200 MPa from which the authors calculated a partition  
82 coefficient between the aqueous fluid and the silicate melt of  $D_{\text{fluid/melt}}^{\text{Br}} = 17.5 \pm 0.6$ .  
83 Bureau et al. (2010) found smaller values with  $D_{\text{fluid/melt}}^{\text{Br}}$  ranging from 2.18 to  $9.2 \pm 0.5$   
84 between aqueous fluids/saline fluids and a haplogranitic melt at higher pressures of  
85 0.66 to 1.7 GPa. Using a similar haplogranitic melt, Louvel et al. (2020b) found values of  
86  $D_{\text{fluid/melt}}^{\text{Br}}$  between  $2.0 \pm 0.2$  and  $15.3 \pm 2.0$  at pressures of 0.2 to 1.7 GPa. Louvel and  
87 coworkers did not find a clear correlation with pressure or temperature in their results.  
88 The experiments from Bureau et al. (2010) and Louvel et al. (2020b) were measured in-

89 situ and give a good insight into Br partitioning between melt and fluid, but they were  
90 conducted in compositionally simplified systems (e.g., Fe-free melts) and rather aimed  
91 to study more evolved melts like sediment melt composition with higher SiO<sub>2</sub> content.

92 Cadoux et al. (2018) conducted partitioning experiments for Br between fluid and a  
93 wider range of arc-related rocks: natural basalt, andesite, and rhyodacite at 100-200  
94 MPa. They calculated  $D_{\text{fluid/melt}}^{\text{Br}}$  of 4.6 to 27.9 with basalt at the lower end and  
95 rhyodacite at the upper end of their partition coefficients. Experiments from Cadoux et  
96 al. (2018) show generally higher partition coefficients than the results from Bureau et al.  
97 (2010) which could describe the impact of the lower pressure used by Cadoux et al.  
98 (2018).

99 Not much is known about the effect of the different cations on  $D_{\text{fluid/melt}}^{\text{Br}}$ . Bromine  
100 concentrations vary in water-saturated silicic melts with (Na+K)/Al molar ratio and reach  
101 a minimum at (Na+K)/Al = 1 (Bureau and Métrich, 2003). A comparison to Cl advocates  
102 for the presence of alkalis to increase Br solubility: Cl solubility in melts is controlled by  
103 the abundances of several elements like Mg, Ca, Fe, Na, K, Al, Li, Rb, Cs, Ti, F, and P  
104 (Webster and de Vivo, 2002; Webster et al., 1999). Cochain et al. (2015) demonstrate  
105 that alkalis and especially Na can retain Br in a silicate melt while it degasses more  
106 efficiently from hydrous melts. Louvel et al. (2020b) find that Br prefers Na over OH in  
107 silicate glasses, where it is incorporated in a salt-like structure, like NaBr. Louvel et al.  
108 (2020a) show that Br bonds with network modifiers in granitic melts but does not find  
109 any affinity to prefer Na<sup>+</sup> over e.g., K<sup>+</sup> or Ca<sup>2+</sup> if all three are present.

110 In this study we present new Br degassing experiments from a natural arc-related basalt  
111 into an aqueous fluid and into neon. The experiments were conducted over a pressure

112 range from 0.4 to 1.7 GPa in the closed system of a diamond anvil cell which has  
113 already been used successfully by Bureau et al. (2010), to study Br. Partitioning of Br  
114 between the basalt and the surrounding fluid can be calculated from both in-situ  
115 measurements on melts and on quenched glass.

116

## 117 2. METHODS

### 118 2.1. Diamond anvil cell setup

119 Two series of experiments were performed as hydrous and neon experiments which  
120 refer to the pressure media water and neon, respectively. As the basalt glass with about  
121 2 wt.% of water was also used in the *neon* runs, these runs were not completely dry  
122 *sensu stricto* (for a detailed description of the starting material see further below). The  
123 water-basalt-partitioning experiments (hydrous) were conducted in externally heated  
124 hydrothermal diamond anvil cells (HDAC) of either the Basset type (e.g., Basset, 2003)  
125 or a modified Basset type with pressure-driving membranes (Munsch et al., 2015).  
126 Similar setups have been used successfully in former studies on heavy halogen  
127 behavior in silicate glass and hydrothermal fluids (e.g., Bureau et al., 2010, 2016;  
128 Louvel et al., 2020b). All HDAC are equipped with 2 mm thick diamonds with large  
129 culets of 1 mm diameter. The sample chamber is compressed between two diamonds  
130 and has a diameter of 500  $\mu\text{m}$  which is drilled as a hole into a Re gasket of either 100  
131  $\mu\text{m}$  or 200  $\mu\text{m}$  initial thickness. The aqueous fluid serves as a pressure medium within  
132 the sample chamber. Both diamonds are mounted on tungsten carbide (WC) seats. A  
133 molybdenum wire coiled around each WC seat serves as external heater. The



134 temperature can be measured with K-type thermocouples that are glued with cement to  
135 each of the diamond anvils. The temperature offset between the thermocouple position  
136 and the sample chamber has been calibrated at ambient pressure against the melting  
137 temperature of pure sulfur (112.8 °C), NaNO<sub>3</sub> (308 °C), CsCl (645 °C), and NaCl (801  
138 °C). To avoid oxidation of the diamonds while using the external heaters, the HDAC are  
139 connected to a gas supply system and can be flooded with a reducing gas mix like Ar-  
140 H<sub>2</sub> (4 vol.%).

141 For neon experiments we used an inert gas as pressure medium. We performed neon-  
142 basalt partitioning experiments which were conducted in modified Chervin-type diamond  
143 anvil cells (Chervin et al., 1995). These DAC are equipped with a pressure driving  
144 membrane like the Basset-type HDAC but do not have an external heating system.  
145 Chervin type cells (CDAC) can be installed into the gas loading system e.g., at the  
146 Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC –  
147 Sorbonne Université Paris) where we loaded the sample chamber with neon gas  
148 instead of water as a pressure medium (Couzinet et al., 2003). Neon has a density like  
149 air. It was loaded with an initial pressure of about 0.5 GPa into the DAC. At this  
150 pressure neon behaves as a (supercritical) fluid. The CDAC are equipped with the same  
151 type of diamonds, rhenium gaskets, and the same sample chamber dimensions that  
152 were used for the HDAC. All used DAC types in this study allow observation of the  
153 experiment and laser heating along the pressure axis through the diamond anvils.

154

155 2.2. Experimental runs, heating, and temperature determination

156 For each experiment the sample chambers were filled with 1-3 larger pieces of basalt  
157 glass (about 30-50 vol.%, 55-75 wt.% respectively), and 50-70 vol.% of either water or  
158 neon gas (+ small flakes of gold + ruby spheres in neon experiments for pressure  
159 determination). The samples were compressed to about 1-2 GPa before the run. To  
160 heat the basalt glass to its liquid state, we used two YAG laser that can be focused on  
161 the sample from both sides of the pressure axis – one through each diamond. YAG  
162 laser can be used as the iron content of the basalt glass starting material (8.45 wt.%) is  
163 high enough to provide the required absorption. During the heating the melt was  
164 analyzed with Synchrotron X-Ray Diffraction (SXR) to test for the presence of crystals  
165 in the melt. If crystals (olivine or pyroxene) were present, the laser temperature was  
166 increased stepwise until all the crystals were melted. The laser heating temperature  
167 ranged from 1725 to 2167 °C for the neon experiments. It could not be measured for  
168 hydrous experiments but by monitoring the absence of crystals by XRD we could  
169 ensure to stay above the liquidus. This would be a temperature of 1300 to 1400 °C for  
170 the hydrous basalt. Experimental conditions are listed in Table 1.

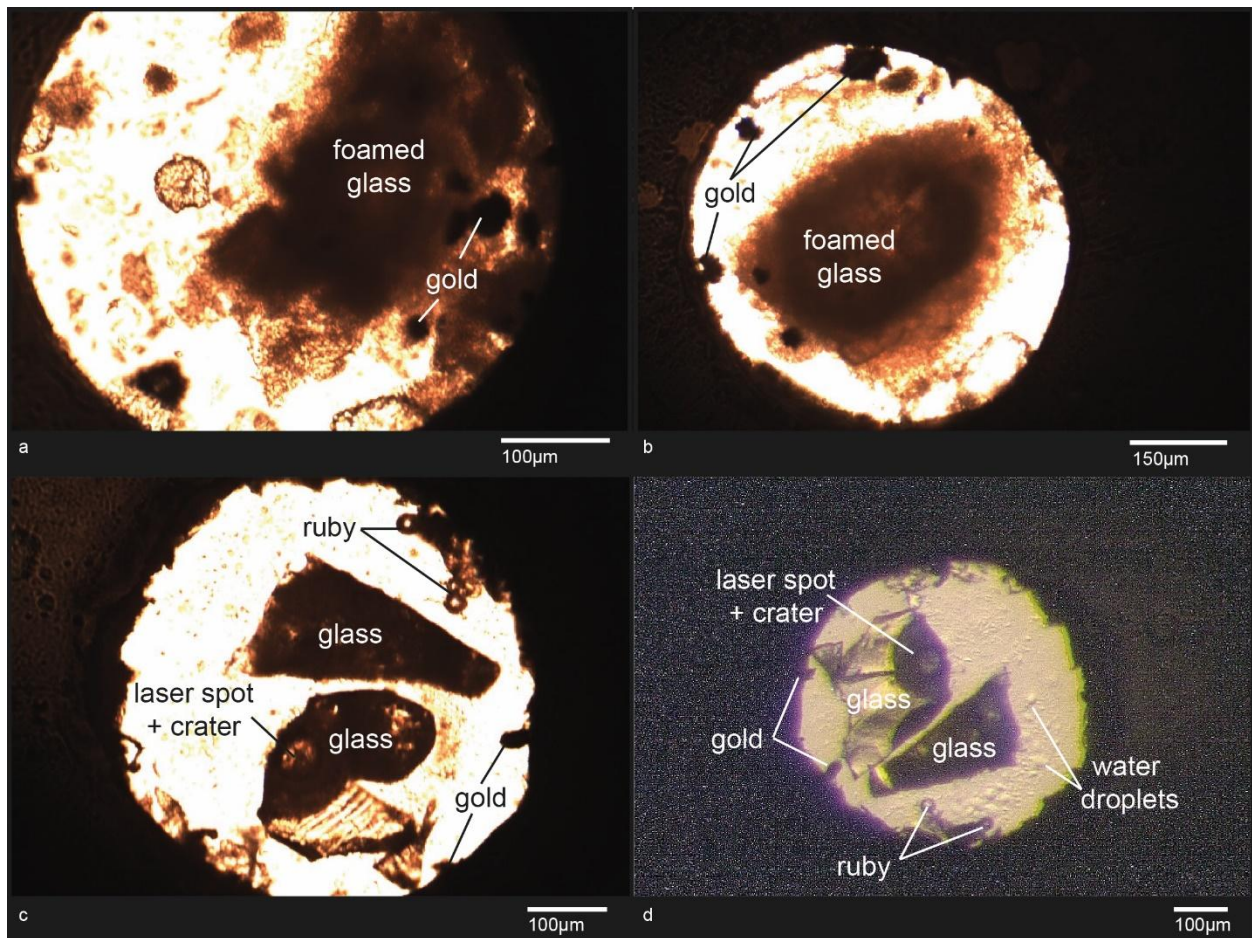
171 For the hydrous experiments heating cycles (usually 5 min at the peak temperature) and  
172 decompression paths were varied between each run: During experiment LN11 and  
173 LN22 the basalt glass was heated with the laser to its liquid state and quenched  
174 afterwards by shutting off the laser. Br concentrations were then analyzed in the glass  
175 and in the fluid. This heating-quenching-analyzing cycle was repeated several times  
176 with a stepwise pressure release in the sample chamber after each cycle to test for  
177 pressure effects on Br partitioning (c.f. Bureau et al., 2010, 2016; Leroy et al., 2019) and  
178 to reach chemical equilibrium (see further below in the Results section for detailed

179 description). Experiment Cpo2 had only one heating-quenching cycle. For experiment  
180 Cpo3 the laser heating was not switched off for the decompression steps, but instead it  
181 was constantly keeping the basalt above the liquidus. The Br concentration was  
182 analyzed in the fluid of Cpo3 while the laser was switched on and the basalt was still  
183 molten. During run Cpo2, Cpo3 and LN22 the external heaters were additionally heating  
184 the sample chamber of the HDAC for the entire run (244 °C, 265 °C and 235 °C  
185 respectively). This minimized the temperature gradient caused by the heating laser and  
186 induced a better circulation and homogenization of the fluid. To test this effect the  
187 external heating system was shut off in experiment LN11: the fluid was not heated  
188 externally, and Br was measured at two fixed positions (Figure 1a): The first spot is next  
189 to the melted and quenched basalt. The second spot is about 200-300  $\mu\text{m}$  away at the  
190 rim of the sample chamber (as it was also the case for all other hydrous experiments).  
191 During the laser heating the temperature of the HDAC measured at the thermocouples  
192 increased to 260 – 280 °C. This was independent from the external heating system  
193 being switched on (LN22, Cpo3) or off (LN11).

194 The neon experiments Hak1 and Hak2 were performed in CDAC with neon as the  
195 pressure medium and with similar heating cycles as described above for LN11 and  
196 LN22: after crossing the basalt glass transition with the laser and keeping the laser for 5  
197 min at the peak temperature, the laser was shut off, Br concentrations were analyzed in  
198 the glass and in the fluid (neon), and the pressure was decreased before starting the  
199 next heating cycle again. During the experiment of Hak1 Br was additionally measured  
200 twice in the basaltic melt during each heating cycles. After the conduction of run Hak1  
201 the cell was kept closed and directly re-compressed to 1.4 GPa to conduct run Hak2 on

202 the same loading. Mar1 had only one long heating cycle: The laser was not switched off  
203 during the decompression steps and for each decompression step in Mar1 Br  
204 concentration was measured in the liquid basalt (600 sec. for each analysis).

205



206  
207 Figure 1 Optical microscope images of sample chambers and experimental  
208 samples LN11, LN22, Hak2 and Hak1. a) LN1: Two spots of measurement for the  
209 aqueous fluid were chosen. One close to the melted glass and one as far away as  
210 possible within the sample chamber. b) LN22: like in a) the basalt glass shows a foam-  
211 like texture after treatment with the heating laser. c) Hak2: In contrast to a) and b) laser  
212 heated glass in coexistence with neon retains its glassy texture. d) Hak1: During heating

213 cycle 3 and ongoing decompression of the cell water droplets could be observed in the  
214 sample chamber.

215

216

## 217 2.3. Pressure determination

### 218 2.3.1. *Setup*

219 Pressure determination in the loaded and compressed DAC was conducted in several  
220 ways using (1) ruby fluorescence, (2) gold SXR, and the (3) water-ice phase transition.

221 (1) For the neon experiments small ruby spheres were added during loading into the  
222 sample chamber of the CDAC. The pressure was measured at room temperature before  
223 and after the run with the fluorescence method at the IMPMC and at Soleil. The  
224 fluorescence wavelength shift of ruby is a commonly used pressure sensor for DAC  
225 experiments (e.g., Chervin et al., 2001; Shen et al., 2020). Ruby fluorescence is  
226 commonly used as a pressure sensor in DAC experiments, but it was not added to the  
227 HDAC experiments as it dissolves quickly in the heated aqueous fluid, possibly causing  
228 chemical pollution.

229 (2) In all experiments small gold particles were added into the sample chambers to  
230 determine the pressure in-situ with SXR during the run. Gold was measured usually  
231 after quenching of the laser heating cycle. The SXR analyses were processed with  
232 DIOPTAS (Prescher and Prakapenka, 2015) and the GSAS-II (Toby and Dreele, 2013)  
233 software. The pressure shift from the equation of state (EOS) for gold was calculated

234 after Dorogokupets and Dewaele (2007) in the web application  
235 <http://kantor.50webs.com/diffraction.htm>. Unlike ruby, the gold flakes do not dissolve in  
236 hydrous experiments. In the neon experiments, the addition of gold allowed us to  
237 compare it to the ruby fluorescence pressures.

238 (3) For the hydrous experiments LN11 and LN22 the pressure was determined  
239 additionally after the run using the EOS for water and following the method described by  
240 Bassett et al. (1993). The water-ice phase transition was used to calculate the fluid  
241 density in the sample chamber: this was done after the experiment (the HDAC were  
242 kept closed) and not during the experimental session at Soleil. The sample chamber of  
243 the HDAC was cooled down with liquid nitrogen and the temperature of the phase  
244 transition between water and ice VI in the aqueous fluid was measured with the  
245 attached thermocouples. Pressures were then calculated from the EOS for the water-ice  
246 transition (Wagner and Pruß, 2002). This is feasible as the use of the EOS of water in  
247 silicate-water systems has been validated by Munsch et al. (2015). Table 2 lists all  
248 calculated pressures from gold, water-ice transition, and ruby.

### 249 *2.3.2. Challenges in pressure determination*

250 Pressure determination in the HDAC is challenging and was often not satisfying during  
251 for the conducted runs. The sample chamber is a closed system during the experiment  
252 and once it has been compressed, the pressure inside remains constant if the cell does  
253 not leak or the pressure is altered – intentionally or by damaging. While the sample is  
254 heated the pressure increases inside the sample chamber due to thermal pressure, but  
255 it decreases again after quenching/during cooling of the sample. Therefore, ruby  
256 fluorescence in neon experiments shows the same pressure before and after the

257 experiment (at room temperature) and confirms that the system remained close (Table  
258 2). To prevent all parts of the loaded cell from damage suffering in hydrous  
259 experiments, the nitrogen cooling for pressure determination with the EOS of the water-  
260 ice transition was only applied after cessation of the experiment while the HDAC were  
261 kept closed. During sample loading of the hydrous experiments no high-pressure  
262 polymorphs of ice were observed in any of the loaded sample chambers at room  
263 temperature. Thus, none of the HDAC samples exceeded pressures of 1.1 GPa during  
264 the pre-experiment compression (c.f. Wagner and Pruß, 2002). The pressure  
265 determination from the water EOS is precise and reliable only for the last heating cycles  
266 performed in the HDAC. Respectively, the limit  $P < 1.1$  GPa is proposed for the first  
267 heating cycles of each experiment (Table 1).

268 Most pressures calculated from the EOS for gold do not agree well with the other two  
269 methods (Table 2). The pressures measured with gold are in average about 1.2 GPa  
270 higher than the pressures determined with water-ice transition or ruby. The difference  
271 between gold and both alternative methods show a moderate positive correlation of  $r =$   
272 0.69 (Figure 2), with -1 or 1 for an excellent correlation and 0 for no correlation.  
273 However, the trend in Figure 2 would be expected to match with  $m = 1$  (dashed line), as  
274 all working pressure calculation methods should give the same results within an error,  
275 or it should describe a nonlinear approach to 1 on a larger pressure scale. We used  
276 only data points where the pressure was measured under the same conditions with two  
277 different methods for Figure 2. The dataset is small, and the range of pressure is limited  
278 to  $< 1.7$  GPa (ruby) which lies in the nature of the experiments of this study. A nonlinear  
279 approach towards the dashed line ( $m = 1$ ) can be expected for pressures  $> 2$  GPa, but

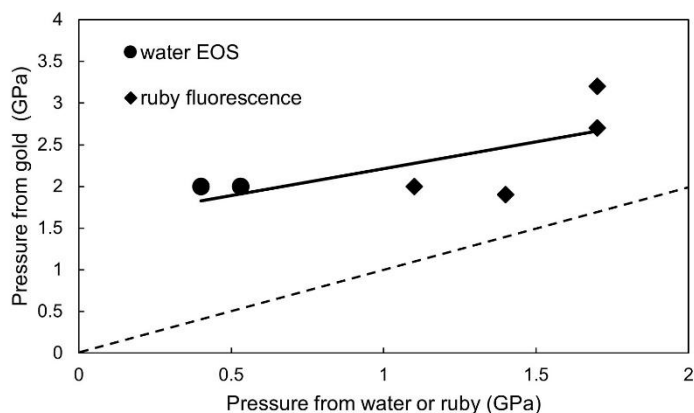
280 at lower pressures the EOS of gold shows a clear shift towards higher pressures (Figure  
281 2) and cause probably pressure overestimation.

282 Pressure values calculated from gold show further unexpected behavior during each  
283 experiment, as for several runs the pressure seem to remain elevated after the last  
284 quenching – relative to the first measured pressure before the start of the experiment.

285 This is not in agreement with ruby fluorescence. Moreover, in experiment LN11 the  
286 pressure seems to drop during the laser heating from 1.9 GPa to 0.8 - 1.2 GPa for the  
287 first four heating cycles but seem to increase to 2.0 GPa after the last heating cycle  
288 (Table 2). A closure (volume change) of the sample chamber could not be observed.

289 We argue therefore that pressure calculations from the EOS of gold are unreliable for  
290 the applied pressure range of this study (< 2 GPa). Pressure data in this range  
291 calculated from gold XRD are rather estimates and must be handled with care.

292



293

294 Figure 2 Pressures in the DAC sample chamber calculated from the EOS for gold  
295 vs. pressures calculated from the EOS for water or from ruby fluorescence. The linear



296 trend (black line) shifts from the expected trend (dashed line) between the applied  
297 methods.

298

#### 299 2.4. Starting material composition

300 For the starting material, we used a natural island arc basalt from the Soufriere volcano  
301 on St Vincent Island, Lesser Antilles arc (STV301 glass Pichavant et al., 2002) that was  
302 enriched in Br and water: The basalt was grounded into a fine grain powder to which 3  
303 wt.% of NaBr and 2 wt.% of H<sub>2</sub>O were added. We melted the powder in a Boyd &  
304 England-type piston cylinder apparatus (Boyd and England, 1960) at the Institut de  
305 Physique du Globe de Paris (IPGP) to obtain a glass of this hydrous, Br-bearing basaltic  
306 mixture. Synthesis conditions for our starting glass were 1.1 GPa, 1300 °C and 30 min  
307 run duration. A sealed Au-Pd capsule prevented major iron loss. Small pieces of the Br-  
308 bearing hydrous glass were used for the in-situ experiments. For the aqueous fluid we  
309 used distilled water.

310 The synthesized basaltic starting material is texturally homogenous. We used an optical  
311 microscope first, and an electron microscope (FEG Zeiss Ultra55) at the IMPMC,  
312 Sorbonne Université Paris to check the glass for impurities. The glass looks  
313 homogenous and no crystals, gas- or water bubbles could be found. Major and minor  
314 elements were analyzed with a JEOL 8530F Plus Electron Probe Microanalyser (EPMA)  
315 at the Centre for Advanced Microscopy, ANU in Canberra, Australia and confirmed that  
316 the basalt glass is also chemically homogenous. The composition of the starting glass  
317 can be found in Table 3. The Br concentration is about  $1.1 \pm 0.1$  wt.% (with EPMA) and

318 was confirmed with Synchrotron X-ray fluorescence (SXRF) in the basalt glass before  
319 each experiment.

320

## 321 2.5. In-situ analysis of Br concentrations

322 Bromine concentration in basalt glass, aqueous fluid, and neon were measured  
323 quantitatively by SXRF in situ analysis in the diamond anvil cells (DAC) at the SOLEIL  
324 Synchrotron on the PSICHÉ beamline. We used a monochromatic beam of 33 keV that  
325 was masked by a pinhole of 50  $\mu\text{m}$  in diameter and focused at  $12 \times 10 \mu\text{m}^2$ . For each  
326 experiment the DAC was positioned perpendicular to the beam. Both SXRF and SXRD  
327 were detected in transmission geometry. SXRF was detected by a SDD detector which  
328 was placed at  $24^\circ$  relative to the beam transmitted through the DAC. Counting times  
329 were usually set to 600 seconds.

330 SXRF analyses were calibrated on a 240  $\mu\text{m}$  thick piece of the NIST silicate glass  
331 certified reference material SRM 610 (e.g., Rocholl et al., 1997). The Br content in NIST  
332 610 is not quantified but NIST 610 is calibrated for multi elemental analyses on glasses  
333 and covers a broad range of elements including elements with  $K\alpha$  peak energies close  
334 to the  $K\alpha$  peak of Br (11.9 keV) e.g., Se (11.2 keV), As (10.5 keV) or Sr (14.1 keV). The  
335 volcanic glass V1 (Mosbah et al. 1995) was measured additionally as standard glasses,  
336 as well as a piece of the Br-H<sub>2</sub>O-doped starting glass (BaM024). To test for any effects  
337 of DAC setup on SXRF measurements NIST 610 was also placed in the DAC at  
338 ambient pressure and temperature. No effects could be found between the different  
339 NIST analyses. All glasses show good agreements for their element concentrations in

340 the energy range of Br (Table 4). During the experiments basalt glass analyses were  
341 conducted in the center of the heated region (the crater-like texture in neon  
342 experiments). The detection limit is typically in the range of of 1-10  $\mu\text{g/g}$ , which is in  
343 good agreement with similar studies (e.g. Louvel et al., 2020a) and with what can be  
344 expected for elements of a similar mass (Rousseau, 2001).

345 The gaskets of each experiment were recovered, and their thickness was measured  
346 after the run to calculate the change in the set-up geometry of the SXRF analyses  
347 during the experiments. To quantify the Br concentration in the basaltic glass, the  
348 aqueous fluid, or in neon all obtained SXRF spectra from standards and experiments  
349 were processed by using the PyMCA software (Solé et al., 2007). We compared the Br  
350 concentration of the starting material with the calculated values from PyMCA for the first  
351 measurement at room temperature for each experiment. If both values were not in  
352 agreement, we assumed that the basalt glass was not touching both diamonds. The  
353 initial thickness of the glass was then calculated using PyMCA by adding a water/neon  
354 layer to fit the calculated Br concentration with the value from the starting material. For  
355 matrix corrections we assumed a  $2.9 \text{ g/cm}^3$  for basalt,  $1\text{-}1.2 \text{ g/cm}^3$  for water and  $0.5$   
356  $\text{g/cm}^3$  for supercritical Neon.

357

### 358 3. RESULTS

#### 359 3.1. Textural observations

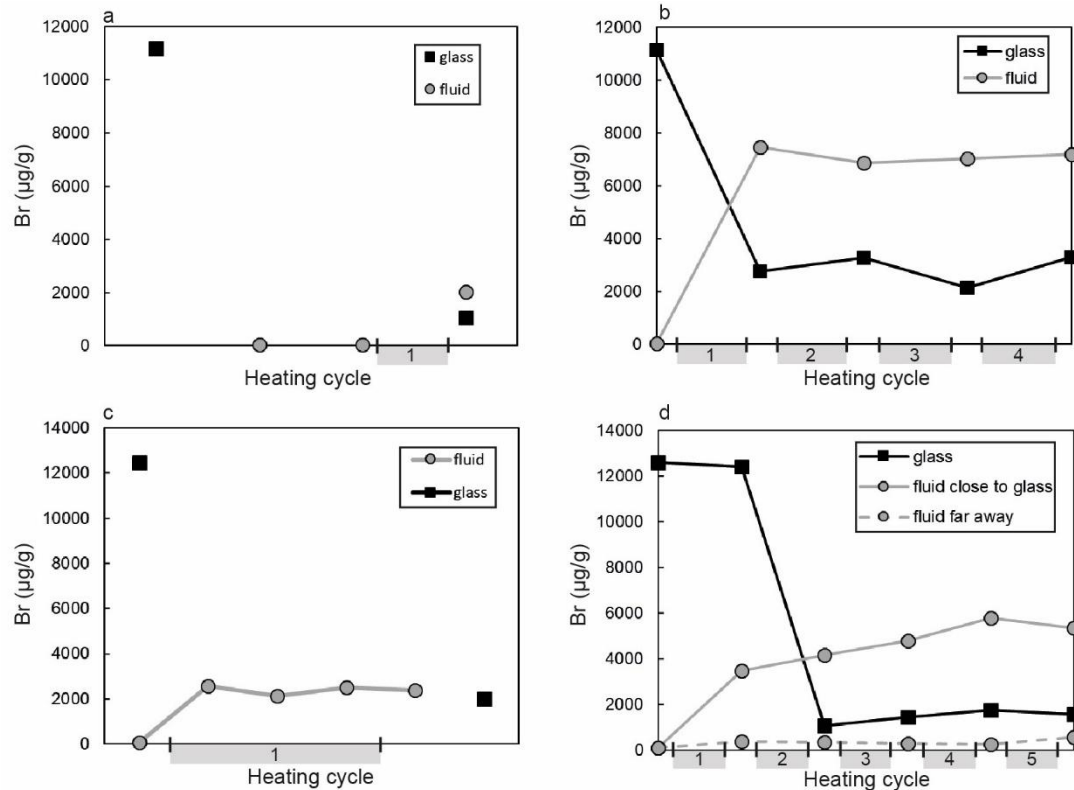
360 Textural changes of the basalt glass were observed after quenching the experiment. In  
361 hydrous experiments the glass has a spongy or foam-like texture after the ultra-fast

362 quenching induced by the laser turn off which causes very fast local water exsolution  
363 (Figure 1a-b). This transformation into a foam affected a volume that is much larger  
364 than the original laser heating spot and is seen at the rim of the glass piece. It shows  
365 therefore that almost the whole glassy volume is melted during the heating. These  
366 textures have not been observed in studies with haplogranite where the external heating  
367 is strong enough to melt the entire glass in the sample chamber of the HDAC and when  
368 temperatures decrease slowly (Bureau et al., 2010; Louvel et al., 2020b). The spongy  
369 textures were not found in neon runs. As a study from Balcone-Boissard et al. (2020)  
370 shows, bromine diffusion in related melts is much lower than that of H<sub>2</sub>O. External  
371 heating was added to lower the temperature gradient and to support the  
372 homogenization of the hydrothermal fluid in several experiments, but temperatures were  
373 not high enough to melt the entire piece of glass or even reach full miscibility between  
374 melt and fluid. Nevertheless, experiments like LN11 and LN22 for water show  
375 reproducible results and equilibration between the Br concentration in the glass and in  
376 the surrounding fluid within their runs.

377 In neon experiments the melting spots of the laser are clearly visible but the glass  
378 around the laser appears to be texturally unharmed (Figure 1c-d). The temperature  
379 gradient is larger than in the hydrous experiments because no external heating was  
380 applied to the CDAC. However, the basalt glass shows no strong reaction with neon.

381 All experimental results are listed in Table 1.

382



383

384 Figure 3 Bromine concentration versus time/heating cycles in hydrous experiments.

385 During each heating cycle step the basalt glass was melted, quenched, and analyzed

386 again. a) Cpo2: Already the first heating cycle reduces the Br concentration in the basalt

387 dramatically. b) LN22: Bromine concentrations in the basalt glass and in the aqueous

388 fluid equilibrate quickly after quenching the first heating cycle and remain on relatively

389 constant levels. The plateau of the curve is a good indicator for chemical equilibrium. c)

390 Cpo3: Bromine concentration in the aqueous fluid equilibrates quickly and remains

391 constant after quenching. d) LN11: Without the usage of external heating the

392 concentration of bromine in the aqueous fluid is not homogenized and shows a distinct

393 difference between the concentrations analyzed close to the melted glass and further

394 away.

395

## 396 3.2. Hydrous Experiments

### 397 3.2.1. Run Cpo2

398 Run Cpo2 shows Br loss to the surrounding aqueous fluid: Br concentration before the  
399 first heating is 11160 µg/g in the glass and 26-48 µg/g in the fluid. For this run the  
400 temperature of the laser could not be measured precisely. After quenching the  
401 concentration changes to 1070 µg/g in the glass and 2029 µg/g in the fluid (Figure 3a).  
402 A partition coefficient of  $D_{\text{fluid/glass}}^{\text{Br}} = 1.9$  was calculated. The pressure could not be  
403 determined precisely, but according to the stability of water and ice VI at room  
404 temperature the pressure in the loaded cell is < 1.1 GPa (Wagner and Pruß, 2002).  
405 Gold SXRD gave a pressure range of 2.6 GPa before the heating and 2.1 GPa after the  
406 heating.

### 407 3.2.2. Run LN22

408 In run LN22 Br concentration before the first heating is 11120 µg/g in the glass and 18  
409 µg/g in the aqueous fluid. The laser temperature could only be estimated but SXRD  
410 confirmed that it was above the solidus of the hydrous basalt. After quenching the  
411 concentrations change to 2124-3282 µg/g in the glass and 6864-7455 µg/g in the fluid  
412 for all four cycles (Figure 3b). A range of  $D_{\text{fluid/glass}}^{\text{Br}} = 2.10 - 3.31$  was calculated. The  
413 pressure range is between 0.4 and 1.1 GPa during the experiment according to water  
414 and decreased slightly from 2.1 GPa to 2.0 GPa according to gold.

415 Br concentration in water and basalt reach a plateau after the first heating cycle (Figure  
416 3b). This is a good indicator that chemical equilibrium has been reached in the  
417 experiment.

### 418 3.2.3. *Run Cpo3*

419 In run Cpo3 Br concentration is 12440  $\mu\text{g/g}$  in the glass and 79  $\mu\text{g/g}$  in the aqueous fluid  
420 before the heating. While the laser keeps the basalt liquid, the Br concentration in the  
421 fluid ranges from 2130 to 2563  $\mu\text{g/g}$ . After quenching the concentrations is 1990  $\mu\text{g/g}$  in  
422 the glass and 2370  $\mu\text{g/g}$  in the fluid (Figure 3c). A value of  $D^{\text{Br}}_{\text{fluid/glass}} = 1.19$  can be  
423 calculated. According to run Cpo3 there are no notable changes in Br concentration  
424 before and after quenching the glass. As for run Cpo2 the pressure is  $< 1.1$  GPa  
425 according to water but increases from 1.6 GPa to 2.1 GPa according to gold.

### 426 3.2.4. *Run LN11*

427 Bromine concentration before the first heating is 12610  $\mu\text{g/g}$  in the glass and 80  $\mu\text{g/g}$  in  
428 the aqueous fluid. After the first quenching the Br concentration remains high in the  
429 glass (12410  $\mu\text{g/g}$ ) but becomes slightly lower after heating-quenching cycle 2-5 (1062-  
430 1752  $\mu\text{g/g}$ ). In the fluid, measurements close to the melted glass show that the Br  
431 concentration ranges from the first to the fifth quenching between 3462 and 5784  $\mu\text{g/g}$ .  
432 Further away from the glass, the values range from 226 to 565  $\mu\text{g/g}$  (Figure 3d). While  
433 Br shows a concentration gradient the partitioning between fluid and glass remains  
434 relatively constant in cycle 2-5 with  $D^{\text{Br}}_{\text{fluid/glass}} = 3.30$  to 3.92 close to the glass and  
435  $D^{\text{Br}}_{\text{fluid/glass}} = 0.13$  to 0.37 at the rim of the sample chamber. The pressure range is  
436 between 0.53 and 1.1 GPa calculated from water EOS and varies between 0.8 and 2.0  
437 GPa calculated from the EOS for gold.

438

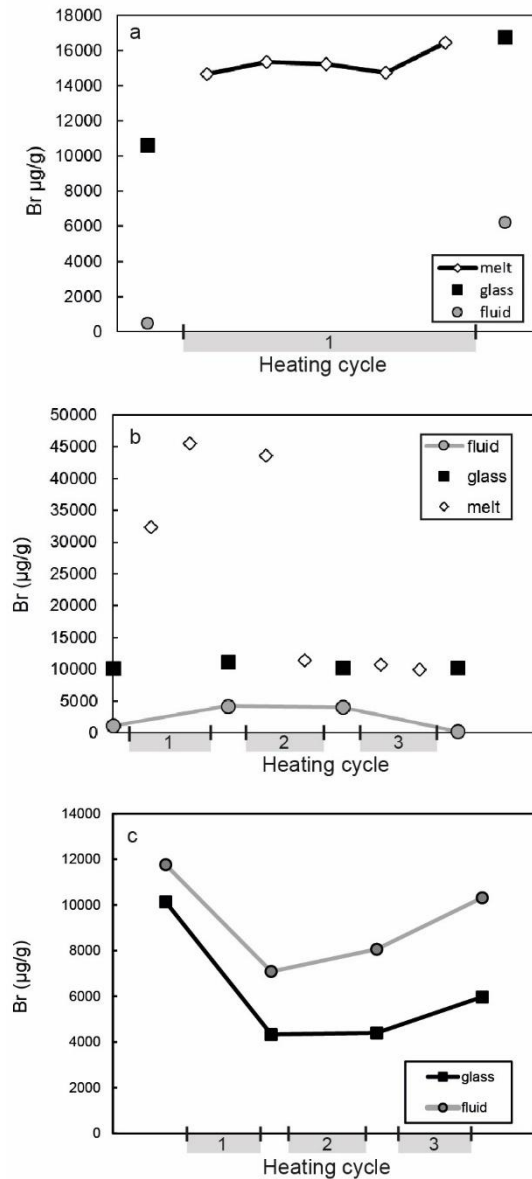
### 439 3.3. Neon Experiments

440 3.3.1. *Run Mar1*

441 In run Mar1 bromine concentration before the first heating is 10620  $\mu\text{g/g}$  in the glass  
442 and 209  $\mu\text{g/g}$  in the neon. During laser heating the concentration increases slightly from  
443 14640 to 16430  $\mu\text{g/g}$  in the melt. It remains high (16430  $\mu\text{g/g}$ ) in the quenched glass  
444 and increased in the neon to 16212  $\mu\text{g/g}$  (Figure 4a). A partition coefficient of  $D^{\text{Br}}_{\text{neon/glass}}$   
445 = 0.37 can be calculated from the Br values in the fluid and in the glass. The pressure is  
446 1.7 GPa according to ruby fluorescence and increases from 2.7 to 3.2 GPa according to  
447 the EOS of gold. We assume that the observed change in concentration comes from  
448 slight variation in the glass thickness between the different heating cycles. The melt can  
449 become spherical and might have extended further in the direction of the beam within  
450 the sample chamber. While Br concentration increased during the ongoing melting the  
451 calculated partitioning between glass and fluid is in good agreement with the Hak1 run  
452 (see below).

453





454

455 Figure 4 Bromine concentration versus time/heating cycles in neon experiments.  
 456 During each further heating cycle step the basalt glass was melted, quenched, and  
 457 analyzed again. a) Mar1: Br concentrations remain high in the basalt glass and low in  
 458 the neon. No changes in concentration appear between melt and glass. b) Hak1: The  
 459 bromine concentrations measured in the neon remain lower than in the basalt glass.  
 460 With ongoing decompression water is released from the hydrous basalt glass during the  
 461 last heating cycle. We suspect bromine to partition into the released water while neon

462 remains depleted in bromine. c) Hak2: Bromine concentration remain higher in the neon  
463 than in the basalt glass over all heating cycles.

464

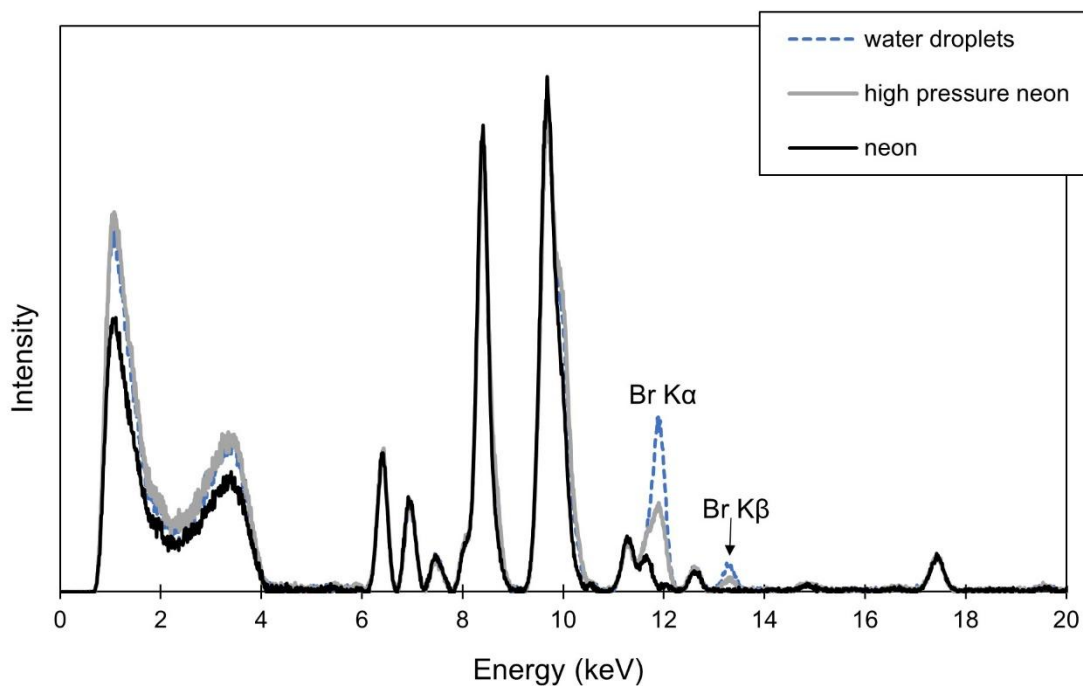
### 465 3.3.2. Run Hak1

466 In run Hak1 bromine concentration before the first heating is 10019  $\mu\text{g/g}$  in the glass  
467 and 1062  $\mu\text{g/g}$  in the neon. During the first heating cycle Br concentration ranges from  
468 11019  $\mu\text{g/g}$  to 45065  $\mu\text{g/g}$  in the melt and in the quenched glass respectively. In the  
469 second and third heating cycles Br concentration remains lower in the melt and in the  
470 glass ranging from 9864  $\mu\text{g/g}$  to 11256  $\mu\text{g/g}$ . In the neon the measured Br concentration  
471 increases to 4153  $\mu\text{g/g}$ , 3985  $\mu\text{g/g}$ , and 208  $\mu\text{g/g}$  after each of the three quenching  
472 cycles. Currently, we cannot fully explain the high Br values in the melt for the first two  
473 heating cycles. Volume changes during the melting could explain the variations.  
474 However, in heating cycle 2 and 3 the Br values decrease and equilibrate with the  
475 values measured in the glass. The  $D^{\text{Br}}_{\text{neon/glass}}$  values are 0.38, 0.39, and 0.02,  
476 respectively (Figure 4b).

477 The pressure is 1.1 GPa after loading the cell measured with ruby fluorescence or 3.3  
478 GPa with gold. At this pressure the diffraction peaks also overlap with neon at 1.2 GPa.  
479 Like in all other experiments with neon, the external pressure (1.1 GPa) is released  
480 stepwise between each heating-quenching cycle. After the last quenching small droplets  
481 of water could be observed as a third phase in the sample chamber (Figure 1d; Figure  
482 5). This observation suggests a pressure  $< 1.1$  GPa after the last quenching but will be

483 discussed in more detail further below. The calculated pressure from gold is 3.1 GPa  
484 (1.2 GPa from neon) at the end of the experiment.

485



486

487 Figure 5 Synchrotron X-ray fluorescence analysis of the pressure medium in run  
488 Hak1. High pressure neon was analyzed at heating cycle 2 while water was absent. The  
489 Br concentration in the HP neon is 4025  $\mu\text{g/g}$  (grey). When the pressure was decreased  
490 in heating cycle 3 water bubbles released from the hydrous basalt could be observed in  
491 the neon (c.f. Figure 1d). With the presence of water Br concentrated in the water  
492 bubbles (blue) and decreased in the neon down to 210  $\mu\text{g/g}$  (black).

493

494 3.3.3. Run Hak2

495 For run Hak2 the closed cell with the sample Hak1 was recompressed and used again  
496 for three heating-quenching cycles. Bromine concentration before the first heating is  
497 10138  $\mu\text{g/g}$  in the glass and already high in the neon from the former run Hak1 with  
498 11760  $\mu\text{g/g}$ . After quenching the concentrations range from 4333 to 5974  $\mu\text{g/g}$  in the  
499 glass and 7087 to 10314  $\mu\text{g/g}$  in the fluid (Figure 4c). A range of  $D^{\text{Br}}_{\text{fluid/glass}} = 1.64 -$   
500 1.83 can be calculated. The ratio calculated from the Br concentrations before the first  
501 heating in this experimental run is  $D^{\text{Br}}_{\text{fluid/glass}} = 1.16$ . The pressure determined with ruby  
502 spheres is 1.4 GPa before the first and after the last run. Gold pressure determination  
503 decreased from 2.8 GPa to 1.9 GPa.

504

## 505 4. DISCUSSION

### 506 4.1 Bromine partitioning between basalt and aqueous fluids

507 The fluid-melt partitioning values from our experiments range from  $D^{\text{Br}}_{\text{fluid/melt}} = 1.19$  to  
508  $3.31 \pm 0.6$  – within the applied pressure and temperature range. These values overlap  
509 with findings from other studies but are slightly lower than the partition coefficients  
510 calculated by Bureau et al. (2010), Cadoux et al. (2018), and Louvel et al. (2020b).  
511 Partition coefficients between haplogranite and an aqueous fluid from Bureau et al.  
512 (2010) range from  $D^{\text{Br}}_{\text{fluid/melt}} = 2.18 \pm 0.4$  to  $15.3 \pm 2$  and values from Louvel et al.  
513 (2020b) range from  $D^{\text{Br}}_{\text{fluid/melt}} = 2 \pm 0.2$  to  $9.2 \pm 1.8$ . Cadoux et al (2018) found partition  
514 coefficients of  $D^{\text{Br}}_{\text{fluid/melt}} = 3.8$  to  $5.2$  from their experiments with basaltic composition  
515 and  $8.6$  to  $27.9$  from rhyodacite. With all calculated  $D^{\text{Br}}_{\text{fluid/melt}} > 1$  the data from all four

516 studies confirm that Br has a slight to strong affinity to partition from the melt into the  
517 aqueous fluid.

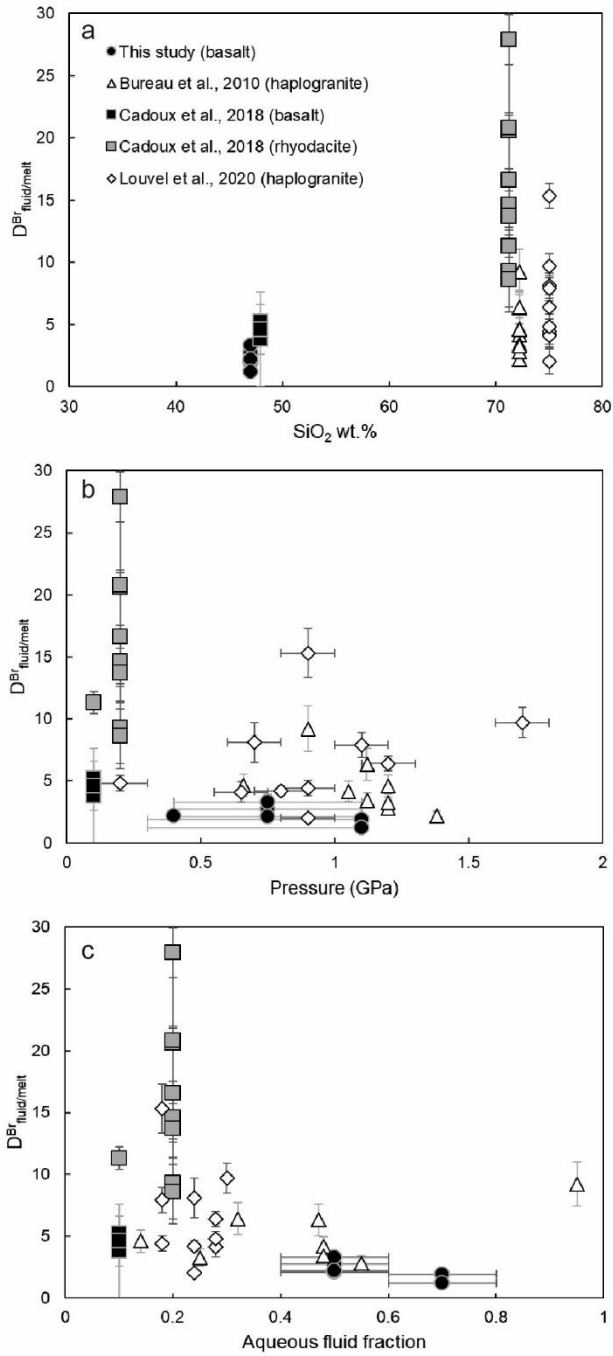
518 Partition coefficients from Cadoux et al. (2018) are generally higher than partition  
519 coefficients from the other three studies for comparable SiO<sub>2</sub> content (Figure 6). One  
520 reason could be that Cadoux et al (2018) did not conduct in-situ experiments and  
521 measured Br concentrations only in the quenched samples. In fact, the three other  
522 studies are all conducted and analyzed in-situ in HDAC – this study at least partially.  
523 Louvel et al. (2020b) argue that differences in the partition coefficients to Cadoux et al.  
524 (2018) might come from the quantification of Br by mass balance as it was used by  
525 Cadoux et al. (2018), or artifacts of the quench cooling that cause Br loss into the fluid.  
526 Louvel et al. (2020b) exclude their data point at 0.2 GPa, as they suspect uncertainties  
527 in the pressure determination below 0.5 GPa. Run Hak1 demonstrates that Br  
528 concentrations do not change significantly in our experiments in neon between basalt  
529 melt and quenched basalt glass (Figure 4b), but it can be the case with water in  
530 externally heated DAC experiments up to 800-900 °C (e.g., Borchert et al., 2009;  
531 Bureau et al., 2010; Leroy et al., 2019). At these temperatures external heating  
532 increases the pressure in the sample chamber. Quenching the experiment can induce a  
533 pressure drop that affects the partitioning of elements like Sr, Rb, (Borchert et al., 2009)  
534 or Br (e.g., Bureau et al., 2010). Due to the selective heating of the laser, the pressure  
535 increase in the cell is small and fast diffusion during cooling plays a minor role in our  
536 experiments. Therefore, differences might also come from uncertainties in pressure  
537 determination or Br quantification in quenched samples.

538 Several trends for partition coefficients were described and suggested in existing  
539 studies on Br partitioning (e.g., Figure 6): Bureau et al (2010) found correlations of  
540 decreasing  $D_{\text{fluid/melt}}^{\text{Br}}$  with increasing pressure and with increasing water content.  
541 Cadoux et al (2018) found a correlation of decreasing  $D_{\text{fluid/melt}}^{\text{Br}}$  with increasing  
542 temperature and with decreasing  $\text{SiO}_2$  concentration within their data. This  
543 compositional effect of the melt was also described by Bureau and Metrich (2003) and  
544 Cochain et al. (2015). Louvel et al., 2020b found the variation in the partition coefficients  
545 to remain small over a large P-T range and do not find any clear trend. They propose  
546 that hydrous granite melts have a Br storage capacity similar to aqueous fluids. This  
547 makes sense as with increasing pressure and temperature, both fluid and melt tend to  
548 be equal before being miscible (Bureau and Keppler, 1999). This could buffer changing  
549 P-T conditions to some extent. Assuming a compositional trend, the basalt from Cadoux  
550 et al. (2018) has a higher  $D_{\text{fluid/melt}}^{\text{Br}}$  than values from this study, which rather overlaps  
551 with the partition coefficients from the haplogranite of Bureau et al. (2010). The  
552 rhyodacite from Cadoux et al. (2018) has about the same amount of  $\text{SiO}_2$  as the  
553 haplogranite but has higher  $D_{\text{fluid/melt}}^{\text{Br}}$  values. This can be best explained with the  
554 pressure trend described by Bureau et al. (2010).

555 As the partition coefficients for basalts are generally smaller than for  $\text{SiO}_2$ -rich melts, the  
556 data from Cadoux et al. (2018) and from this study support the pressure trend, as well  
557 as the general trend of decreasing  $D_{\text{fluid/melt}}^{\text{Br}}$  with increasing water content. However,  
558 given the uncertainties and the data spreading from all five studies and the much  
559 stronger effect melt composition, it is not clear if pressure, melt composition, or fluid  
560 fraction have the strongest effect on the partitioning.

561

562



563

564 Figure 6 Aqueous fluid-melt partition coefficients for bromine from Bureau et al.

565 (2010) (triangle), Cadoux et al. (2018) (box), Louvel et al. (2020b) (diamond) and this

566 study (Cpo2, Cpo3, LN22 in circles) vs. a) SiO<sub>2</sub> content in the silicate glass; b) vs.  
567 pressure; c) vs. aqueous fluid fraction.

568

#### 569 4.2. Bromine partitioning between basalt glass and neon

570 The calculated neon-melt partition coefficients in the experiments Hak1 and Mar1 are in  
571 the range of  $D_{\text{fluid/melt}}^{\text{Br}} = 0.38 \pm 0.06$  and imply that Br favors to remain in the basalt  
572 liquid over partitioning into the neon, an inert fluid phase (Table 1). To the authors'  
573 knowledge there are no further studies on halogen partitioning between a silicate glass  
574 and neon or any other dry gaseous phase such as CO<sub>2</sub>. We argue that Br has a strong  
575 affinity to bond with water but a low affinity to bond with neon which can be a good  
576 analogue for CO<sub>2</sub>, the second major volatile degassed by volcanoes. Both neon and  
577 CO<sub>2</sub> do not have a strong bonding affinity to halogens. Therefore, Br tends to remain in  
578 the basaltic melt. However, partition coefficients from experiment Hak2 range from 1.16  
579 to 1.83. This discrepancy within the neon-related experiments needs to be addressed:

580 We used a hydrous basalt with about 2 wt.% of H<sub>2</sub>O as starting material for the  
581 experiments of this study. In experiment Hak1 water droplets released from the hydrous  
582 basalt could be observed in the sample chamber after the last heating cycle (Figure 1d;  
583 Figure 5). The water droplets were visible at the end of run Hak1 and could explain the  
584 decrease of Br concentration in the neon from 3985 to 208 µg/g Br after the last heating  
585 cycle: As soon as small amounts of water appear as a third phase in the sample  
586 chamber, Br partitions from neon into water leaving the neon fluid with much lower Br  
587 concentration than in the former heating-quenching cycles.



588 The cell remained closed for the next experiment Hak2 but after recompression of the  
589 cell the water droplets could not be observed during the experiment Hak2. At  $\geq 1.4$  GPa  
590 and ambient temperature liquid water is not stable but instead ice VI (Wagner and Pruß,  
591 2002). However, neither water nor ice VI were observed before and during the Hak2  
592 experiment. In the lack of Br partitioning data between ice VI and neon we assume that  
593 not much Br can be incorporated in the structure of ice VI and that most of the Br goes  
594 back into neon when water transforms into ice during the re-compression of the sample.

595 The partition coefficients between basalt and (dry) neon are represented by the first two  
596 heating cycles of Hak1 (0.38 and 0.39) before water droplets were observed. The higher  
597 partition coefficients over several heating-quenching cycles in Hak2 (1.16 – 1.83) must  
598 be related to the presence of water. At this stage the basalt crossed the glass transition  
599 several times (heating and quenching cycles) and Br should partition from the neon  
600 back into the basalt while the system equilibrates. Instead, Br concentrations and  
601  $D_{\text{neon/glass}}^{\text{Br}}$  remain higher than in Hak1.

602 A mixed fluid of “wetted” or hydrous neon probably explains the elevated concentrations  
603 and partitioning values. During heating of the Hak2 experiment neon takes up the water  
604 (initially stored in liquid droplets or ice) and increases its Br storage capacity as it  
605 becomes slightly hydrous. In Hak1 the water release from the basalt liquid has been  
606 initially prevented by the high pressure in the first cycles. After external decompression  
607 in the last cycle of Hak1 water could be released from the basalt glass. This is a very  
608 likely scenario as the water solubility in the basalt glass strongly relies on pressure (e.g.,  
609 Dixon et al., 1995). As the basalt dehydrates during the melting, experiments with dry  
610 basalt would be needed to clarify Br behavior in neon.

611

### 612 4.3 Volcanic bromine degassing and global bromine fluxes

613 Bromine concentrations in natural melts, fluids, or volcanic gases are usually in the  
614 range of low  $\mu\text{g/g}$ . Monitoring of Br cycling, or volcanic degassing remains challenging,  
615 and so far, the data are scarce relative to e.g., the lighter halogens fluorine (F) and Cl  
616 (e.g., Webster et al., 2018). To calculate a (global) flux for volcanic halogen degassing,  
617 two methods can be applied: (1) Volatile degassing can be measured directly at active  
618 volcanoes or (2) halogen concentration in melt inclusions can be studied as a  
619 petrological approach (for detailed reviews of both methods: Wallace, 2005; Pyle and  
620 Mather, 2009; Webster et al., 2018, and references therein).

#### 621 4.3.1. Volcanic halogen degassing

622 Halogen flux calculations from present-day emissions have been applied to accessible  
623 volcanoes – most of them are related to arc volcanism (Pyle and Mather, 2009). Due to  
624 its high concentration in volcanic gasses  $\text{SO}_2$  is the easiest volatile to measure in  
625 volcanic plumes. Measured halogen concentrations can be scaled up using e.g.,  
626  $\text{HF}/\text{SO}_2$  or  $\text{HCl}/\text{SO}_2$  ratios (Wallace, 2005). For Br either  $\text{HBr}/\text{HCl}$  or  $\text{HCl}/\text{SO}_2$  are  
627 commonly in use as ratios. However, halogen- and  $\text{SO}_2$  degassing show large spatial  
628 variations and can vary dramatically at one volcano during different phases of activity  
629 (c.f. Edmonds et al., 2001, 2002). This can have large impacts on global flux upscaling  
630 (Pyle and Mather, 2009, Webster et al., 2018, Cadoux et al., 2022). Recent flux  
631 estimates for halogens from volcanic gas data range therefore over two orders of

632 magnitude for F and Cl, and over four orders of magnitude for Br and iodine (Webster et  
633 al., 2018).

634 Several values for global Br flux from volcanic arc degassing have been calculated  
635 based on HBr measurements and the comparison to HBr/HCl or HCl/SO<sub>2</sub> ratios: Halmer  
636 et al. (2002) calculated  $2.6\text{-}43.2 \times 10^9$  g/y, Aiuppa et al. (2005) calculated  $13 \times 10^9$  g/y,  
637 Pyle and Mather (2009) calculated  $5\text{-}15 \times 10^9$  g/y, and Webster et al. (2018) calculated  
638  $10.5 \times 10^9$  g/y (Table 5). Several studies on volatile degassing show that halogen  
639 degassing from non-arc volcanism is rather negligible for global flux calculations of e.g.,  
640 Cl (5.5 wt. % of the annual global flux) and for heavy halogens like Br (0.6 wt. %;  
641 Webster et al., 2018; with data from: Gerlach, 2004; Aiuppa et al., 2009; Shinohara,  
642 2013).

#### 643 *4.3.2. Global flux calculation from melt inclusions*

644 The calculation of global halogen flux from melt inclusions compares the concentration  
645 of halogens measured in pre-eruptive melt inclusions with post-eruptive glass of the  
646 final degassed lava (e.g., Webster et al., 2018; d'Augustin et al., 2020). This approach  
647 allows to estimate volatile flux from volcanic eruption of the past. Chlorine and fluorine  
648 exsolve at low pressures with  $< 100$  MPa for Cl and  $< 10$  MPa for F (Aiuppa et al., 2009;  
649 Webster et al., 2018). This implies late degassing of both halogens during magma  
650 ascent and a good preservation of initial Cl and F contents in pre-eruptive melt  
651 inclusions. Not much is known about the behavior of Br but the small pressure effect on  
652 melt-fluid partitioning in basalts suggests also shallow degassing of Br.

653 Following the method described in Wallace (2005), we can calculate an annual bromine  
654 flux  $q_{\text{Br}}$ :

$$q_{\text{Br}} = \frac{Q \times \rho_B}{c_{\text{fl}}}$$

655 with  $\rho_B$  as the density for basalt (2.8 g/cm<sup>3</sup>). For the annual magma flux  $Q$ , we use a  
656 global arc magma flux of  $2.5 \times 10^{15}$  cm<sup>3</sup>/y from Carmichael (2002). Instead of using Br  
657 measurements from post-erupted glasses, the bromine concentration in the  
658 fluid/degassing phase  $c_{\text{fl}}$  can be calculated as

$$c_{\text{fl}} = c_{\text{mi}} \times W \frac{D}{D + 1}$$

659 with  $c_{\text{mi}}$  as bromine concentration in melt inclusions and  $D$  as the newly gained partition  
660 coefficient  $D^{\text{Br}}_{\text{fluid/melt}}$  for aqueous fluid experiments from this study. The addition of the  
661 factor  $W$  considers that the fluid fraction in our experiments is higher than in natural  
662 systems: Experiments from this study have a fluid fraction of 25 to 45 wt.%. Arc  
663 magmas can have water contents up to 20 wt.%, but probably not all over the globus  
664 (Urann et al., 2022). Assuming a water content between 5 and 12 wt.% would lead to a  
665 factor  $W = 3$  to 7.

666 The amount of data for bromine concentration in melt inclusions ( $c_{\text{mi}}$ ) are rather limited  
667 relative to the lighter halogens F and Cl. Webster et al. (2018) compiled a dataset of  
668 175 measurements for Br and 4710 measurements for Cl in melt inclusions. They find  
669 that primitive arc magmas have in general Br concentrations  $< 10$  µg/g. Higher  
670 concentrations are however possible: Straub and Layne (2003) found melt inclusions  
671 with Cl concentration of 9400 µg/g from the Izu Bonin arc. According to typical Cl/Br

672 mantle ratios of about 300, primitive melts at the Izu Bonin arc could have Br  
673 concentrations of 30  $\mu\text{g/g}$  (Bureau et al., 2010). But for a global Br distribution in  
674 primitive arc magmas an average concentration of 5  $\mu\text{g/g}$  is more likely (e.g., dataset  
675 from Webster et al., 2018) and is also in good agreement with other recent findings with  
676 about 3-5  $\mu\text{g/g}$  Br in melt inclusions from arc basalts (Kutterolf et al., 2013; Vidal et al.,  
677 2016).

678 With 5  $\mu\text{g/g}$  as initial average Br concentration the calculated global Br flux from arc  
679 volcanoes ranges from  $23.5 \times 10^9$  g/y to  $72.9 \times 10^9$  g/y in respect to the minimum and  
680 maximum values of our experimentally determined partition coefficients  $D_{\text{fluid/glass}}^{\text{Br}} =$   
681 1.19 and  $D_{\text{fluid/glass}}^{\text{Br}} = 3.92$  and the water content of arc magmas. The calculated flux is  
682 higher than values from degassing data (Table 5), but these values could be  
683 underestimated as they assume a  $\text{SO}_2$  fluxes of  $14 \times 10^{12}$  g/y (Aiuppa et al., 2005),  
684  $15 \times 10^{12}$  g/y (Pyle and Mather, 2009),  $16.8 \times 10^{12}$  g/y (Webster et al., 2018), or  $16.8 \times 10^{12}$   
685 g/y (Cadoux et al., 2022) for their calculations of the Br flux. Recent findings of a higher  
686  $\text{SO}_2$  flux of  $23 \pm 2 \times 10^{12}$  g/y (Carn et al., 2017) would lead also to higher results for  
687 corrected Br degassing values with fluxes of  $21.4 \times 10^9$  g/y,  $8\text{-}23 \times 10^9$  g/y,  $14.4 \times 10^9$  g/y,  
688 or  $12.3 \times 10^9$  g/y, respectively (Table 5). Given all uncertainties for volatile flux  
689 estimations in general, these values for the global Br flux and the newly calculated flux  
690 based on our experiments are in a very good agreement.

691

692 5. CONCLUSION

693 We present a new experimental dataset for Br partitioning between basalt and an  
694 aqueous fluid and between basalt and neon. To our knowledge these are the first  
695 experimental data measured in-situ for Br degassing from basalt. We calculated  
696 partition coefficients of  $D^{\text{Br}}_{\text{fluid/melt}} = 1.19$  to  $3.92$  at  $0.4$  to  $1$  GPa for magma degassing in  
697 water-rich magmas (aqueous fluids in equilibrated experiments). The values are in good  
698 agreement with partition coefficients from ex-situ experiments at lower pressures with  
699 basalt (Cadoux et al., 2018) and confirm a slight negative correlation with pressure, as  
700 well as a strong positive correlation with  $\text{SiO}_2$  content.

701 Experiments with an inert gas analogue for  $\text{CO}_2$  as pressure medium (neon) give  
702 partition coefficients  $< 1$  ( $D^{\text{Br}}_{\text{fluid/melt}} = 0.38 \pm 0.01$  at  $1.1$  GPa) for magma degassing  
703 under almost dry (2 wt.% water) conditions, as neon and Br have no bonding affinity.  
704 These experiments propose less Br degassing for e.g., dry intra-plate volcanism relative  
705 to hydrous eruptions in arcs, in good agreement with natural observations.

706 From the calculated partition coefficients for the presented anhydrous experiments and  
707 from global Br concentration values in melt inclusions from arc magmas, we calculated  
708 a global Br flux of  $23.5 - 72.9 \cdot 10^9$  g/y. This flux is higher than most values calculated  
709 from active volcano degassing (Aiuppa et al., 2005; Pyle and Mather, 2009; Webster et  
710 al., 2018) but agrees well with new findings on global  $\text{SO}_2$  degassing (Carn et al., 2017).  
711 Former calculated fluxes may be slightly underestimating the annual Br degassing.

712

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724

## 725 7. Appendix A. Supplementary Material

726 The supplementary material contains the raw data of all SXRF spectra and SXRD  
727 pattern that were analyzed and processed in this study.

728

729 8. REFERENCES

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Experiment-Run	Pressure (GPa)	Heating cycle	Laser Temperature °C	Pressure medium/fluid	Bromine concentration (µg/g)			D <sup>Br</sup> <sub>fluid/melt</sub>
					melt	glass	fluid	
<i>hydrous experiments</i>								
Cpo2	< 1.1	0	RT	water		11160 <sup>a</sup>	48 <sup>a</sup>	
	< 1.1		RT	water			26 <sup>a</sup>	
	< 1.1	1 <sup>b</sup>	nd <sup>g</sup>	water		1070	2029	1.9
LN22	< 1.1	0	RT	water		11120 <sup>a</sup>	18 <sup>a</sup>	
	< 1.1	1 <sup>b</sup>	nd <sup>g</sup>	water		2739	7455	2.72
	< 1.1	2 <sup>b</sup>	nd <sup>g</sup>	water		3267	6864	2.10
	< 1.1	3 <sup>b</sup>	nd <sup>g</sup>	water		2124	7027	3.31
	0.4 <sup>f</sup>	4 <sup>b</sup>	nd <sup>g</sup>	water		3282	7178	2.19
Cpo3	< 1.1	0	RT	water		12440 <sup>a</sup>	79 <sup>a</sup>	
	< 1.1		nd <sup>g</sup>	water			2563	
	< 1.1	1 <sup>b</sup>	nd <sup>g</sup>	water			2130	
	< 1.1		nd <sup>g</sup>	water			2498	
	< 1.1		RT	water		1990	2370	1.19
LN11	< 1.1	0	RT	water		12610 <sup>a</sup>	-/80 <sup>a,d</sup>	
	< 1.1	1	nd <sup>g</sup>	water		12410	3462/358 <sup>d</sup>	0.28/0.03 <sup>e</sup>
	< 1.1	2	nd <sup>g</sup>	water		1062	4161/326 <sup>d</sup>	3.92/0.31 <sup>e</sup>
	< 1.1	3	nd <sup>g</sup>	water		1438	4783/267 <sup>d</sup>	3.33/0.19 <sup>e</sup>
	< 1.1	4	nd <sup>g</sup>	water		1752	5784/226 <sup>d</sup>	3.30/0.13 <sup>e</sup>
	0.53 <sup>f</sup>	5	nd <sup>g</sup>	water		1545	5337/565 <sup>d</sup>	3.45/0.37 <sup>e</sup>
<i>neon experiments</i>								
Mar1	1.7	0	RT	Neon		10620 <sup>a</sup>	209 <sup>a</sup>	
	1.7	1	1875	Neon	14640			
	1.7		1810	Neon	15350			

	1.7		≈ 1800	Neon	15200			
	1.7		≈ 1800	Neon	14720			
	1.7		≈ 1800	Neon	16430			
	1.7		RT	Neon		16760	6212	0.37
Hak1	1.1	0	RT	Neon		10019 <sup>a</sup>	1062 <sup>a</sup>	
			2005	Neon	32046			
		1	2120	Neon	45065			
	1.1		RT	Neon		11019	4153	0.38
			nd	Neon	43095			
		2	2167	Neon	11256			
	1.1		RT	Neon		10148	3985	0.39
			2057	Neon	10623			
		3	2057	Neon	9864			
	< 1.1		RT	Neon		10128	208	0.02
Hak2	≥ 1.4	0	RT	Neon <sup>c</sup>		10138 <sup>a</sup>	11760 <sup>a</sup>	1.16
	≥ 1.4	1	≈ 1725	Neon <sup>c</sup>		4333	7087	1.64
	≥ 1.4	2	≈ 1725	Neon <sup>c</sup>		4398	8060	1.83
	1.4	3	≈ 1725	Neon <sup>c</sup>		5974	10314	1.73

897

- <sup>a</sup> Initial bromine concentration measurements were done in a compressed cell at ambient temperature before the first heating.
- <sup>b</sup> External heating kept the temperature at 235-265 °C when the las was shut off to enable fluid circulation.
- <sup>c</sup> The Neon fluid became enriched in water that was first released from the basalt glass in run Hak1-3 and together recompressed for Hak2 runs.
- <sup>d</sup> Two separate fluid analyses were conducted: '*next to the melted glass*'/'200 μm away from the glass'.
- <sup>e</sup> Partition coefficients calculated for the fluid '*next to the melted glass*'/'200 μm away from the glass'.
- <sup>f</sup> Determined by ice-water transition from Nitrogen cooling after the experiment.
- <sup>g</sup> Laser temperature was above the liquidus temperature for hydrous basalt (> 1300 °C). The absence of crystals was monitored with SXR.

898

899 Table 1 Experimental runs. Bromine was analyzed with synchrotron x-ray fluorescence. Uncertainties on the  
900 bromine concentrations are of 10% relative. RT = room temperature; nd = not detectable. The volume of the fluid fraction  
901 was estimated from sense of proportion and ranges from 25 to 45 wt.%.

Experiment-Run	Heating cycle	Pressure		
		water-ice VI transition	ruby	gold
Cpo2	0	< 1.1 <sup>a</sup>		2.6 <sup>b</sup>
	1	-		2.1
LN22	0	< 1.1 <sup>a</sup>		2.1 <sup>b</sup>
	1	-		-
	2	-		-
	3	-		-
	4	0.4 <sup>c</sup>		2.0 <sup>c</sup>
Cpo3	0	< 1.1 <sup>b</sup>		1.6 <sup>b</sup>
		-		-
	1	-		-
		-		-
		< 1.1		2.1
LN11	0	< 1.1 <sup>b</sup>		1.9 <sup>b</sup>
	1	< 1.1		-
	2	< 1.1		0.8
	3	< 1.1		0.9
	4	< 1.1		1.2
	5	0.53		2.0
Mar1	0		1.7 <sup>b,c</sup>	2.7 <sup>b,c</sup>
			1.7	-
			1.7	-
	1		1.7	-
			1.7	-
			1.7 <sup>c</sup>	3.2 <sup>c</sup>
Hak1	0		1.1 <sup>b,c</sup>	3.3 <sup>b,c,d</sup>
	1		1.1	-
	2		1.1	-
	3		< 1.1	3.1 <sup>d</sup>
Hak2	0		1.4 <sup>b</sup>	-
	1		≥ 1.4	2.8
	2		≥ 1.4	2.4
	3		1.4 <sup>c</sup>	1.9 <sup>c</sup>

- a Water-ice transition measurements were conducted after the experiment and after the cell cooled down to room temperature.
- b Initial pressure measurements were done in a compressed cell at ambient temperature before the first heating.
- c Pressure values are used for the method correlation in Figure 2.
- d Diffraction peaks could be also neon at 1.2 GPa.

903

904 Table 2 Experimental pressures calculated from the equation of state (EOS) of  
 905 water-ice VI transition, ruby fluorescence, and EOS of gold.

906

SiO <sub>2</sub>	44.9(2)
TiO <sub>2</sub>	1.08(3)
Al <sub>2</sub> O <sub>3</sub>	14.5(1)
Cr <sub>2</sub> O <sub>3</sub>	0.09(2)
FeO	8.45(7)
MnO	0.15(2)
NiO	0.03(2)
MgO	11.8(1)
CaO	10.66(6)
Na <sub>2</sub> O	2.61(6)
K <sub>2</sub> O	0.50(1)
P <sub>2</sub> O <sub>5</sub>	0.10(2)
Total	95.6(3)

907

908 Table 3 Major and minor element composition of the basaltic glass stating material  
 909 measured with electron microprobe analysis. Uncertainties (1 s.d.) are given in  
 910 parentheses showing the first significant digit.

911

Sample	Bromine ( $\mu\text{g/g}$ )
BaM024	10812
Cpo2-0	11160

LN22-0	11120
Cpo3-0	12440
LN11-0	12610
Mar1-0	10620
Hak1-0	10019
Mean	11254
SD	726

912

913 Table 4 Bromine concentration in the starting glass measured by synchrotron x-ray  
 914 fluorescence and electron microprobe analysis. Uncertainties on the bromine  
 915 concentrations are of 10% relative.

<b>HBr (Gg/year)</b>		<b>Study</b>
<i>volcanic flux</i>		
based on SO <sub>2</sub> flux from the respective study	with SO <sub>2</sub> flux from Carn et al. (2017)	
2.6-43.2	-	Halmer et al. (2002)
13		21.4 Aiuppa et al. (2005) Pyle and Mather (2009)
5-15		8-23 Webster et al. (2018)
10.5		14.4 Cadoux et al. (2022)
9		12.3
<i>melt inclusions</i>		
23.5-72.9		this study

916

917 Table 5 Estimates of annual global volcanic bromine flux to the atmosphere.

918