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

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25 **Abstract**

26 Volcanogenic halogens, in particular bromine, potentially play an important role in the ozone
27 depletion of the atmosphere. Understanding bromine behaviour in magmas is therefore crucial
28 to properly evaluate the contribution of volcanic eruptions to atmospheric chemistry and their
29 environmental impact. To date, bromine partitioning between silicate melts and the gas phase
30 is very poorly constrained, with the only relevant experimental studies limited to investigation
31 of synthetic melt with silicic compositions. In this study, fluid/melt partitioning experiments
32 were performed using natural silicate glasses with mafic, intermediate and silicic
33 compositions. For each composition, experiments were run with various Br contents in the
34 initial fluid (H₂O-NaBr), at T - P conditions representative of shallow magmatic reservoirs in
35 volcanic arc contexts (100-200 MPa, 900-1200°C). The resulting fluid/melt partition
36 coefficients ($D_{\text{Br}}^{\text{f/m}}$) are: 5.0 ± 0.3 at 1200°C -100 MPa for the basalt, 9.1 ± 0.6 at 1060°C -
37 200 MPa for the andesite and 20.2 ± 1.2 at 900°C - 200 MPa for the rhyodacite. Our
38 experiments show that $D_{\text{Br}}^{\text{f/m}}$ increases with increasing SiO₂ content of the melt (as for
39 chlorine) and suggest that it is also sensitive to melt temperature (increase of $D_{\text{Br}}^{\text{f/m}}$ with
40 decreasing temperature). We develop a simple model to predict the S-Cl-Br degassing
41 behaviour in mafic systems, which accounts for the variability of S-Cl-Br compositions of
42 volcanic gases from Etna and other mafic systems, and shows that coexisting magmatic gas
43 and melt evolve from S-rich to Cl-Br enriched (relative to S) upon increasing degree of
44 degassing. We also report first Br contents for melt inclusions from Etna, Stromboli, Merapi
45 and Santorini eruptions and calculate the mass of bromine available in the magma reservoir
46 prior to the eruptions under consideration. The discrepancy that we highlight between the
47 mass of Br in the co-existing melt and fluid prior to the Merapi 2010 eruption (433 and 73
48 tons, respectively) and the lack of observed BrO (from space) hints at the need to investigate
49 further Br speciation in 'ash-rich' volcanic plumes. Overall, our results suggest that the Br

50 yield into the atmosphere of cold and silicic magmas will be much larger than that from hotter
51 and more mafic magmas.

52

53 **Keywords:** bromine, fluid/melt partitioning, degassing, arc magmas, atmospheric chemistry

54 **1. Introduction**

55 Volcanic degassing is an important process in sustaining the composition of Earth's
56 atmosphere (e.g., Gaillard and Scaillet, 2014; Mather, 2015). Whilst much progress has been
57 made constraining global volcanic fluxes, uncertainties remain regarding the emissions of the
58 key halogen species, especially the trace Br- and I-bearing species (Pyle and Mather, 2009).
59 However, improvements in remote sensing techniques and analytical techniques, and their
60 application to an increasing number of active volcanoes, have provided new data on the
61 concentrations of these minor components in volcanic gases (e.g., Gerlach, 2004; Aiuppa et
62 al., 2005; Aiuppa, 2009; Bobrowski et al., 2015), which in turn can be used to better constrain
63 their global fluxes to the atmosphere (Pyle and Mather, 2009). Bromine has received
64 particular attention over the last decade, owing to its important role in atmospheric chemistry
65 in general (e.g., Oppenheimer et al., 2006; Roberts et al., 2009; 2014) and ozone depletion in
66 the troposphere and stratosphere in particular (von Glasow et al., 2009; Kutterolf et al., 2013;
67 Cadoux et al., 2015). Global compilations show that Br sources (emissions to the atmosphere)
68 and sinks (removal routes from the atmosphere) are not strictly balanced, hinting at a missing
69 natural source of Br (Montzka et al., 2011). The direct detection of HBr and BrO in volcanic
70 plumes (Bobrowski et al., 2003; Aiuppa et al., 2005) suggests that volcanic activity may be
71 one such a source.

72 The correct evaluation of the contribution of past volcanic eruptions to atmospheric chemistry
73 depends on our ability to evaluate Br behaviour in magmas, in particular its partitioning
74 between silicate melt and gas phases. So far, only a few experimental studies have been
75 performed on this topic, and have investigated Br behaviour in synthetic albite to rhyolite melt
76 compositions (Bureau et al., 2000; Bureau and Métrich, 2003). However, natural silicate melt
77 compositions can depart significantly from such model systems, in particular by having
78 elevated contents of Fe, Mg or Ca, which (as Na) can complex with halogens thereby

79 enhancing their solubility in silicate melts (Cochain et al., 2015). The relationship between
80 halogen solubility and their complexation with cations has been shown for Cl; chlorine
81 solubility in most silicate melts is dominantly controlled by the abundances of Mg ~ Ca > Fe
82 > Na > K > network-forming Al > Li ~ Rb ~ Cs, but Ti, F, and P also have strong influences
83 (e.g., Webster et al., 1999; Webster and De Vivo, 2002). There is thus a need to evaluate the
84 role of melt composition on Br behaviour in magmas, which is the main motivation of the
85 present study. To that end, we have performed fluid/melt partitioning experiments on natural
86 basalt, andesite and rhyodacite compositions under P-T-H₂O-redox storage conditions
87 relevant to shallow arc magmas. Combining our Br partition coefficient for the basaltic
88 composition, with other experimental data on S and Cl behaviour, and volcanic gas
89 compositions from the literature, we develop a simple first-order model to predict the S-Cl-Br
90 degassing behaviour in mafic systems. We also measure Br contents of melt inclusions from
91 Etna, Stromboli, Merapi and Santorini eruptions and estimate the mass of bromine in the pre-
92 eruptive magmas, this allows us to address the atmospheric contribution of open-vent mafic
93 volcanoes versus that of intermediate-silicic volcanoes.

94

95 **2. Fluid/melt partitioning experiments**

96

97 *2.1 Starting material*

98 The selected starting materials are natural volcanic rocks: a hawaiitic basalt from a 2002 Etna
99 eruption (Lesne et al., 2011a, b; Iacono-Marziano et al., 2012), a calc-alkaline andesite and a
100 rhyodacite from the Santorini Upper Scoria-2 (USC-2) and Minoan eruptions, respectively
101 (Cadoux et. al., 2017). The whole-rocks were crushed and ground in an agate mortar. About
102 10 g of the powders were melted twice (and ground in between), to ensure homogenization, in
103 a platinum crucible at 1400 °C - 1 atm for 3-4 hours in a piezoceramic oven, and quenched in

104 cold water. The resulting dry glasses were ground to powder and constituted the starting
105 material for both (i) bromine standard glasses synthesis (Cadoux et al., 2017) used to calibrate
106 bromine analyses (section 3) and (ii) partitioning experiments. The compositions of the
107 starting glasses are given in Table 1.

108

109 *2.2 Experimental procedure*

110 Equilibrium partitioning experiments (neglecting kinetic effects) were performed in an
111 Internally Heated Pressure Vessel equipped with a rapid quench device at the Institut des
112 Sciences de la Terre d'Orléans (ISTO, Orléans, France). The chosen experimental T-P- fO_2
113 conditions are representative of those in shallow crustal reservoirs in volcanic arc contexts
114 (Martel et al., 1999; Di Carlo et al., 2006; Cadoux et al., 2014; Kahl et al., 2015) and are
115 reported in Table 2: T ($\pm 10^\circ\text{C}$) = 900, 1060 and 1200°C, P (± 2 MPa) = 100 and 200 MPa,
116 and fO_2 estimated around the Ni-NiO (NNO) buffer, on the basis of the partial pressure of H_2
117 imposed in the vessel (~ 2 bars; Di Carlo et al., 2006; Cadoux et al., 2014).

118 We deliberately used a fluid solely composed of H_2O and Br. Experiments with simplified
119 fluids are necessary for comparison with future experiments which will include additional
120 volatile species (e.g., CO_2 , S), and will permit us to assess whether or not the presence of
121 other volatile species can modify Br behaviour.

122 Capsules were always loaded so that the mass ratio between the aqueous fluid and the glass
123 (silicate) phases was equal to or lower than 0.1 (Table 2), which avoids significant silicate
124 dissolution into fluid during experiments. About 50 to 100 mg of glass powder was loaded
125 into Au or Au-Pd capsules (2.5 mm internal diameter, 20-30 mm in length) together with 3-8
126 mg of a solution composed of distilled water and dissolved NaBr salt. These amounts of
127 solution (6-10 wt%) ensure the attainment of fluid saturation of the silicate melts at the
128 investigated T-P conditions. Different solutions with Br contents between 0.1 and 14 wt% Br

129 were employed. The runs lasted between 24 and 92 hours, depending on the temperature
130 (Table 2). Chlorine partitioning experiments of Alletti et al. (2009) performed at 1200°C with
131 a basaltic melt showed that 3-4 hours were sufficient to attain equilibrium at 1200°C and $P >$
132 1 MPa. Considering that Br diffusion coefficient appears to be 2–5 times lower than the other
133 halogens in basaltic melts (at 500 MPa to 1.0 GPa, 1250 to 1450 C and at anhydrous
134 conditions, Alletti et al., 2007), we chose a 24 hour run duration for our experiments at
135 1200°C-100 MPa including the basaltic composition, to ensure the attainment of equilibrium.
136 For our experiments at 900°C- 200 MPa including the silicic composition, a run duration of
137 92 hours was chosen on the basis of previous experiments with chlorine. Kravchuk and
138 Keppler (1994) performed partitioning experiments with silicic melts at lower T (800°C) and
139 same P with duration varying between 93h to 1142h, which yielded similar results, thus
140 demonstrating that 93h was sufficient to attain equilibrium (at 800°C).
141 The run duration for the experiment at 1060°C (48h) with andesite and rhyodacite
142 compositions was chosen as intermediate between that at 900°C and that at 1200°C.
143 Experiments were terminated by drop quench (Di Carlo et al., 2006). Upon opening the
144 capsules, hissing and fluid escape occurred, indicating the presence of excess fluid, and thus
145 that fluid saturation was achieved at the target P-T conditions. All runs produced crystal-free
146 glasses, those of rhyodacitic composition being rich in fluid inclusions (Fig. A.1 in
147 Supplementary Material).

148

149 **3. Analytical techniques**

150

151 *3.1. Major element analysis*

152 Experimental glasses and natural melt inclusions were analysed for their major elements by
153 electron microprobe (EMP) using the joint ISTO-BRGM SX-Five microbeam facility

154 (Orléans, France). The operating conditions were: 15 kV accelerating voltage, 4-6 nA beam
155 current, 10 seconds counting time on peaks, 5 seconds on background. The standards used
156 were: albite for Si and Na, TiMnO_3 for Ti and Mn, Al_2O_3 for Al, Fe_2O_3 for Fe, MgO for Mg,
157 andradite for Ca and orthose for K. Alkalis were analyzed first and a defocused beam was
158 used to minimize alkali migration: 20 μm diameter for experimental glasses, and 6-10 μm for
159 melt inclusions. Between 5 and 10 analyses were performed on each charge. The EMP
160 detection limit for Na (component of the aqueous solution used in the experiments and thus
161 considered in the calculation of the Br partition coefficients; Supplementary Information) was
162 generally < 700 ppm.

163

164 3.2. *Volatile analysis*

165 Br abundances in the experimental glasses were determined either by Laser Ablation
166 Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) or with a Secondary Ion Mass
167 Spectrometer (SIMS), using Br glass standards synthesized with the same starting
168 compositions as those used for the partitioning experiments presented here (Table 1, Cadoux
169 et al., 2017). LA-ICP-MS has been shown to be a technique suited to analyse Br contents of
170 hundreds to thousands ppm in experimental glasses, while SIMS and synchrotron X-ray
171 fluorescence (SR-XRF) are more appropriate techniques for lower Br contents (Cadoux et al.,
172 2017). Moreover, the spatial resolutions of SIMS and SR-XRF are significantly higher than
173 that of LA-ICP-MS (Cadoux et al., 2017), we therefore analysed bromine contents in melt
174 inclusions from Santorini, Merapi and Etna volcanoes by SIMS and SR-XRF.

175 The abundance of water dissolved in most of the experimental glasses was determined by
176 SIMS.

177

178 3.2.1. *Bromine analysis by LA-ICP-MS*

179 LA-ICP-MS analyses were performed at the Istituto Nazionale di Geofisica e Vulcanologia
180 (INGV, Palermo, Italy). The laser used is a Compex Pro 102, 193 nm ArF excimer laser
181 mounted on an ablation system GeoLas Pro, which is connected to an Agilent 7500ce ICP-
182 MS. Analyses were done on polished glass chips set in epoxy resin.

183 Analyses were performed with a fluence of 15 J/cm² and a pulse energy of 100 mJ. The
184 samples were ablated during ~50 seconds on a 90 µm diameter area, with a pulse repetition
185 rate of 10 Hz. Three to ten analyses were collected for every sample, to check sample
186 homogeneity. With this configuration, Br contents of >100 ppm are quantifiable with
187 accuracy generally within 20% (Cadoux et al., 2017).

188 Data reduction was performed using GLITTER™ software (Griffin et al., 2008), using ²⁴Mg
189 as the reference element (Mg contents from EMP analyses), and in-house bromine glass
190 standards B3000 and B6000 (with 2694 ± 5.1 and 5968 ± 3.5 ppm Br, respectively; Cadoux et
191 al., 2017), as external standards. The error on the measured ⁷⁹Br/²⁴Mg ratio was always < 4%.

192

193 3.2.2. Bromine analysis by SIMS

194 Polished chips of experimental glasses were set into indium and coated with gold, while
195 individual crystals from Santorini Minoan eruption, Merapi 2010 eruption and Etna 2006
196 eruption were mounted in epoxy resin, polished and coated with gold for melt inclusion
197 analysis.

198 Analyses were conducted at the Centre de Recherches Pétrographiques et Géochimiques
199 (CRPG, Nancy, France) with a Cameca IMS 1280 HR2. The Cs⁺ primary ion beam was
200 accelerated at 10 kV with an intensity of 5 nA, and focused on a 15 µm diameter area. The
201 electron gun was simultaneously used for charge compensation. Negative secondary ions
202 were extracted with a 10 kV potential, and the spectrometer slits set for a mass resolving
203 power (MRP = M/ΔM) of ~20,000. A single collector (EM) was used in ion-counting mode,

204 and the spectrum scanned by peak jumping. Each analysis consisted of 8 or 6 successive
205 cycles. Each cycle began with background measurement at the mass 75.8, followed by
206 $^{28}\text{Si}^{16}\text{O}_3^-$ (75.963 amu), $^{30}\text{Si}^{16}\text{O}_3^-$ (77.959 amu), $^{79}\text{Br}^-$ and $^{81}\text{Br}^-$, with measurement times of 4,
207 4, 4, 10 and 30 s, respectively (waiting time of 2 s). More details about the analytical
208 configuration can be found in Cadoux et al. (2017).

209 We used three different sets of in-house bromine glass standards (Cadoux et al., 2017): a
210 basaltic set containing 1 to 6,000 ppm Br (B1 to B6000), an andesitic set containing 10 to
211 1,000 ppm Br (A10 to A1000), and a rhyodacitic set containing 10 to 5,000 ppm Br (RD10 to
212 RD5000).

213 The bromine content of the samples was calculated using the measured $^{81}\text{Br}/^{28}\text{SiO}_3$ and
214 known Br (ppm)/ SiO_2 (wt%) ratios of the standards (Cadoux et al., 2017).

215 The three glass sets define distinct linear calibration curves with slopes decreasing with
216 increasing degree of melt polymerization (Cadoux et al., 2017). The equation of the
217 calibration lines passing through zero is:

$$\left(\frac{^{81}\text{Br}}{^{28}\text{SiO}_3}\right) = a \left(\frac{\text{Br}}{\text{SiO}_2}\right)$$

218 where the slope a is a function of SiO_2 content.

219 The error on the measured $^{81}\text{Br}/^{28}\text{SiO}_3$ ratio was generally $< 3\%$ (most often $< 2\%$).

220

221 3.2.3. *Br analysis by SR-XRF*

222 Bromine in Etna and Stromboli melt inclusions was analysed via SR-XRF at the UK
223 national synchrotron facility, Diamond Light Source (Didcot, Oxfordshire), on I18, the
224 Microfocus Spectroscopy beamline. Analyses were performed on polished olivine-hosted
225 melt inclusions set in epoxy resin, using a beam of $\sim 5 \times 5 \mu\text{m}^2$ and an analysis time of 120 s
226 (details in Cadoux et al., 2017). Fluorescence spectra were processed by PyMca (Solé et al.,

227 2007), by identifying the K-lines of Br and applying an iterative Gaussian peak fitting
228 procedure to quantify the net peak areas free of background and interference from other
229 elements.

230 Background- and baseline-subtracted net peak areas for the MI samples were converted into
231 Br concentrations from comparison with peak areas measured for the basaltic standards of
232 known Br composition (Cadoux et al., 2017). Based on tests made on the standards (Cadoux
233 et al., 2017), the Br detection limit is inferred to be < 1 ppm, Br contents ≤ 5 ppm
234 (representative of Br contents in most natural volcanic glasses) are measured with an accuracy
235 $< 26\%$ and with a precision of 30% .

236

237 3.2.4. *Water analysis by SIMS*

238 The analysis of water dissolved in the experimental glasses was performed on the CRPG
239 Cameca 1280 HR2. Spot analyses of secondary ions ^{17}O , $^{16}\text{O}^1\text{H}$, ^{18}O , ^{29}Si , ^{30}Si were obtained
240 using a 3 nA, 20 μm diameter primary beam of Cs^+ ions. The electron gun was
241 simultaneously used for charge compensation. The measurements were made at a mass
242 resolution of $\sim 7,700$ to separate $^{17}\text{O}^-$ and $^{16}\text{O}^1\text{H}^-$. An energy filtering was set at $+30 \pm 10$ eV in
243 moving the energy slit off axis, to minimize both matrix effect and instrumental background.
244 A 10×10 μm raster was used for 1 minute prior to analysis at each spot in order to pre-
245 sputter through the gold coat and remove surface contamination. The beam position in the
246 field aperture and the magnetic field centering was checked before each measurement. Each
247 analysis on one spot consisted of 18 cycles of measurements, with counting times and
248 switching times of 3 and 1 s respectively at each peak. The errors on the measured $^{16}\text{O}^1\text{H}/^{30}\text{Si}$
249 ratios were $< 1\%$.

250 Concentrations of H_2O were calculated using a best-fit quadratic polynomial regression to
251 count-rate ratios (normalized to ^{30}Si) versus variable known concentration ratios (referenced

252 to wt% SiO₂) of experimental glass standards of basaltic (sample N72, Kamtchatka; Shishkina
253 et al., 2010), trachy-andesitic (sample TAN25, Tanna Island, Vanuatu; Metrich & Deloué,
254 2014), dacitic and rhyolitic (Pinatubo, Philippines; Scaillet & Evans, 1999) compositions,
255 with H₂O contents ranging from 0 to ~6 wt%.

256

257 **4. Results**

258 *4.1. Major element compositions*

259 Average major element compositions of experimental glasses and melt inclusions are
260 presented in Tables 3 and A2, respectively. Comparison of the experimental products (Table
261 3) with the corresponding starting dry glasses (Table 1) shows a systematic gain in Na₂O due
262 to the addition of sodium through the H₂O-NaBr solution in the experimental charges (10 to
263 153 µg of Na were incorporated into the final glass, Table A.1), and a loss in FeO (up to 14%
264 taking into account standard deviations) in experiments ≥ 1060 °C, most likely due to Fe
265 alloying with the AuPd capsule. Other elements were generally comparable with the starting
266 glasses within standard deviations.

267

268 *4.2. H₂O and Br dissolved in experimental glasses*

269 The concentrations of both H₂O and Br dissolved in quenched glasses are reported in Table
270 2. Melt water contents (H₂O_{melt}) vary between 2.9 up to 7.3 wt%, encompassing the range of
271 pre-eruptive H₂O_{melt} of arc magmas (e.g., Scaillet et al., 1998; Di Carlo et al., 2006; Cadoux et
272 al., 2014). Bromine concentrations range from 69 (M4-RD1; Table 2) to 9112 ppm (M2-B),
273 comparable to the range explored in previous experimental studies (Bureau et al., 2000;
274 Bureau and Métrich, 2003). Repeat analyses of either H₂O (n = 5-7) or Br (n = 3-10) in
275 quenched glasses show them to be homogeneous within analytical uncertainty (including error
276 on calibration and error on sample measurements), indicating that the run durations (1 to 4

277 days according to T-P conditions; Table 2) were sufficient to attain chemical equilibrium
278 between the co-existing melt and fluid phases.

279

280 4.3. *Fluid/melt bromine partitioning*

281 Assessment of the partition coefficients requires the calculation of the ratio between Br
282 concentration (in ppm) in coexisting aqueous fluid and silicate melt at the experimental
283 conditions. In natural magmatic systems, besides from being dissolved in the silicate melt, Br
284 can exist as a gas species in the vapour phase and/or be dissolved in hydrosaline liquid phase
285 (brine), as has been shown for Cl. This raises the question as to whether a brine rich in Br
286 could have been present in our capsules at run conditions. Solubility experiments of Bureau et
287 al. (2003) have shown that silicic melts can contain up to 7850 ppm Br at P-T conditions of
288 100-200 MPa and 900-1080°C without brine occurrence. Our experiments were run at similar
289 conditions, with Br contents lower than 2000 ppm (Table 2). We thus conclude that our silicic
290 melts did not co-exist with a brine, and that only a gas phase was present. There is no data
291 about Br solubility in mafic melts but the results of our experiment #3 (basalt, andesite,
292 rhyodacite in the same experimental P-T-H₂O-[Br^o] conditions; Table 2) suggest a higher
293 ability for Br to enter in mafic melts, so that, by comparison with the values for silicic melts
294 given above, we might expect that brine saturation in andesitic and basaltic melts occurs for
295 Br contents higher than 8000 ppm. Hence, as for the silicic melts, we conclude that basaltic-
296 andesitic charges were co-existing solely with a gas phase during the experiments.

297 Whereas the amount of Br dissolved in the melt ([Br]_{melt}) was directly analysed (by SIMS or
298 LA-ICP-MS in run product glasses, section 3; referred to as '[Br] measured in final glass' in
299 Table 2), the Br amount of the coexisting aqueous fluid phase ([Br]_{fluid}) was determined by
300 mass balance, knowing the original bulk Br content (the amount of Br loaded in the capsule as
301 H₂O+NaBr solution; hereafter [Br^o]), the measured amount of Br dissolved in the final glass

302 ([Br]_{melt}), and assuming that the difference between these two figures represents the amount of
303 Br left over for the fluid phase.(details of the calculation are given in Supplementary
304 Information and in Table A.1). For each run product, we estimated the errors on the calculated
305 [Br]_{fluid} and $D_{\text{Br}}^{\text{f/m}}$ by propagating the errors coming from the preparation of the experimental
306 charges to the analysis of Br, Na and H₂O contents of the glasses (Supplementary Information
307 and Table A.1). The resulting errors on [Br]_{fluid} are < 51% (and mostly < 34%), except for one
308 run-product (M1-B). As the main source of error for $D_{\text{Br}}^{\text{f/m}}$ is [Br]_{fluid}, the resulting errors on
309 $D_{\text{Br}}^{\text{f/m}}$ are close to those for [Br]_{fluid}: they do not exceed 54% and are mostly <45%, except for
310 M1-B (112%; Table A.1). Note that, as underlined in previous studies (e.g., Alletti et al.,
311 2014), such rigorous error propagation overestimates the real errors, due to the complex
312 covariation of individual errors. The large error associated with the $D_{\text{Br}}^{\text{f/m}}$ estimated for M1-B
313 is due to the low fluid/melt mass ratio of the experimental charge (0.06 compared to 0.08-0.11
314 for the others): the mass of initial fluid is small relative to the weighing error (Table A1).
315 Therefore, the calculated mass of fluid has a larger associated relative error of 19% (<15% for
316 the other run products), which increases the error on the calculated value for [Br]_{fluid} and
317 $D_{\text{Br}}^{\text{f/m}}$. This observation is consistent with the uncertainty analysis for the mass balance
318 calculations of Zajacz et al. (2012), which shows that the determination of D for elements
319 with low D values in experiments with low volatile/mass ratio may bear large uncertainties
320 due to error propagation. Their modeling (Fig. 1 in Zajacz et al., 2012) predicts relative error
321 of 10 up to 100% for volatile/mass ratios lower than 0.1. The error on the $D_{\text{Br}}^{\text{f/m}}$ estimated for
322 M1-B being > 100% ($D_{\text{Br}}^{\text{f/m}} = 3.8 \pm 4.5$), we conclude that this value, taken alone, is
323 meaningless. Overall, the error on $D_{\text{Br}}^{\text{f/m}}$ is particularly sensitive to the error on the measured
324 [Br]_{melt} (i.e., Br content of the run product glasses). The precision of the Br measurements is
325 crucial for the accuracy of $D_{\text{Br}}^{\text{f/m}}$.

326 The main data of the partitioning experiments are listed in Table 2 (details in Table A1) and
327 displayed on Figures 1 to 5.

328 The basaltic products of runs #1 to 3 performed at 1200°C, 100 MPa, with various [Br^o]
329 contents apparently show a linear relationship between the measured [Br]_{melt} and the
330 calculated [Br]_{fluid} (Fig. 1). Linear regression forced through zero yields a $D_{Br}^{f/m} = 5.0 \pm 0.3$
331 for the basaltic composition. At the same T-P-[Br^o] conditions (experiment #3; Table 2),
332 $D_{Br}^{f/m}$ increases steadily from basalt ($D_{Br}^{f/m} = 4.6 \pm 2.0$), to andesite ($D_{Br}^{f/m} = 6.4 \pm 3.5$), to
333 rhyodacite ($D_{Br}^{f/m} = 11.3 \pm 0.9$). At 1060°C, 200 MPa, ~NNO (Fig. 2), experiments on
334 andesite and rhyodacite melts yields linear trends between [Br]_{melt} and [Br^o] (Fig. 2a) or
335 [Br]_{fluid} (Figs. 2b and 2c). Linear regression of the latter data forced through zero yields $D_{Br}^{f/m}$
336 = 9.1 ± 0.6 for andesite, and $D_{Br}^{f/m} = 14.0 \pm 0.6$ for rhyodacite. At 900°C - 200 MPa, (Fig. 3),
337 the same pattern is again observed resulting in $D_{Br}^{f/m} = 20.2 \pm 1.2$ for rhyodacite, slightly
338 higher than that of Bureau et al. (2000) for albitic melts (17.5 ± 0.6).

339 The experiments show a two-fold increase of $D_{Br}^{f/m}$ from basalt (5.0 ± 0.3) to rhyolite melts
340 (11.3 ± 0.9) at 1200°C - 100 MPa (Fig. 4). The same trend of an increase of $D_{Br}^{f/m}$ with SiO₂
341 is noted at 1060°C - 200 MPa, with a slightly higher slope. At 900°C, we did not work on
342 basaltic/andesitic compositions because of their extensive crystallization (which would have
343 driven the residual liquids toward higher SiO₂ content). Our data on silicic compositions,
344 along with those of Bureau et al. (2000) (Fig. 4), suggest a similar trend of increasing $D_{Br}^{f/m}$
345 with increasing SiO₂ at 900°C. Figure 4 also suggests a general trend of an increase in $D_{Br}^{f/m}$
346 as temperature decreases, at least for more silicic compositions. For instance, for rhyolitic
347 melts (71 wt% SiO₂), a linear extrapolation of our data set ($D_{Br}^{f/m} = -0.0299 \times T(^{\circ}C) + 46.673$,
348 $r^2 = 0.97$) yields $D_{Br}^{f/m} = 26$ at 700°C (Fig. 5).

349 We did not attempt to explore the effect of pressure in a systematic way. Previous work has
350 shown that $D_{Br}^{f/m}$ strongly increases as pressure decreases, from about 20 at 200 MPa up to

351 over 300 at near atmospheric pressure in silicic melts (synthetic haplogranitic composition;
352 Bureau et al., 2010). In contrast, our experiment at 100 MPa (experiment #3) does not show
353 any significant increase in $D_{\text{Br}}^{f/m}$, with $D_{\text{Br}}^{f/m}$ being instead generally lower than those at 200
354 MPa (experiments #4 and #5; Table 2). However, the fact that temperatures between our 100
355 and 200 MPa runs are different, does not allow us to make definitive conclusions on this
356 aspect. We suggest that our results should be used to model degassing processes in the crustal
357 reservoir and not for simulating decompression processes between the reservoir and surface.

358

359 *4.4. Br contents in melt inclusions*

360 Table A.2 reports the Br contents of melt inclusions from (i) basaltic magmas erupted at
361 Mount Etna and Stromboli, (ii) the andesitic magma erupted in 2010 at Mount Merapi, and
362 (iii) the rhyodacitic magma of the 1613 BC Minoan eruption of Santorini volcano. Melt
363 inclusions from Mt. Etna and Stromboli are hosted by olivine crystals, while those from Mt.
364 Merapi and Santorini volcano are in pyroxenes and plagioclase crystals, respectively.

365 Br abundance ranges from 2.5 to 10 ppm, without any clear correlation with melt inclusion
366 major element composition; there is no notable difference between basaltic, andesitic and
367 rhyodacitic melt inclusions. The Br contents of these melt inclusions are comparable to those
368 of submarine back-arc and arc glasses (Kendrick et al., 2014).

369

370 **5. Discussion and applications**

371

372 *5.1. Halogen behaviour*

373 This section aims to place our novel Br partitioning data in the wider framework of
374 halogen behaviour. Hereafter, we provide a brief, non-exhaustive review of chlorine, fluorine
375 and iodine partitioning and make comparisons with bromine.

376 Many studies have been dedicated to understanding the partitioning behaviour of halogens
377 between fluids and silicate melts (e.g., Webster, 1990; Webster and Holloway 1990; Webster
378 1992a,b; Webster et al. 1999; Signorelli and Carroll, 2000; Bureau et al., 2000; Botcharnikov
379 et al., 2004, 2007, 2015; Dolejs and Baker 2007a,b; Alletti, 2008; Stelling et al. 2008;
380 Chevychelov et al., 2008b; Webster et al., 2009; Borodulin et al., 2009; Alletti et al. 2009,
381 2014; Beermann 2010; Zajacz et al. 2012; Webster et al., 2014; Beermann et al., 2015).
382 Nevertheless, most of these studies have focused on chlorine, mainly because of its
383 importance as a ligand for ore metals (e.g., Carroll and Webster, 1994; Aiuppa et al., 2009).

384

385 *5.1.1 General behaviour*

386 Chlorine partitions preferentially into fluids relative to melts for the vast majority of terrestrial
387 magmas at shallow-crustal pressure and temperature conditions, due to its highly solubility in
388 aqueous and aqueous-carbonic fluids (e.g., Webster et al., 2018 and references therein). The
389 few partitioning experiments performed with bromine and iodine show a similar behaviour
390 (Bureau et al., 2000; Bureau et al., 2016; this study). In contrast, fluorine concentrations in
391 aqueous and aqueous-carbonic fluids at magmatic conditions are much lower than those of the
392 other halogens (e.g., Carroll and Webster, 1994), and can be therefore enriched in the silicate
393 melt with respect to the fluid phase (e.g., Webster, 1990; Webster and Holloway 1990).

394

395 *5.1.2 The effect of melt composition*

396 In this study, we show that the partitioning of bromine between aqueous fluid and melt
397 appears to be influenced by the melt composition (Figs. 1, 2, 4). We estimate $D_{\text{Br}}^{f/m}$ of $4.6 \pm$
398 2.0 , 6.4 ± 3.5 and 11.3 ± 0.9 for basaltic, andesitic and rhyodacitic compositions respectively,
399 with $[\text{Br}^\circ] = 2.4$ wt.%, at 1200°C, 100 MPa and $f\text{O}_2$ close to NNO (exp. #3, Table 2). If $D_{\text{Br}}^{f/m}$
400 of the basalt and andesite are comparable taking into account the error bars, the difference

401 between the mafic-intermediate compositions on one hand, and the silicic composition on the
402 other hand, is significant. In addition, we observe the same trend at 1060°C, 200 MPa where
403 $D_{\text{Br}}^{f/m}$ of the silicic composition (14.0 ± 0.6) is significantly higher than that of the
404 intermediate composition (9.1 ± 0.6). This relationship between melt composition and Br
405 partitioning is consistent with the higher Br solubility in melts with lower SiO_2 observed by
406 Bureau and Métrich (2003). The recent study of Cochain et al. (2015) on Br speciation in
407 hydrous alkali silicic melts at high pressure (up to 7.6 GPa) confirms this trend. Similarly,
408 several studies have demonstrated the strong effect of melt composition on fluid/melt
409 partitioning of chlorine (Webster 1992a,b; Webster et al. 1999). Like $D_{\text{Br}}^{f/m}$, $D_{\text{Cl}}^{f/m}$ also
410 increases with increasing SiO_2 contents of the melts (i.e., with increasing melt polymerization
411 and thus decreasing Br and Cl solubility in melt; e.g., Webster, 1992a,b; Signorelli and
412 Carroll, 2000; Botcharnikov et al., 2004; Webster, 2004; Webster et al., 2006; Webster et al.,
413 2009). Most experimental values of $D_{\text{Cl}}^{f/m}$ for basaltic systems are <10 (Stelling et al 2008;
414 Beermann 2010; Baker and Alletti 2012), but Alletti et al. (2009) observed $D_{\text{Cl}}^{f/m}$ of 8-34 in
415 trachybasaltic melt in equilibrium with aqueous fluids at $f\text{O}_2$ near NNO. Values of $D_{\text{Cl}}^{f/m}$ for
416 intermediate (andesitic and phonolitic) and silicic melts exceed those for mafic melts (e.g.,
417 Webster et al. 1999; Stelling et al., 2008; Chevychelov et al., 2008b; Alletti et al., 2009;
418 Beermann, 2010; Beermann et al., 2015); with values >160 determined for silicic melts at 200
419 MPa (Webster, 1992a). Note that $D_{\text{Cl}}^{f/m}$ also varies strongly with Cl concentration (Webster
420 1992a,b; Webster et al. 1999; Stelling et al. 2008) and a decrease of $D_{\text{Cl}}^{f/m}$ by up to the order
421 of one magnitude can be observed when the Cl concentration in the system decreases (from
422 several wt.% to <1 wt.% Cl). At low Cl system concentrations (<1 wt% Cl in andesite, Zajacz
423 et al., 2012; or in basalt, Beermann et al., 2015; Stelling et al., 2008), $D_{\text{Cl}}^{f/m}$ seems to achieve
424 values close to or even below unity. From our data, we do not observe any systematic
425 relationship between Br concentration in the system ($[\text{Br}^\circ]$) and $D_{\text{Br}}^{f/m}$: the apparent decrease

426 of D-values for andesite (M4-A) relative to $[\text{Br}^\circ]$ at 1060°C and 200 MPa (Table 2) is actually
427 not significant taking into account the errors on D. More experiments are necessary to
428 investigate the potential relationship between $D_{\text{Br}}^{f/m}$ and the Br concentration in the system.
429 Unlike bromine and chlorine, values of $D^{f/m}$ for fluorine are lower in silicic melts (typically
430 well below unity; Webster, 1990; Webster and Holloway 1990; Dolejs and Baker 2007a,b;
431 Borodulin et al., 2009) than in mafic melts coexisting with aqueous fluids (ca. 3 to 38; Alletti,
432 2008; Chevychelov et al., 2008b).

433

434 *5.1.3 Temperature and pressure effects*

435 Our data suggest that $D_{\text{Br}}^{f/m}$ is sensitive to melt temperature (increase of $D_{\text{Br}}^{f/m}$ with decreasing
436 temperature; Figs. 4 and 5), though more experiments are required to confirm this trend.
437 Currently there are insufficient data available to constrain the temperature effect for the other
438 halogens. The few existing data concern Cl in phonolitic and trachybasaltic melts and suggest
439 that there is no strong influence of temperature (Chevychelov et al., 2008a; Stelling et al.,
440 2008).

441 We do not systematically investigate the effect of pressure on $D_{\text{Br}}^{f/m}$. Experiments conducted
442 on haplogranite melts coexisting with iodine-bearing aqueous fluids indicate an increase of
443 $D^{f/m}$ of iodine with pressure decrease (from ~2 at 1.5 GPa to 41 at 0.1 GPa; Bureau et al.,
444 2016). Contrastingly, $D^{f/m}$ of fluorine decreases with decreasing pressure as suggested by
445 experiments on trachybasaltic melts (Alletti, 2008; Chevychelov et al., 2008b). Available data
446 for chlorine show no clear pressure effect on $D_{\text{Cl}}^{f/m}$ for most compositions and contrasting
447 effects for phonolitic ones (Signorelli and Carroll, 2000; Baker and Alletti, 2012; Alletti et al.
448 2014).

449 We conclude that more systematic experiments are necessary for all halogens to assess the
450 effect of pressure and temperature on their fluid/melt partitioning, in order to interpret
451 degassing processes of ascending and cooling magmas comprehensively.

452

453 *5.1.4 Effect of fluid composition*

454 Experiments with trachybasaltic melts coexisting with aqueous fluids have shown that the
455 addition of CO₂ to the system leads significant reductions of $D^{f/m}$ of fluorine.

456 Several studies have investigated the effect of fluid composition on Cl partitioning in
457 chemically complex O-H ± C ± S ± Cl fluids and show variable influence of CO₂ or S on
458 $D_{Cl}^{f/m}$, no systematic trend appears (e.g., Botcharnikov et al. 2004; Webster et al. 2003;
459 Botcharnikov et al., 2007; Alletti et al., 2009; Beermann 2010, Zajacz et al. 2012; Webster et
460 al., 2014). As we do not explore the effect of other volatile species on Br partitioning in this
461 study, we will not enter into the details of those studies (for a review on this topic, see
462 Webster et al., 2018). Clearly, further investigations are needed to better understand the
463 effects of other volatile species on halogens partitioning.

464

465 *5.1.5 Role of ionic radius?*

466 On the basis of their results ($D_{Cl}^{f/m} = 8.1$, $D_{Br}^{f/m} = 17.5$, $D_I^{f/m} = 104$ with an albitic melt),
467 Bureau et al. (2000) suggested that bromine and iodine partitioned even more strongly into the
468 fluid phase than chlorine and that it could be correlated to the increasing ionic radius of the
469 halide ions (Cl⁻ = 1.81 Å, Br⁻ = 1.96 Å, I⁻ = 2.20 Å; Shannon, 1976). Nevertheless, our brief
470 review above shows that chlorine fluid/melt partition coefficients as high as that of iodine
471 may be reached with a rhyodacitic melt ($D_{Cl}^{f/m} = 115$, Table 2 in Webster et al., 2009)
472 depending on the initial Cl content in the bulk system. In addition, we show in section 5.2.
473 below that the range of Br and Cl composition of volcanic gases and melts from mafic

474 systems requires a lower $D_{\text{Br}}^{f/m}$ (= 5) than the $D_{\text{Cl}}^{f/m}$ value (8.6); this questions the general
475 applicability of the higher volatility of Br as shown by the experimental results of Bureau et
476 al. (2000) and Mungall and Brenan (2003) and attributed to the larger ionic radius of Br vs.
477 Cl.

478

479 5.2. *S-Cl-Br degassing behaviour in mafic magma systems*

480 Our partition coefficients for Etnean melts set the basis for initializing the first basic
481 models to evaluate Br degassing behaviour in mafic systems. Our aim is to derive model-
482 based evidence for Br abundance in magmatic gases coexisting with mafic melts at shallow
483 crustal conditions, and to compare this with available information on the measured
484 compositions of volcanic gases, the ultimate product of magmatic degassing. Figure 6a shows
485 a selection of volcanic gas plume compositions (in the S-Cl-Br system) from some open-vent
486 mafic volcanoes (for data provenance, see caption of Figure 6). The wide range of volcanic
487 gas S/Br compositions observed points to a mechanism fractionating Br, relative to sulfur,
488 during magmatic degassing or systematic variations in melt compositions, e.g., between
489 different tectonic settings. In comparison, volcanic gases exhibit a far more restricted range of
490 Cl/Br ratios (see Fig. 6a and Gerlach, 2004; Aiuppa et al, 2005, 2009; Webster et al., 2018),
491 which suggests that less Cl/Br fractionation takes place during degassing and/or less
492 comparative variation in melt compositions. The relatively constant Cl/Br ratios in our gas
493 dataset also indicate that Cl vs. Br decoupling due to fractionations among coexisting brine
494 and vapour (Foustoukos and Seyfried, 2007; Seo and Zajacz, 2016), or by halite precipitation
495 (Foustoukos and Seyfried, 2007), are unlikely to occur at the mafic, halogen-poor melt
496 conditions explored here (Webster et al., 2009, 2018). We consider below our new Br
497 partitioning data, in tandem with previous information on S and Cl from the literature, to
498 provide a simple model verification for these volcanic gas-based inferences.

499 Rigorous quantitative calculation of magmatic gas compositions would require a theoretical
500 and/or empirical model that describes solubilities, fluid/melt partition coefficient, and
501 diffusivities of all involved volatiles over the range of P-T-X conditions experienced by
502 magmas upon ascent, storage, and eruption. Such quantitative information is increasingly
503 available for S (see review of Baker and Moretti, 2011), still limited for Cl (Webster et al.,
504 1999, 2015, 2018), but virtually absent for Br. Given this limitation, we base our model
505 calculations on a modified version of the empirical degassing model of Aiuppa et al. (2002)
506 and Aiuppa (2009). The original model described the evolution of the SO₂-HCl-HF magmatic
507 gas phase exsolved during progressive degassing of a basaltic magma, using a Rayleigh-type
508 open-system degassing model assumption, and with constant S, Cl and F fluid/melt partition
509 coefficients. Based on fair agreement between model results and volcanic gas compositions, it
510 was concluded that a Rayleigh-type open-system process could suitably reproduce the
511 relatively shallow exsolution of halogens from basaltic magmas that often dominates the gas
512 signature (Métrich and Wallace, 2008; Métrich et al., 2001, 2004, 2010; Spilliaert et al., 2006;
513 Edmonds et al., 2009; Webster et al., 1999, 2015; Mather et al., 2012).

514 Here we adapt and extend the methodology of Aiuppa (2009) to bromine, and develop a
515 simple model to account for the variability of S-Cl-Br compositions of volcanic gases (Fig.
516 6a). We use similar sets of Rayleigh-type open-system equations as in Aiuppa (2009) but,
517 contrarily to previous work, we do not derive fluid/melt partition coefficients using an
518 empirical best-fit procedure to volcanic gas data, but rather use independent information
519 (from Alletti et al., 2009; Aiuppa, 2009; and this work) (see below).

520 We use equations (1) and (2) to calculate the evolving S/Cl and S/Br (molar) ratios in the
521 magmatic gas phase produced upon increasing extents of degassing of a mafic silicate melt:

$$522 \quad \left(\frac{S}{Cl}\right)_{\text{gas}} = \left(\frac{S}{Cl}\right)_{\text{melt}_0} \cdot \frac{D_S}{D_{Cl}} \cdot R^{\left(1 - \frac{D_{Cl}}{D_S}\right)} \quad (1)$$

523
$$\left(\frac{S}{Br}\right)_{\text{gas}} = \left(\frac{S}{Br}\right)_{\text{melt}_0} \cdot \frac{D_S}{D_{Br}} \cdot R^{\left(1 - \frac{D_{Br}}{D_S}\right)} \quad (2)$$

524 where $\left(\frac{S}{Cl}\right)_{\text{gas}}$ and $\left(\frac{S}{Br}\right)_{\text{gas}}$ are the molar volatile ratios in the gas phase; $\left(\frac{S}{Cl}\right)_{\text{melt}_0}$ and
 525 $\left(\frac{S}{Br}\right)_{\text{melt}_0}$ are the original volatile ratios in the parental (un-degassed) melt; D_S , D_{Cl} and D_{Br}
 526 are the fluid/melt (molar) partition coefficients for the three volatiles; and R is the residual
 527 fraction of sulfur in the melt (ranging from 1 at onset of degassing to 0 if S is totally exsolved
 528 from the melt).

529 To resolve the model equations, $\left(\frac{S}{Cl}\right)_{\text{melt}_0}$ and $\left(\frac{S}{Br}\right)_{\text{melt}_0}$ are here set at 1.7 and 1320,
 530 respectively, from the characteristic S (0.27 wt%), Cl (0.18 wt%) and Br (5.1 ppm) contents
 531 in our most primitive, un-degassed glass inclusions from Etna (inclusion E2 from the 2001
 532 eruption; Table A.2). The molar fluid/melt partition coefficients are obtained from our
 533 experimental results on Etnean melts for Br ($D_{Br}^{f/m} = 5.0$ on weight basis; Fig. 1) and those of
 534 Alletti et al. (2009) for Cl ($D_{Cl}^{f/m} = 8.6$ on weight basis), obtained at the same pressure (100
 535 MPa), temperature (1200°C), redox conditions (NNO) and melt composition. These
 536 conditions are appropriate to describe halogen behaviour in mafic magmas at shallow crustal
 537 conditions and to extrapolate to shallow degassing, in view of the minor pressure-dependence
 538 of halogen fluid/melt partition coefficients (Alletti et al., 2009). It is noteworthy that the
 539 experiments of Alletti et al., (2009) were run at the low Cl concentrations (< 0.4 wt %) typical
 540 of mafic (basaltic to andesitic) melts (Webster et al., 2009), similar to those characteristic of
 541 the volcanoes we report gas data for in Figure 6. At such Cl -under-saturated conditions
 542 (absence of brine formation) the minor (if any) dependence of $D_{Cl}^{f/m}$ on total Cl contents
 543 justifies the use of a constant $D_{Cl}^{f/m} = 8.6$ throughout the entire degassing path. For S , a
 544 fluid/melt partition coefficient of 86 (on weight basis) is adopted based on the results of

545 Aiuppa (2009), who found that volcanic gas measurements from Etna and several mafic arc
546 volcanoes worldwide can satisfactorily be reproduced with a D_S/D_{Cl} ratio (ratio between
547 fluid/melt weight partition coefficients) of 10. Our inferred $D_S = 86$ agrees well with results
548 obtained from S thermodynamic modelling (Moretti and Ottonello, 2005) of Etna-like melts at
549 $P \leq 100$ MPa, \sim NNO and ~ 3 wt.% H_2O (Aiuppa et al., 2007), and is within the range of D_S
550 values (3-236, by weight) obtained by Beermann et al., (2015) in their partitioning
551 experiments between fluid and Etna-like melts at 100-200 MPa, and at either reducing or
552 oxidizing redox conditions. We are aware that, at redox conditions close to the sulfide-sulfate
553 transition, such as at \sim NNO (Jugo et al., 2010), D_S can exhibit large variations for even subtle
554 redox variations (Beermann et al., 2015), and that therefore keeping D_S constant in our model
555 is an over-simplification that does not completely reflect the real S degassing behaviour in
556 natural (basaltic) systems. However, incorporation of such complexities (including the non-
557 linear S partition behaviour, and its dependence on the total S content in the system;
558 Beermann et al., 2015) into an S-Cl-Br degassing model is currently hampered by our very
559 preliminary understanding of Br partitioning behaviour. In view of this, we find it safer to
560 assume a constant D_S value (of 86) in our preliminary model, keeping in mind that our
561 inferred D_S/D_{Cl} ratio is derived from empirical fitting of hundreds of volcanic gas data, and is
562 thus likely to describe the “averaged” S degassing behaviour in mafic systems at shallow (\ll
563 3 km; Spilliaert et al., 2006) conditions relevant to halogen degassing.

564 With these numbers, and with R varied from 1 (start of degassing) to 0 (complete S exsolution
565 from the melt), the magmatic *vapour model line* shown in Figure 6a is obtained. The evolving
566 volatile composition of the coexisting melt is obtained by mass balance (e.g., by subtracting
567 from the initial volatile contents, at each degassing step, the volatile fractions partitioned into
568 the vapour phase), and is illustrated by the *melt model line* (solid red line) in Fig. 6b.

569 Our model results predict that the coexisting magmatic gas and melt (Fig. 6a, b) should both
570 evolve with increasing degassing, from S-rich (*early gas* and *early melt*) to Cl-Br rich
571 (relative to S) (*late gas* and *late melt*). The *vapour model line* reproduces the observed
572 compositional range of volcanic gas samples from Etna and other mafic systems well (Fig.
573 6a). Our calculations, therefore, provide a first, though simplistic, model to interpret Br
574 abundance in volcanic gases from basaltic systems. We propose that high S/Br (along with
575 S/Cl ratios; Aiuppa, 2009) gas compositions reflect shallow degassing of fertile (volatile-rich)
576 magmas in basaltic volcano plumbing systems; while more soluble Cl and Br will prevail in
577 gas released by later degassing stages (e.g., during near-surface syn-eruptive degassing). Our
578 conclusions are opposite to those of Bobrowski and Giuffrida (2012) who, based on
579 observational evidence and use of BrO gas measurements (that under-estimate total Br),
580 proposed that low S/Br ratios mark “deep” degassing episodes of fresh basaltic magmas (at
581 Etna). We stress, instead, that our model calculations more closely reproduce the similar
582 *shallow* degassing behaviour of Cl and Br, which is supported by the limited variability of
583 Cl/Br volcanic gas ratios (Fig 6a). We caution, however, that additional experimental
584 observations, especially at low pressure, and rigorous thermodynamic models, are required to
585 more fully constrain the fate of Br during ascent and degassing of mafic melts.

586 Our *melt model line* also suitably reproduces the compositional trends exhibited by Etna’s and
587 Stromboli’s melt inclusions (data from Table A.2). Curiously, a set of model calculations
588 initialised as above but with initial volatile contents from Stromboli’s most primitive
589 inclusion (ST82c 137; S = 0.2 wt.%; Cl = 0.17 wt.%; and Br = 4.8 ppm; Table A.2) output a
590 *melt model line* (orange line) that is very close to the Etna-like model trend above (Fig. 6b).
591 An additional set of two model lines, calculated using slightly different initial Br contents to
592 encompass the whole range of glass inclusion compositions observed, are also illustrated in
593 the Figure 6b (dashed lines).

594

595 5.3. *Bromine contribution of volcanism to the atmosphere*

596 Global compilations show that Br sources and sinks are not strictly balanced, hinting
597 at a missing natural source of Br (Khalil et al., 1993; Montzka et al., 2011). Methyl bromide
598 CH₃Br (mainly produced by marine phytoplankton, biomass burning and fumigants in
599 agriculture) is the largest source of bromine to the atmosphere, and is believed to play a key
600 role in tropospheric and stratospheric ozone depletion (e.g., Mano and Andreae, 1994;
601 Warwick et al., 2006). However, methyl bromide alone cannot explain the total amount of
602 active Br species involved in the ozone destruction process (e.g., Warwick et al., 2006).
603 Following the first detection of bromine monoxide (BrO) in a volcanic plume (Bobrowski et
604 al., 2003), volcanic degassing (both passive and active) has been recognized as a potentially
605 major source of reactive bromine species to the atmosphere (e.g., Gerlach, 2004;
606 Oppenheimer et al., 2006).

607 Possible approaches to quantify the volcanogenic bromine contribution to the atmosphere
608 include: (i) direct measurements from volcanic fumaroles and plumes or (ii) calculation from
609 bromine contents of pre-eruptive melts (i.e., undegassed crystal-hosted melt inclusions).

610 Below we apply the second approach to Etna, Merapi and Santorini volcanoes, and compare
611 to direct gas measurements when possible.

612

613 5.3.1 *Bromine emission from an open-vent mafic volcano: the case of Mount Etna*

614 Mount Etna is a persistently degassing basaltic volcano with frequent eruptive activity. We
615 measured the Br contents of olivine-hosted melt inclusions from the trachybasaltic magma
616 erupted during the 2006 Etna eruptions (Table A.2). This eruptive period began in mid-July
617 2006 and continued intermittently for 5 months (Neri et al. 2006; Behncke et al., 2008); it was
618 characterized by strombolian and effusive activity along fissures and at different vent

619 locations and by a short episode of lava fountaining (more details in Behncke et al., 2009 and
620 references therein).

621 *Br in the pre-eruptive magma versus Br released in the atmosphere*

622 Taking into account (i) an average Br content of 5.6 ppm dissolved in the pre-eruptive melt
623 (Table A.2), (ii) a ‘dense-rock equivalent’ (DRE) erupted volume of 0.012-0.013 km³
624 (Supplementary Information) and (iii) 25 vol% of phenocrysts (Ferlito et al., 2010), we
625 estimate that 125-141 tons of Br were dissolved in the melt prior to the eruption (SI).

626 The bromine output (as BrO) of this eruptive period, calculated from gas monitoring data
627 (using an average SO₂ flux of 3444 tons/day, from Aiuppa et al., 2008; and a molar volcanic
628 gas BrO/SO₂ ratio of 1.1×10^{-4} ; from Bobrowski and Giuffrida, 2012) was 85 tons. However,
629 this is a minimum estimate since BrO is not emitted directly from the magma, but forms by
630 conversion from HBr after emission (e.g. Oppenheimer et al 2006; Martin et al., 2009; von
631 Glasow, 2010; Roberts et al., 2014). Thermodynamic equilibrium calculations indicate that
632 HBr is the primary Br species at Etnean magmatic temperatures (in the 500-1100 °C
633 temperature range and 0.1 MPa pressure; Aiuppa et al., 2005). The HBr output was
634 unfortunately not determined during the 2006 eruption. If we assume the same mean HBr/SO₂
635 (7×10^{-4} by mass) as measured in 2004 (Aiuppa et al., 2005) then this yields a Br emission of
636 425 tons.

637 It is preferable to base the estimate on data from the actual 2006 eruption; however the
638 percentage of BrO of the total emitted bromine is difficult to determine. BrO/SO₂ depends on
639 factors including the plume age (distance from the vent, wind velocity), meteorology, time of
640 day, etc (e.g., Bobrowski and Giuffrida, 2012). Observations and models suggest that BrO
641 contents may represent 20 to ~50 % of total bromine within a few tens of minutes after plume
642 release (von Glasow, 2010; Roberts et al., 2014). The total mass of bromine emitted during
643 the 2006 Etna eruption would therefore be between 170 and 425 tons, which is comparable to

644 or larger than the mass of bromine in the pre-eruptive melt (125-141 tons, see above and SI),
645 suggesting that Br was efficiently degassed from the basaltic melt.

646 *Estimate of Br annual flux at Mount Etna*

647 On the basis of the 2006 BrO gas monitoring data encompassing non-eruptive and eruptive
648 periods (i.e., Aiuppa et al., 2005; Bobrowski et al., 2012), we calculate a time-averaged Br
649 emission rate of 0.7 kt/yr (assuming that BrO = 40% of Br total, Oppenheimer et al., 2006;
650 SI). This is similar to the estimate for the 2004 eruption from Aiuppa et al. (2005). However,
651 as highlighted by Collins et al. (2009), the 2004 and 2006 eruptions were “gas-poor
652 eruptions” thus 0.7 kt/yr should be considered as a minimum Br annual flux for Etna.

653

654 *5.3.2 Bromine emission from an andesitic volcano: the 2010 Merapi plinian eruption*

655 Merapi volcano (Java, Indonesia) is one of the most active and hazardous volcanoes in the
656 world. The 2010 eruption (VEI 4; Solikhin et al., 2015) was the volcano’s largest since 1872.
657 In contrast to the prolonged and effusive dome-forming eruptions typical of Merapi’s activity
658 of the last decades, the 2010 eruption began explosively, before a new dome was rapidly
659 emplaced. This new dome was subsequently destroyed by explosions, generating pyroclastic
660 density currents. The initial explosive phase generated an ash plume that rose to 18 km
661 altitude (Solikhin et al., 2015). The entire eruption released ~0.44 Tg of SO₂ (cumulative SO₂
662 output based on satellite observations; Surono et al., 2012), much more than previous Merapi
663 eruptions (from 1992 to 2007; Surono et al., 2012). The SO₂ emission rates of the 2010
664 eruption greatly exceed background and eruptive emissions recorded at Merapi between 1986
665 and 2007 (Nho et al., 1996; Humaida et al., 2007; Surono et al., 2012). On the basis of the
666 ‘petrological method’, Surono et al. (2012) and Preece et al. (2014) calculated that the magma
667 volume needed to account for the amount SO₂ released is at least an order of magnitude
668 higher than the estimated DRE volume of magma erupted. They inferred the existence of an

669 exsolved S-rich fluid phase in the pre-eruptive magma body, consistent with the conclusion
670 given by Scaillet et al. (1998b, 2003) and Keppler (1999) to explain the common excess of
671 sulfur upon explosive eruptions. According to VolatileCalc modelling by Preece et al. (2014),
672 the vapour phase would have represented 1 wt% of the magma and degassing occurred in
673 closed- (i.e., gas bubbles remained in physical contact and equilibrium with their host melt)
674 rather than in open-system conditions prior to the explosive phase of the 2010 eruption.

675 The GOME-2 satellite instrument measured SO₂ SCD (slant column densities) of up to
676 8.9×10^{18} molecules.cm⁻² (paroxysmal phase of November 5, 2010; Hormann et al., 2013),
677 while BrO/SO₂ ratios were extremely low (8×10^{-6} maximum), indicating that Br was virtually
678 absent. Yet, considering a magma density of 2550 kg/m³, 55 wt% of phenocrysts (Preece et
679 al., 2014) and an average Br content of 9 ppm in the melt inclusions (this study, Table A.2),
680 433 tons of Br were available in the pre-eruptive melt. In addition, if we consider the presence
681 a free fluid phase in the reservoir (1 wt%; Preece et al., 2014) and the $D_{\text{Br}}^{\text{f/m}} = 9.1$ in andesitic
682 melt (Fig. 2b), 73 tons of Br were stored in the fluid and hence immediately available during
683 eruption. Note that we observe the same large discrepancy between the satellite-based
684 estimate of the chlorine yield and the petrological one (see SI). In our opinion, the two most
685 probable explanations are: (1) the paroxysmal phase of the eruption being ash-rich (opacity)
686 and occurring in the middle of the night, the production of BrO was prevented until many
687 hours later (as the reactions are UV-enabled) and is probably lower than in ash-poor plumes
688 (2) satellite instruments measure gases which reached the stratosphere more effectively than
689 those that remain lower in the atmosphere (significant amount of bromine might have been
690 scavenged in the troposphere). Additional causes might include: (i) preferential S degassing
691 owing to kinetic factors (e.g., Fiege et al., 2014), (ii) Br uptake by brine saturation during
692 magma uprise, (iii) the involvement of other volatile species (e.g. CO₂) which may alter Br
693 partitioning.

694 The case of Merapi 2010 eruption hints at the need of studies on Br speciation in ash-rich
695 volcanic plumes and additional experimental constraints, in particular on the effect of
696 volatiles other than H₂O on Br systematics.

697

698 *5.3.3. Bromine emission during the cataclysmic Minoan eruption of Santorini volcano*

699 The Late-Bronze age Minoan eruption discharged 38-86 km³ DRE of rhyodacitic magma (e.g.
700 Pyle, 1990; Johnston et al., 2014). Petrological studies have shown that the pre-eruptive melt
701 was rich in halogens, particularly in chlorine (2500-6000 ppm), and was most probably in
702 equilibrium with an exsolved H₂O-Cl-rich fluid phase (Cadoux et al., 2014; Cadoux et al.,
703 2015; Druitt et al., 2016). Here, we have measured for the first time the Br content of
704 plagioclase-hosted melt inclusions from the Minoan plinian fallout deposit (Table A.2). They
705 give an average value of 7.3 ± 0.8 ppm, which multiplied by the $D_{\text{Br}}^{\text{f/m}}$ of 20.2 (obtained in
706 this study for a rhyodacitic composition at 900°C, 200 MPa and ~NNO; Fig. 3), indicate that
707 the pre-eruptive fluid phase contained 147 ppm Br.

708 Assuming a minimum erupted volume of 39 km³ DRE and a magma crystallinity of 10%, the
709 Minoan pre-eruptive melt would have contained 0.6 Mt of Br. Recent studies have shown
710 that, in silicic magma systems, Br is efficiently degassed with water during eruption (Bureau
711 et al., 2010; Cochain et al., 2015). If we assume that all the Br was degassed from the melt
712 (i.e. we consider 0 ppm of Br in the interstitial melt), the Br output of the Minoan eruption
713 was 0.6 Mt. If we add the contribution of the fluid phase (assuming that it represents 5 wt% of
714 the magma mass, as in Cadoux et al., 2015), then the total Br output would have reached 1.3
715 Mt. These Br yields are consistent with previous estimates of 0.1-1.5 Mt (Cadoux et al., 2015)
716 obtained by multiplying the chlorine yields by the mean molar Br/Cl ratio of 0.0022 of
717 volcanic arc gases (Gerlach, 2004).

718 The estimated Br output of this single large explosive event (VEI 6-7) is > 100 times higher
719 than the annual Br flux at a persistently degassing volcano such as the Etna (0.0007 Mt, see
720 before) and the estimated global Br flux at volcanic arcs (0.005-0.015 Mt/yr; Pyle and Mather,
721 2009).

722

723 **6. Conclusions**

724 Determining halogen behaviour in magmatic systems is important to understand their role in
725 the Earth's element cycles and to provide reliable constraints on the contribution of volcanism
726 to atmospheric and ocean chemistry. The behaviour of the heavier halogens such as Br in
727 magmatic systems is less well understood than that of Cl and F. We have experimentally
728 determined the fluid/melt partitioning of bromine at shallow crustal pressure and temperature
729 conditions (100-200 MPa, 900-1200°C) with mafic, intermediate and silicic natural melts.
730 $D_{\text{Br}}^{\text{f/m}}$ values range from 5.0 ± 0.3 at 100 MPa – 1200°C for the basalt to 20.2 ± 1.2 at 200
731 MPa - 900°C for the rhyodacite. Our data confirm previous experimental constraints on
732 synthetic model magma compositions (Bureau et al., 2000). They also show that $D_{\text{Br}}^{\text{f/m}}$
733 increases with increasing SiO₂ content of the melt (as for chlorine) and it also appears to be
734 sensitive to melt temperature (increase of $D_{\text{Br}}^{\text{f/m}}$ as temperature decreases). These results
735 suggest that the Br yield into atmosphere from relatively cold and silicic magmas will be
736 much larger than that from hotter and more mafic magmas. The partition coefficients of this
737 study will permit better estimates of the Br yield of past explosive eruptions, provided their
738 pre-eruptive temperature is well known.

739 Our Br partition coefficient for Etna basalt, together with literature data on S and Cl
740 behaviour, and S-Cl-Br volcanic gas compositions in mafic volcanic systems, allow first order
741 quantitative modelling of S-Cl-Br degassing behaviour in shallow magma reservoirs,
742 permitting a better interpretation of gas-monitoring data.

743

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1209 **Figure Captions**

1210

1211 **Figure 1.** Partitioning of bromine between melt and fluid in the run products at 1200°C, 100
1212 MPa and $fO_2 \sim NNO$. The $D_{Br}^{f/m}$ of the basaltic composition, determined by linear regression
1213 through the origin, is: 4.95 ± 0.33 . The error on the partition coefficient corresponds to the
1214 error on the slope of the regression line, as determined by the least squares method.

1215

1216 **Figure 2. (a)** Melt Br contents versus bulk Br contents (ppm) for the andesitic and rhyodacitic
1217 compositions at 1060°C, 200 MPa and $fO_2 \sim NNO$. **(b)** and **(c)** Partitioning of bromine
1218 between melt and fluid in the andesitic and rhyolitic run products, respectively, at those
1219 conditions. The $D_{Br}^{f/m}$ determined by linear regression through the origin are: 9.1 ± 0.6 for the
1220 andesite and 14.0 ± 0.6 for the rhyodacite. The errors on $D_{Br}^{f/m}$ are the errors on the regression
1221 lines slope, see Figure 1 caption.

1222

1223 **Figure 3.** Partitioning of bromine between melt and fluid for the rhyodacitic composition, at
1224 900°C, 200 MPa, $\sim NNO$. At lower temperature, the $D_{Br}^{f/m}$ of the rhyodacite increases: $20.2 \pm$
1225 1.2 . Error on $D_{Br}^{f/m}$: see Figure 1 caption. The results are consistent with those of Bureau et al.
1226 (2000) on synthetic albitic composition.

1227

1228 **Figure 4.** $D_{Br}^{f/m}$ as a function of SiO_2 (wt%) of the run products of this study. The data for the
1229 900°C – 200 MPa experiment of Bureau et al. (2000) is also plotted. This figure shows the
1230 effect of melt composition on $D_{Br}^{f/m}$ and also suggests an effect of the temperature, at least for
1231 the more silicic melts.

1232

1233 **Figure 5.** $D_{\text{Br}}^{f/m}$ of the rhyodacite composition versus partition experiment temperature (°C).

1234 Data at 900°C and 1060°C are at 200 MPa and data at 1200°C is at 100 MPa.

1235

1236 **Figure 6. (a)** Triangular plot of S-Cl-Br*300 compositions of volcanic gas samples from
1237 selected mafic arc volcanoes. All data refer to near-vent in-situ measurements with filter
1238 packs, and are thus representative of gas species SO₂, HCl and HBr (the main S and halogen
1239 reservoirs in near-vent plumes, Aiuppa et al., 2005). Volcanic gas data sources: Reunion
1240 Island (Indian Ocean): Allard et al (2011); Nyiragongo (Congo): Bobrowski et al. (2015);
1241 Hawaii (Pacific Ocean): Mather et al., (2012); Etna (Sicily): Aiuppa et al. (2005), Aiuppa,
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1243 (Nicaragua): Witt et al, (2008); Mount Asama (Japan): Aiuppa, (2009), Aiuppa, unpublished
1244 results; Myike-jima (Japan): Aiuppa, (2009), Aiuppa, unpublished results; Gorely
1245 (Kamchatka, Russia): Aiuppa et al. (2012); Villarrica (Chile): Sawyer et al., (2011). For
1246 comparison, the model-derived compositions of gas initially coexisting with an Etna-like
1247 primitive melt (S: 0.27 wt.%, Cl: 0.18 wt.%, and Br: 5.1 ppm) are shown by the thick solid
1248 green curve. Dashed green lines are examples of Etna-like melt model trends obtained using
1249 same initial S and Cl contents (S: 0.27 wt.%, Cl: 0.18 wt.%) but slightly different initial Br
1250 contents (of respectively 3 and 6.1 ppm), within the range observed in glass inclusions (see
1251 Table A.2). The initial Br contents for the 3 Etna runs are labeled in the plot. Model lines are
1252 obtained using the Rayleigh-type open-system equations described in the text. Extent of
1253 degassing along both model lines varies from top (“early gas”) to bottom (“late gas”) (R
1254 values for specific points are shown in italics). See text for discussion. **(b)** The glass inclusion
1255 compositions from Etna and Stromboli (data from Table A.2) are displayed against the model-
1256 derived compositions, ranging from S-rich “*early melts*” to halogen-enriched (relative to S)
1257 “*late melts*”. The melt model line (solid red curve) is derived from the same Etna-like

1258 primitive melt composition given above (S: 0.27 wt.%, Cl: 0.18 wt.%, and Br: 5.1 ppm).
1259 Dashed red lines are examples of Etna-like melt model trends obtained using same initial S
1260 and Cl contents (S: 0.27 wt.%, Cl: 0.18 wt.%) but slightly different initial Br contents (of
1261 respectively 3 and 6.1 ppm), within the range observed in glass inclusions (see Table A.2).
1262 The initial Br contents for the 3 Etna runs are labeled in the plot. The melt model trend
1263 initialized at conditions representative of a Stromboli's primitive melt (S: 0.2 wt.%, Cl: 0.17
1264 wt.%, and Br: 4.8 ppm; see Table A.2) is depicted by the orange solid line. R values for
1265 specific points are shown in italics.

1266

1267 **Table Captions**

1268

1269 **Table 1.** Major element composition of the starting dry glasses used for the partitioning
1270 experiments.

1271

1272 **Table 2.** Results of the fluid/melt partitioning experiments.

1273

1274 **Table 3.** Major element composition (wt%) of the partition experiment products.

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

Volcano: Eruption	Etna: 11/22/2002		Santorini: USC-2		Santorini: Minoan	
Sample name	ET02PA27 ^a		S09-22 ^b		S82-30 ^c	
<i>Major oxides (wt%)</i>	<i>n = 32</i>	$\pm 1\sigma$	<i>n = 8</i>	$\pm 1\sigma$	<i>n = 22</i>	$\pm 1\sigma$
SiO ₂	47.95	0.82	58.88	0.43	71.24	0.26
TiO ₂	1.67	0.11	1.28	0.05	0.45	0.04
Al ₂ O ₃	17.32	0.27	16.16	0.17	14.87	0.15
FeO _{tot}	10.24	0.13	8.18	0.25	2.85	0.18
MnO	nd	nd	0.20	0.09	0.08	0.05
MgO	5.76	0.28	2.77	0.09	0.73	0.05
CaO	10.93	0.37	6.46	0.12	2.34	0.14
Na ₂ O	3.45	0.16	4.07	0.15	4.24	0.08
K ₂ O	1.99	0.10	1.67	0.06	3.08	0.11
P ₂ O ₅	0.51	0.12	0.31	0.06	0.13	0.04
Original sum	99.82		96.66		98.40	

Major element analyses performed by electron microprobe

a: from Iacono-Marziano et al. (2012)

b: from Cadoux et al. (2017), recalculated to 100%

c: from Cadoux et al. (2014, 2017), recalculated to 100%

n: number of analyses, and σ : standard deviation of the average of *n* analyses

nd: not determined

These dry glasses were also used to synthesize Br standards characterized in Cadoux et al. (2017)

Table 2. Results of the fluid/melt partitioning experiments

	[Br ^o] ^a (ppm)	fluid/melt mass ratio	[Br] _{melt} ^b (ppm)	± 1σ	[H ₂ O] _{melt} ^c (wt%)	± 1σ	[Br] _{fluid} ^d (ppm)	± error (ppm)	D _{Br} ^{f/m}	± error
Experiment #1: Au-Pd capsule, 1200°C, 100 MPa, ~NNO (pH₂ = 2 bars), 24 hours										
Run product # (B for basalt)										
M1-B	72181	0.06	3753	168	n.d.		14298	1595	3.8	4.3
								8		
Experiment #2: Au-Pd capsule, 1200°C, 100 MPa, ~NNO (pH₂ = 2 bars), 24 hours										
M2-B	14251	0.08	9112	464	n.d.		47027	1265	5.2	1.4
								7		
Experiment #3: Au-Pd capsules, 1200°C, 100 MPa, ~NNO (pH₂ = 2 bars), 24 hours										
Run product # (B for basalt, A for andesite, RD for rhyodacite)										
M3-B	24222	0.12	2034	290	3.4	0.0	9370	3845	4.6	2.0
M3-A	24222	0.12	1912	376	4.8	0.1	12298	6227	6.4	3.5
M3-RD	24222	0.12	1426	42	2.9	0.0	16065	1073	11.3	0.9
Experiment #4: Au-Pd capsules, 1060°C, 200 MPa, ~NNO (pH₂ = 2 bars), 48 hours										
M4-A1	999	0.11	69.5	0.1	7.2	0.1	948	138	13.7	2.0
M4-A2	4968	0.11	359	48	7.3	0.1	4439	1498	12.3	4.5
M4-A3	9874	0.11	733	79	7.3	0.2	8396	2462	11.5	3.6
M4-A4	24222	0.12	1960	34	7.2	0.1	16908	2499	8.6	1.3
M4-RD1	999	0.11	69	10	5.2	0.1	662	204	9.3	3.3
M4-RD2	4968	0.11	240	82	4.9	0.2	4968	1437	20.6	9.3
M4-RD3	9874	0.11	591	24	5.4	0.3	8626	966	14.6	1.8
M4-RD4	24222	0.12	1483	242	5.1	0.1	20314	4418	13.7	3.8
Experiment #5: Au capsules, 900°C, 200 MPa, ~NNO (pH₂ = 2 bars), 92 hours										
M5-RD1	999	0.12	79	6	6.8	0.4	701	162	8.6	2.2
M5-RD2	4968	0.11	226	31	6.0	0.3	6307	981	27.9	5.9
M5-RD3	9874	0.11	608	97	6.5	0.5	10113	2704	16.6	5.2
M5-RD4	24222	0.11	1251	214	5.6	0.1	26037	4452	20.8	5.1

Uncertainties on T and P are ± 10°C and ± 2 MPa, respectively.

a: calculated Br content loaded into capsule in H₂O+NaBr solution

b: measured by LA-ICP-MS in run-product glasses from experiments #1 and 2 (average of 3 to 10 analyses per charge), by SIMS in glasses from experiments #3 to 5 (3-6 analyses per charge)

c: H₂O content determined by SIMS (5-7 analyses per charge) in run-product glasses from exp. #3 to 5. H₂O_{melt} was not measured in run products from exp. #1 and 2.

d: calculated by mass balance (see supplementary material for details)

1275

1276

Table 3. Major element composition (wt%) of the partitioning experiment glassy products

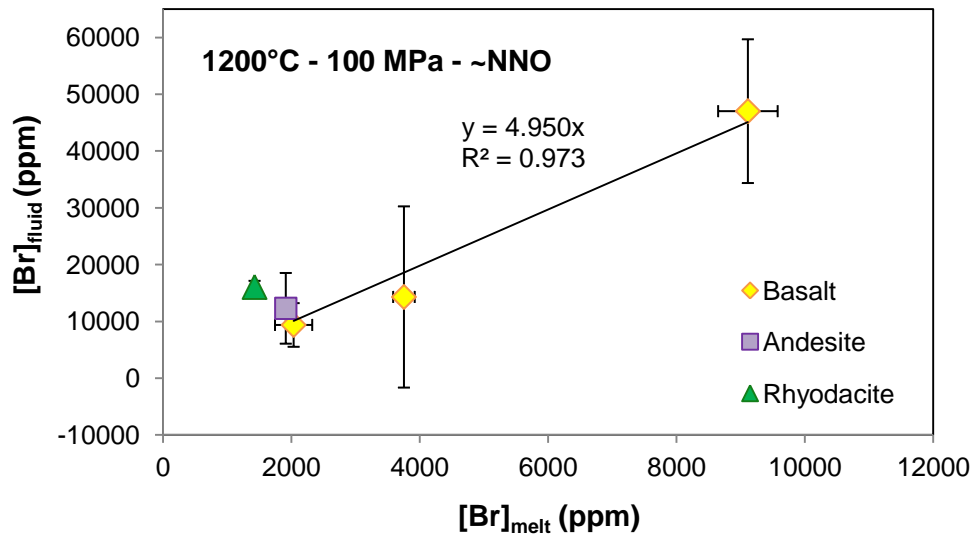
Experiment #	Run product ID	<i>n</i>	SiO ₂	TiO ₂	Al ₂ O ₃	FeO _{tot}	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Original Sum
1	M1-B	1	48.47 (37)	1.77 (9)	16.79 (18)	10.07 (32)	0.17 (10)	5.83 (20)	10.83 (25)	3.51 (16)	1.98 (14)	0.59 (8)	94.11
		0											
2	M2-B	1	48.36 (29)	1.75 (9)	16.84 (15)	9.89 (30)	0.17 (9)	5.85 (17)	11.01 (31)	3.61 (12)	1.92 (21)	0.60 (9)	94.37
		0											
3	M3-B	7	48.96 (59)	1.65 (16)	17.05 (19)	9.12 (38)	0.17 (12)	6.15 (5)	10.82 (26)	3.60 (10)	2.07 (20)	0.40 (12)	95.01
"	M3-A	7	59.54 (30)	1.27 (14)	16.32 (20)	7.36 (29)	0.10 (8)	2.74 (6)	6.33 (14)	4.46 (8)	1.66 (7)	0.21 (15)	95.14
"	M3-RD	6	71.31 (30)	0.40 (6)	14.77 (18)	2.15 (15)	0.10 (12)	0.72 (3)	2.40 (8)	4.90 (9)	3.20 (10)	0.07 (6)	95.56
4	M4-A1	6	59.50 (33)	1.28 (14)	16.37 (13)	7.66 (41)	0.19 (8)	2.73 (9)	6.35 (6)	4.11 (9)	1.59 (6)	0.22 (12)	93.51
"	M4-A2	6	59.52 (38)	1.36 (17)	16.45 (28)	7.50 (39)	0.18 (9)	2.68 (8)	6.35 (9)	4.14 (11)	1.56 (7)	0.27 (15)	92.77
"	M4-A3	6	59.70 (43)	1.33 (18)	16.55 (10)	7.19 (22)	0.20 (14)	2.66 (5)	6.31 (11)	4.12 (5)	1.61 (10)	0.31 (18)	93.18
"	M4-A4	6	59.44 (54)	1.38 (11)	16.27 (18)	7.73 (19)	0.28 (9)	2.71 (5)	6.34 (14)	4.17 (9)	1.51 (5)	0.16 (20)	92.81
"	M4-RD1	6	71.77 (26)	0.51 (4)	14.85 (20)	2.18 (28)	0.14 (5)	0.69 (4)	2.47 (7)	4.41 (34)	2.88 (19)	0.10 (6)	92.93
"	M4-RD2	5	71.48 (73)	0.48 (9)	14.92 (5)	2.35 (12)	0.05 (5)	0.69 (4)	2.46 (7)	4.51 (7)	2.86 (13)	0.19 (10)	92.35
"	M4-RD3	6	71.49 (61)	0.46 (7)	15.05 (19)	2.28 (25)	0.08 (11)	0.66 (2)	2.45 (11)	4.64 (9)	2.83 (11)	0.05 (8)	92.40
"	M4-RD4	7	71.68 (37)	0.45 (8)	14.63 (22)	2.40 (21)	0.09 (7)	0.71 (4)	2.37 (6)	4.58 (10)	2.90 (10)	0.18 (9)	92.10
5	M5-RD1	8	71.56 (31)	0.49 (8)	14.49 (29)	2.88 (21)	0.06 (8)	0.71 (3)	2.34 (8)	4.35 (8)	3.01 (19)	0.11 (6)	91.79
"	M5-RD2	8	71.47 (39)	0.42 (10)	14.40 (21)	3.01 (30)	0.08 (8)	0.70 (5)	2.41 (11)	4.41 (8)	2.97 (12)	0.11 (10)	92.69
"	M5-RD3	9	71.50 (31)	0.46 (10)	14.39 (13)	2.96 (19)	0.07 (7)	0.72 (4)	2.37 (6)	4.45 (14)	3.00 (19)	0.09 (10)	92.37
"	M5-RD4	7	71.31 (52)	0.41 (11)	14.44 (22)	2.89 (20)	0.05 (6)	0.71 (4)	2.38 (9)	4.58 (9)	3.07 (17)	0.16 (5)	93.19

Major element analyses recalculated to 100%

n is the number of analyses per product

Numbers in parentheses indicate one standard deviation of *n* analyses in terms of smallest units cited

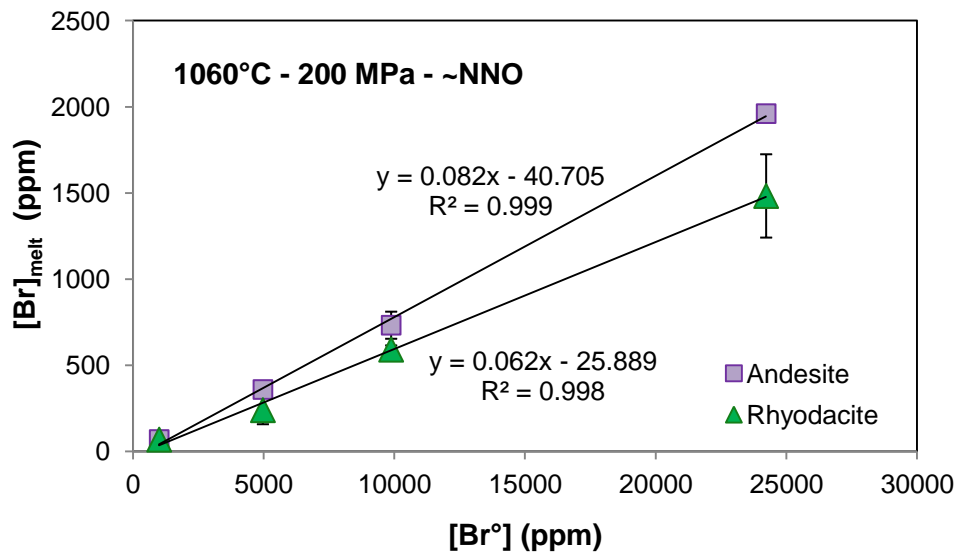
1277 **Figure 1**



1278

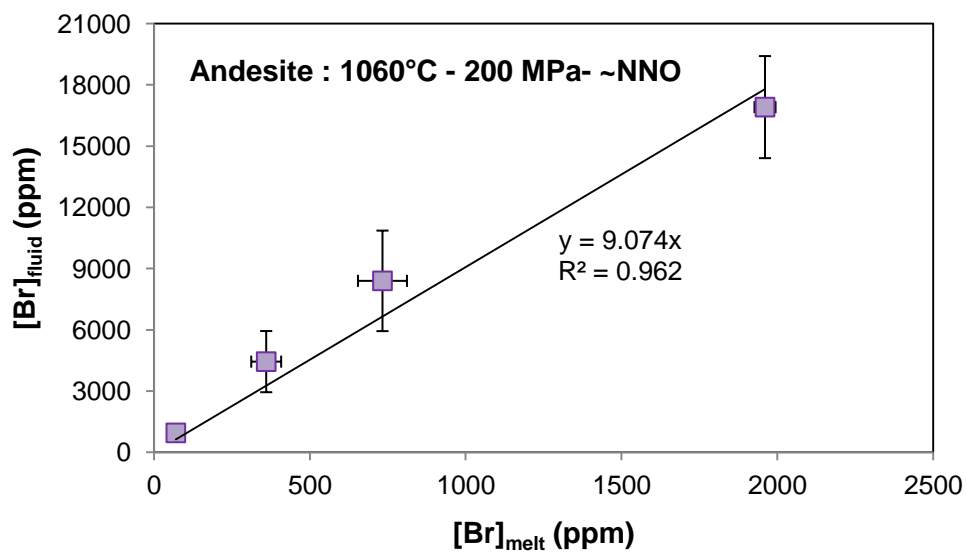
1279

1280 **Figure 2 (a)**



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1282 **(b)**



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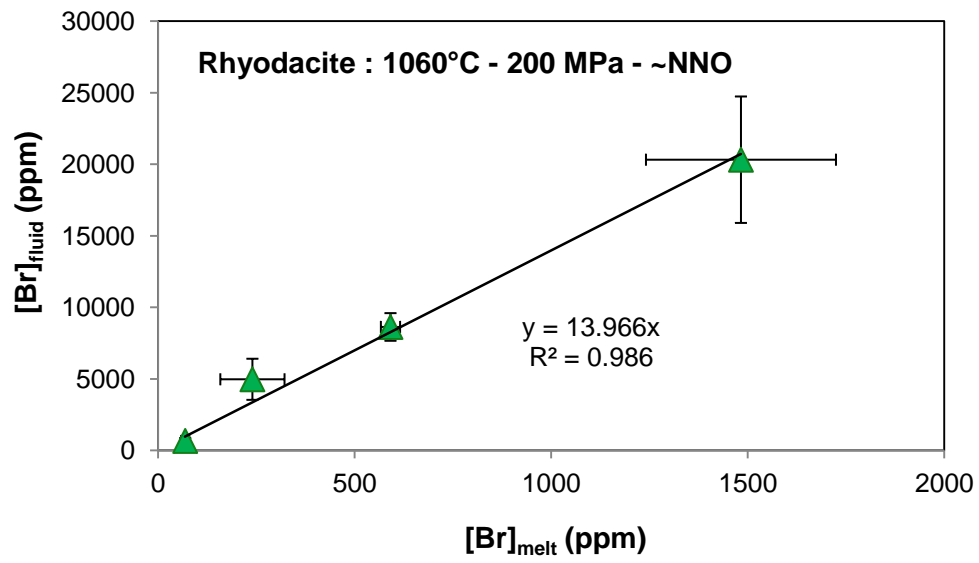
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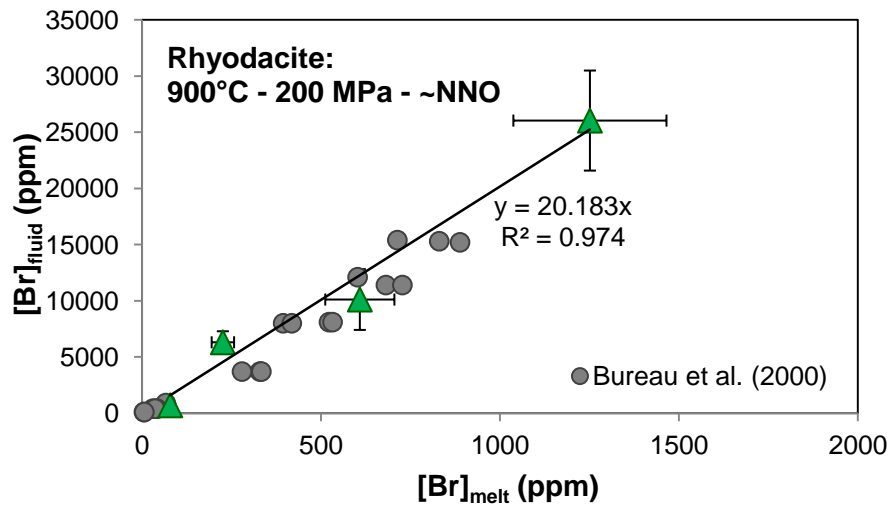
1289 (c)



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1291

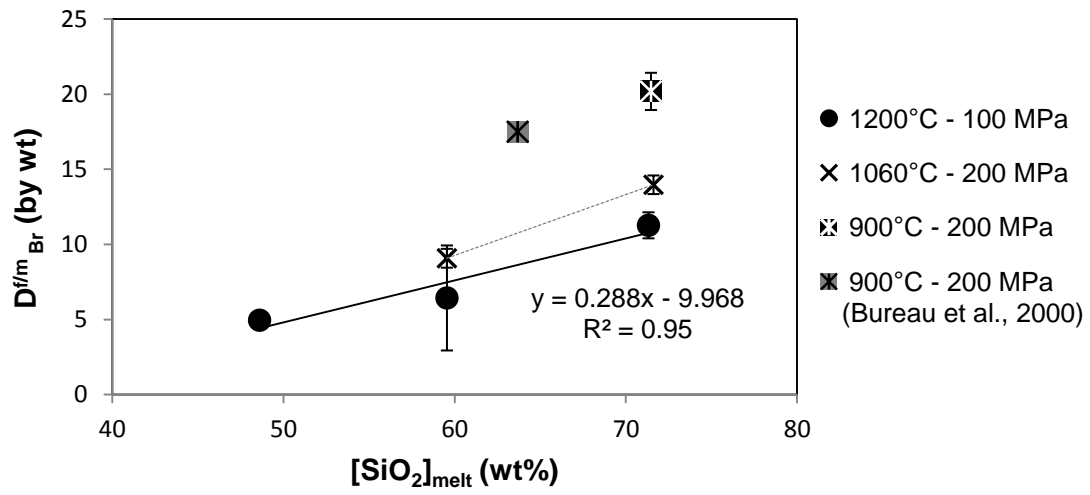
1292 **Figure 3**



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1294

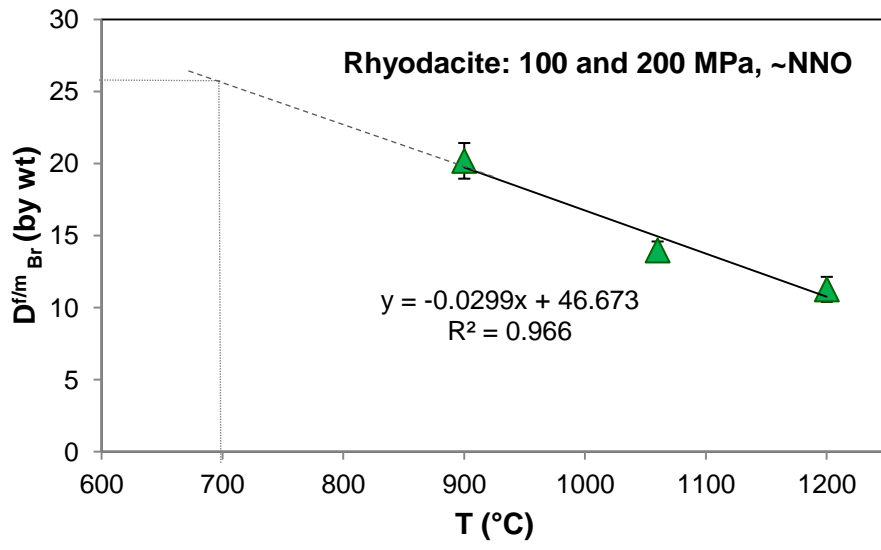
1295 **Figure 4**



1296

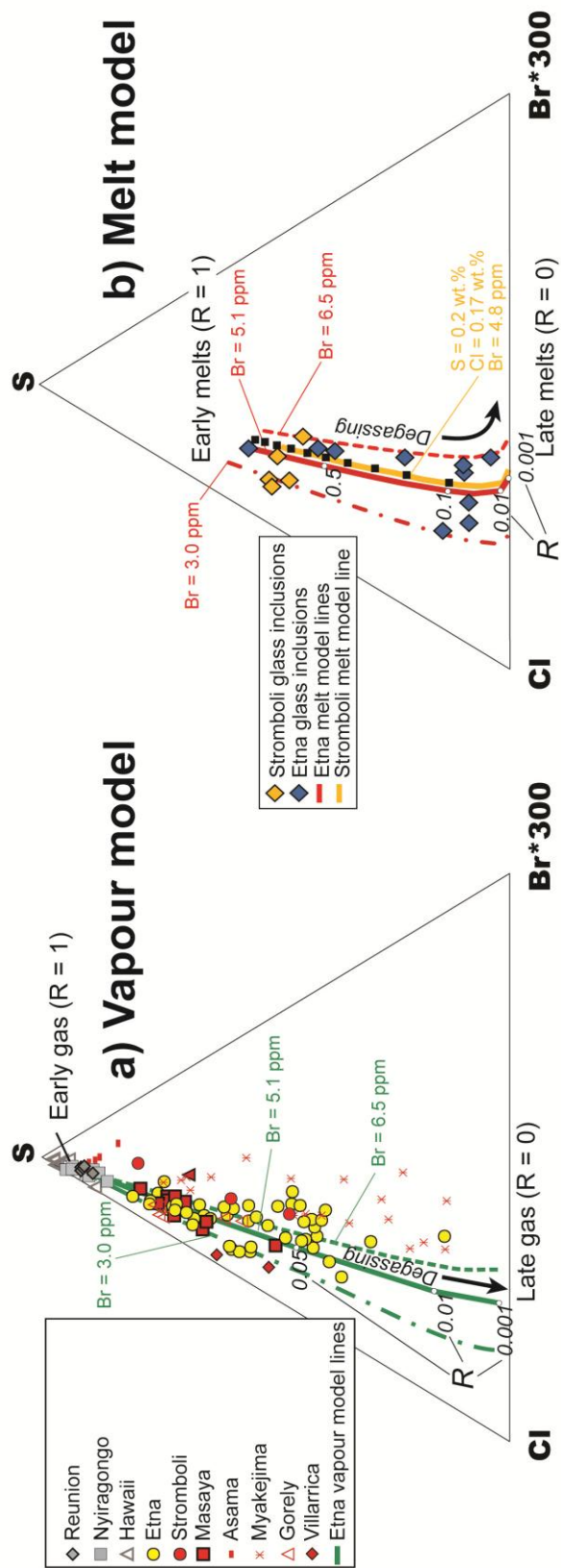
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1298 **Figure 5**



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