Halogens (F, Cl, Br, I) in thirteen USGS, GSJ and NIST international rock and glass reference materials

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Abstract

Fluorine, Cl, Br and I measurements are reported for 8 international rock reference materials (BHVO-2, BCR-2, BIR-1a, RGM-2, AGV-2, GSP-2, JB-2, JR-1) and new F data are reported for 5 silicate glass reference materials (NIST SRM 610 and 612, BHVO-2G, BCR-2G, BIR-1G). Fluorine was measured by SHRIMP in the silicate glasses and in Li-borate flux glasses prepared from the rock powders. Chlorine, Br and I were measured in vacuum encapsulated rock powders by the noble gas method (extended $^{40}Ar/^{39}Ar$ methodology). The methods yield reliable results: F has a repeatability of 1-16% in the flux glasses compared to 2-4% in the silicate glasses, which suggests incomplete homogenisation during flux melting, but F was not lost during fusion of flux glasses at 1080 °C. The noble gas method gave repeatability's of 1-2% for samples included in a single irradiation and reproducibility's of 2% for Cl, 2-3% for Br and 3-10% for I in samples included in two irradiations. The accuracy of the measurements varies from 5% to 10%, based on the reproducibility of our results, the agreement of different standardisation procedures and uncertainty in experimentally determined neutron capture cross sections. Our results significantly improve upon the precision with which some of the halogens have been characterised in the selected standards previously.

Introduction

Halogens play unique roles in a variety of natural processes. Fluorine is the most electronegative element in the periodic table and readily substitutes for the OH-group or O^{2-} in a variety of minerals (e.g. Dalou et al., 2012; Elliott, 2002; Pan and Fleet, 2002; Wu and Koga, 2013). Chlorine can also substitute for the OH-group in many hydrous minerals, but is strongly partitioned into fluid phases when present, and the chloride ligand plays a critical role in the transport of many other elements in solution (Hanor, 1994; Yardley, 2005). Bromine and iodine are trace elements that are strongly partitioned into fluid phases, however, both elements play important roles in biochemical pathways (Crockford, 2009; Kuepper et al., 2013) and consequently have elevated abundances (μg/g levels) in organic-rich sedimentary rocks (Muramatsu et al., 2007; Price and Calvert, 1977). Halogens are widely used as geochemical tracers in silicate melts and aqueous fluids (Kendrick and Burnard, 2013; Kendrick et al., 2017), and volcanic degassing of halogens has a significant impact on atmospheric chemistry (Kutterolf et al., 2013; Pyle and Mather, 2009).

Despite the importance of halogens to a variety of geological, biological and atmospheric processes, there are a limited number of techniques available to precisely analyse the abundances of all halogens in silicate rocks and minerals. Furthermore, relatively few reference materials have been adequately characterised for multiple halogens, which limits the traceability of analytical results obtained by different techniques or in different laboratories (e.g. Balcone-Boissard et al., 2009; Chai and Muramatsu, 2007; Marks et al., 2017; Michel and Villemant, 2003). To address this problem, this study aimed to refine previous F measurements of international glass standards (NIST SRM 610 and 612; BHVO-2G, BCR-2G, BIR-1G; Marks et al., 2017) and characterise all four halogens in a suite of widely available international rock standards which are available as powders (JR-1, JB-2, BHVO-2, BCR-2, BIR-1a, RGM-2, AGV-2, GSP-2). The combined results from this study and Marks et al. (2017) are intended

56 to provide a dataset for F, Cl, Br and I in rock powders and glasses that can be collectively used
57 to calibrate or compare results between a variety of bulk and micro-analytical techniques.

58 Microbeam techniques applicable to halogen measurement include electron probe
59 microanalysis (EPMA) for Cl (and F at high concentrations), laser ablation inductively coupled
60 plasma mass spectrometry (LA-ICPMS) for Cl and Br (Marks et al., 2017), and secondary ion
61 mass spectrometry (SIMS) for F, Cl, Br and I (Goswami et al., 1998; Hoskin, 1999; Straub and
62 Layne, 2003). However, to date *in situ* analysis of Br and I have been restricted to halogen-
63 rich minerals (Hammerli et al., 2013; Kusebauch et al., 2015) and analysis of typical low ng/g
64 concentrations of Br and I in many geological materials requires bulk analytical techniques.
65 The bulk techniques available require highly variable sample sizes (mg- to g-size) and most of
66 them rely on first extracting halogens from their matrix, often by pyrohydrolysis, to produce a
67 halogen bearing solution or concentrate (e.g. techniques including ion selective electrode, ion
68 chromatography, inductively coupled plasma mass spectrometry and radiochemical neutron
69 activation analysis; Balcone-Boissard et al., 2009; Chai and Muramatsu, 2007; Deruelle et al.,
70 1992; Jambon et al., 1995; Magenheim et al., 1995).

71 The current study applied two independent methods for F, and Cl, Br and I
72 measurement that do not require chemical extraction of the halogens. Firstly, sensitive high
73 resolution ion micro-probe (SHRIMP) was used to measure F in the silicate glass standards
74 and Li-borate flux glasses prepared from the international rock standard powders. Secondly,
75 Cl, Br and I were measured in the rock standards by the noble gas method, which is based on
76 measuring irradiation-produced noble gas proxy isotopes (e.g. ^{40}Ar-^{39}Ar methodology; Böhlke
77 and Irwin, 1992; Johnson et al., 2000; Kendrick, 2012; Kendrick et al., 2013; Marks et al.,
78 2017). In contrast with the previous study on glass chips (Marks et al., 2017), the rock powders
79 investigated in this study were vacuum encapsulated prior to irradiation. This was undertaken
80 because fine grained powders might be sensitive to loss of irradiation-produced noble gases

prior to analysis. Vacuum encapsulation precludes possible loss of $^{39}Ar_K$ and $^{37}Ar_{Ca}$ by recoil during irradiation or loss of $^{38}Ar_{Cl}$, $^{80}Kr_{Br}$ and $^{128}Xe_I$ by thermal processes (Magloughlin et al., 2001; Smith et al., 1993). The results for all the halogens investigated show reasonable agreement with previous studies but significantly improve upon precision in several cases.

Methods

Fluorine analysis by SHRIMP

SHRIMP was used to measure F in: i) international glass standards (NIST SRM 610 and 612, BHVO-2G, BCR-2G, BIR-1G); ii) international rock standards prepared as Li-borate flux glasses (JR-1, JB-2, BHVO-2, BCR-2, BIR-1a RGM-2, AGV-2, GSP-2); and iii) synthetic MORB glasses prepared in either a gas mixing furnace or a piston cylinder, which were intended as additional in house standards. The SHRIMP was calibrated for these measurements using either: i) a suite of natural silicate glasses with known F concentration (see Kendrick et al. 2017); or ii) in house Li-borate flux glass standards prepared from CaF_2-doped oxide mixtures with the major element composition of average MORB (Fig 1a).

The Li-borate flux glasses (rock reference materials and calibration standards) were prepared following standard XRF protocols. The rock powders and CaF_2-doped oxide mixtures were mixed with Sigma X-ray Flux (35.3% Li tetraborate and 64.7% Li metaborate) in a ratio of 1:3 in platinum crucibles. A few drops of ammonium nitrate was added to the powder and dried in a furnace at 400 °C for 10 minutes. The sample mixtures were then placed in a second furnace and melted at 1080 °C for 10 minutes during which time they were continuously agitated. The melt was quenched by removal from the furnace. A Li-borate glass (with no sample) was prepared as a blank for this procedure and was found to contain 5 µg/g F. Every

104 sample was prepared in two or more beads (denoted –a, -b, -c, -d) to test the reproducibility of
105 the glass making as well as the SHRIMP measurements.

106 To test alternative methods of sample/standard preparation synthetic silicate glasses
107 were also prepared from the same CaF_2-doped oxide mixtures, without the addition of a flux.
108 The majority of these silicate glasses were prepared in gas mixing furnaces on Pt and Re wires
109 by heating the sample to 1200 °C over a period of 2 hours and then quenching the melt by
110 removal from the furnace. However, to test if F was lost by degassing of samples prepared at
111 atmospheric pressure, a single aliquot of a mixture with 506 ± 25 µg/g F was also melted in the
112 piston cylinder at 1300 °C and 6 kbar for 30 minutes.

113 Chips of the glass calibration standards (natural silicate glasses and Li-borate flux
114 glasses); international reference materials analysed as unknowns (silicate glasses and Li-borate
115 flux glasses) and synthetic silicate glasses prepared in the gas mixing furnaces and piston
116 cylinder were mounted in epoxy discs and polished to a 1 µm finish. The polished mounts
117 were ultrasonically cleaned with acetone and ethanol, dried overnight in a vacuum furnace at
118 100 °C and given a 10 nm thick gold coat before loading into the SHRIMP-II or SHRIMP-SI
119 for analysis (below).

120 The SHRIMP technique utilised in both SHRIMP-II and –SI sessions was similar to
121 that of Beyer et al. (2016). The sample mount was held in the SHRIMP ultrahigh-vacuum
122 sample chamber at a potential of -10 kV and targeted with a primary Cs^+ ion beam focused to
123 a ~30 µm spot on the sample. The ion beam generated with a Kimball Physics Cs gun (IGS-4)
124 was 2 nA and had an initial energy of 5 kV, making a total impact energy of 15 keV. Charge
125 neutralisation was achieved by focusing a 2 kV electron beam generated with a Kimball
126 Physics electron gun onto the sample mount. A two minute raster was performed around the
127 target area prior to each analysis and secondary ions of $^{19}F^-$ and $^{18}O^-$ were measured by Faraday
128 cup multi-collection (10^{11} and 10^{12} Ω resistors). The instrument was configured to give

129 resolution of 3,500 (1% peak height definition), which is adequate for complete resolution of
130 known interferences. Data was collected over four 20 s integration periods in static mode (total
131 measurement time 80 s). The measured ^{19}F signal was calibrated using ^{18}O as an internal
132 standard and the calibration curve constructed with either silicate glasses (Kendrick et al.,
133 2017) or F-doped Li-borate flux glasses (Fig 1a). Measurements on Li-borate glasses were
134 corrected for the 'blank' of 5 μg/g F associated with the flux.

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137 **Chlorine, Br and I analysis by the noble gas method**

138 The majority of sample powders were vacuum encapsulated and then analysed for
139 halogen-derived noble gas isotopes produced in two different irradiations. Silica glass tubes
140 with an internal diameter of 1 mm were cut to lengths of ~6 cm and fused at one end. The
141 tubes were filled with sample powder to a depth of ~1-1.5 cm, corresponding to ~5-16 mg of
142 sample, dependent on packing density. The silica tubes were connected to a vacuum manifold
143 via Swagelok fittings and evacuated to a pressure of 10^{-8} torr. An acetylene torch was used to
144 heat the evacuated tubes just above the sample and the tube was pinched off to produce a silica
145 capsule containing the sample powder while maintaining vacuum in both the capsule and
146 manifold. Care was taken to perform this procedure quickly and without heating the sample.
147 Additional ~25 mg aliquots of JR-1 and BHVO-2 sample powder were packed in Al-foil
148 packets (e.g. un-encapsulated).

149 The vacuum capsules were labelled and loaded into two silica glass irradiation canisters
150 together with the un-encapsulated aliquots of JR-1 and BHVO-2, Ca- and K-salts, the ^{40}Ar-
151 ^{39}Ar flux monitor Hb3gr (1072 Ma; Roddick, 1983) and aliquots of 3 scapolite gems used as
152 Br and I standards (Kendrick, 2012; Kendrick et al., 2013). The samples included in both
153 canisters were irradiated in the central position of the McLellan Research and Reactor Centre

154 at UC Davis. Irradiation RS#4 on the 20th January 2017 had a duration of 47 hrs and received
155 a total neutron fluence of 3.6×10^{18} neutrons cm^{-2}. Irradiation RS#5 on the 23rd January 2018
156 had a duration of 45 hrs and received a total neutron fluence of 3.3×10^{18} neutrons cm^{-2}. The
157 samples received neutron fluxes with thermal/fast neutron ratios of close to one in both
158 irradiations.

159 Following return to the ANU noble gas laboratory the irradiated samples were
160 unloaded. The sample packets or capsules were cleaned with acetone and placed in an ultra-
161 high vacuum furnace sample holder and baked at ~120 °C for 24 hours to achieve ultra-high
162 vacuum. Each sample was successively dropped into the tantalum resistance furnace and
163 heated to 1600 °C for a period of 30 mins. The extracted gases were exposed to a Ti-foil bulk
164 getter at 650 °C throughout the 30 minute heating step and then further purified over a second
165 period of 30 minutes using a series of three SAES® Zr-Al getter pumps, which remove active
166 gases (e.g. H_2O, CO_2, N_2). The purified noble gases were expanded into the MAP 215-50 noble
167 gas mass spectrometer, and analysed for irradiation-produced and naturally occurring isotopes
168 of Ar, Kr and Xe. The measurements were made in static vacuum in 7 cycles of peak jumping
169 over a period of ~45 minutes. Following the initial sample analysis one or two further steps
170 at 1600 °C were repeated to ensure complete outgassing of the capsule and maintain low blanks
171 for subsequent samples. Together with blanks and calibrations, this procedure enabled the
172 analysis of 1-4 samples per day.

173 The relative abundances of Cl, Br, I, K and Ca were calculated from signals of
174 irradiation-produced $^{38}Ar_{Cl}$, $^{80}Kr_{Br,}$ $^{128}Xe_{I,}$ $^{39}Ar_{K}$ and $^{37}Ar_{Ca}$ and noble gas production ratios
175 ($^{38}Ar_{Cl}$/Cl, $^{80}Kr_{Br}$/Br, $^{128}Xe_{I}$/I, $^{39}Ar_{K}$/K, $^{37}Ar_{Ca}$/Ca) determined from the irradiation monitors
176 (Kendrick, 2012; Kendrick et al., 2013). Small corrections were made for instrument blanks
177 equivalent to less than ~3 ppm K, ~2 ppm Cl, ~6 ppb Br and ~1 ppb I, ^{37}Ar decay and other
178 standard Ar-interference reactions (see Kendrick, 2012 for details). The concentrations of Cl,

Br and I in the encapsulated sample powders investigated here were obtained using K as an internal standard (cross checked with Ca). This differs to the usual procedure based on noble gas abundance data and sample mass (e.g. Marks et al., 2017) and was necessary because finite quantities of sample powder were sucked into the vacuum during encapsulation, meaning that the encapsulated sample masses were not precisely known. However the reliability of the procedure is demonstrated because both data reduction methods give indistinguishable results for the precisely weighed un-encapsulated aliquots of JR-1 and BHVO-2 (below). Uncertainties are quoted at the 1 standard deviation level.

Results

SHRIMP Fluorine measurements

The F results obtained for the glass and rock standards analysed as unknowns in four different SHRIMP sessions, which were calibrated by two different methods, are summarised in Table 1 and compared with data from previous studies in Fig 1b and Table 2. The repeatability of F concentrations in the international glass standards analysed in a single SHRIMP session varies from better than 1% (Relative Standard Deviation, RSD) in cases where spots are sited close to one another (e.g. SRM 610 in session 1) to 4% in cases where a greater number of spots have been analysed on multiple chips (e.g. SRM 610 in session 2 and BCR-2G in session 1). The reproducibility of the results between different SHRIMP sessions with different calibration curves varies from 2% for BHVO-2G with 411 ± 7 µg/g F to 6 % for SRM 610 with 287 ± 16 µg/g F to 12% for BIR-1G, which has only 34 ± 4 µg/g F (Table 1).

Individual flux glass beads prepared from the international rock standards were less repeatable than the silicate glass standards within any given SHRIMP session (Table 1). Most of the flux glasses had repeatability of better than 10%, but the repeatability varied from a best value of 0.4% for the flux glass of BIR-1a-a in session 2 (49 µg/g F, n = 6), to a worst value of

16% for the flux glass of AGV-2-b in session 4 (413 µg/g F, n = 5; Table 1). The reproducibility of different beads of the same sample and the reproducibility of individual beads between different sessions is similar at the 5-10% level for all the samples with more than 100 µg/g F (Table 1). However, while the different beads of BIR-1a and JB-2 appear to have been reproduced quite well in session 4 (allowing for charging affects on the mount containing these samples), the low concentrations of F in these samples were poorly reproduced between sessions 2 and 4 (e.g. 20% level, Table 1).

The typical variability of ~10-15% in the F concentrations of individual flux glass beads and between different beads of the same sample analysed in the same session indicates incomplete homogenisation of the flux glass, which could be related to either heterogeneity in the sample powder that was melted or temperature gradients within the molten sample (e.g. Soret effect). In contrast, the lower reproducibility of ~20% obtained for the low concentrations of F in samples BIR-1a and JB-2 between different SHRIMP sessions is explained by the very low concentrations of F in these flux glasses. Note that the concentration of F measured in each flux glass is 25% of the value reported for the sample, which is diluted by the flux. In the case of BIR-1a with 63 ± 12 µg/g F, the flux glass would have contained ~12-19 µg/g F, which is lower than the calibrated range of 145-8200 µg/g F (Fig 1a) and is only 2-4 times higher than the concentration of ~5 µg/g F determined in the Li-borate flux glass prepared as a blank (Table 1).

Despite the measured heterogeneity of 10-15% in the flux glasses, the F concentrations obtained for each of the rock standards are within the ranges of previously published values (Fig 1b; Table 2). The F concentration measured in the MORB glass prepared in the piston cylinder (590 ± 47 µg/g F) was also within the 95% confidence limit of the doped value (506 ± 25 µg/g F; Fig 1b). Taken together, the generally good agreement of: i) F concentrations determined in individual standards in different SHRIMP sessions, calibrated with either silicate

229 glasses or Li-borate flux glasses; and ii) F concentrations measured by SHRIMP in diverse
230 rock standards (ranging from basalt to rhyolite) prepared as Li-borate flux glasses and
231 previously reported results (Fig 1b; Table 2); show that F was not lost from the samples during
232 flux melting at 1080 °C and that matrix effects associated with F analysis by SHRIMP are small
233 (e.g. < 10%).

234 In contrast with the flux glasses and silicate glass prepared in the piston cylinder, which
235 did not lose F during melting, the silicate glasses prepared in the gas mixing furnaces at
236 atmospheric pressure all gave F concentrations much lower than the doped values. This is
237 attributed to F loss during melting the silicates at atmospheric pressure and the results are not
238 reported for these samples. The loss of F from silicate glasses prepared in the gas mixing
239 furnaces and the retention of F in Li-borate glasses, which were all prepared at atmospheric
240 pressure, could be explained by a number of factors including i) the different melting
241 temperatures of 1200 versus 1080 °C, respectively; the different heating durations of 2hrs
242 versus 10 mins, respectively; or the very high concentration of Li in the borate flux, which
243 might have stabilised F in the melt.

244 Further work is required to assess if Cl behaves like F and is retained in the flux glasses,
245 and if it has a sufficiently low concentration in the flux to enable simultaneous measurement
246 of Cl and F in whole rock samples by this SHRIMP technique. However, it is unlikely that this
247 approach is applicable to Br or I which have very low abundances in whole rocks (e.g. ng/g)
248 and significantly higher volatility than Cl or F.

249

250 **Noble gas method Cl, Br and I results**

251 The new Cl, Br and I results obtained for repeat analyses of international rock standards in this
252 study are tabulated in Table 3 and are summarised and compared with results from other
253 techniques in Fig 2 and Table 4.

The concentrations of Cl in the rock powders, calculated by internal standardisation to K, had a repeatability of better than 1% for most of the duplicates included in a single irradiation, and a reproducibility of about 2% between irradiations RS#4 and RS#5 (Table 3). In contrast, the duplicates of GSP-2 included in RS#4, had a repeatability for Cl concentration of only 8% (Table 3). The low repeatability of the Cl measurements in GSP-2 is explained by the large amount of ^{40}Ar in this standard, which was prepared from a ~1.4 Ga granodiorite (Wilson, 1998). The large amount of ^{40}Ar in this sample necessitated splitting the sample gas and resulted in a sub-optimal aliquots of halogen-derived $^{38}Ar_{Cl}$, $^{80}Kr_{Br}$ and $^{128}Xe_{I}$ for analysis.

The Br concentrations of 260-2250 ng/g measured in encapsulated duplicate aliquots of RGM-2, BHVO-2 and JR-1 included in two irradiations have reproducibility's of 2-3%, compared to 11% for BCR-2 with 192 ± 22 ng/g Br (Table 3). The I concentrations of 51-91 ng/g measured in encapsulated duplicate aliquots of RGM-2, BHVO-2, BCR-2 and JR-1 included in two irradiations have reproducibility's of 3-10% (Table 3).

The encapsulated and un-encapsulated aliquots of JR-1 and BHVO-2 included in RS#5 gave indistinguishable results for Cl (Table 3), demonstrating that irradiation-produced $^{37}Ar_{Ca}$, $^{38}Ar_{Cl}$ and $^{39}Ar_{K}$ used for Ca, Cl and K measurement were retained in the un-encapsulated aliquots of both samples, which is consistent with the powders grain sizes (~2-80 μm, measured by laser diffraction) greatly exceeding the dimensions over which ^{37}Ar and ^{39}Ar recoil effects are significant (Onstott et al., 1995). In contrast, while the Br and I results for the encapsulated and un-encapsulated aliquots of JR-1 are indistinguishable, the un-encapsulated aliquot of BHVO-2 (BHVO-2d) gave anomalously low Br and I concentrations that suggest that ~13% of the irradiation-produced $^{80}Kr_{Br}$ and ~94% of irradiation-produced $^{128}Xe_{I}$ was lost from the un-encapsulated aliquot of this sample prior to analysis. Further work is required to test if this effect is reproducible, to determine its cause and evaluate if it influences other sample materials. However, the discrepancy between our results demonstrate the value of vacuum

encapsulating sample powders, which might be susceptible to gas loss because of their fine grain size.

Comparison with previous studies and accuracy

Fluorine

The F concentrations determined by SHRIMP analysis of flux glasses for diverse rock standards ranging from basalt to rhyolite (JB-2, JR-1, BHVO-2, BCR-2, AGV-2 and GSP-2) are within the ranges previously reported for these samples at the quoted levels of uncertainty (Table 2; Fig 1b; Balcone-Boissard et al., 2009; Imai et al., 1995; Michel and Villemant, 2003; Shimizu et al., 2006; Wang et al., 2014; Wang et al., 2010). The SHRIMP data indicate a concentration of 325 ± 30 µg/g F in RGM-2, which is within the range previously reported for RGM-1 (Table 2; Michel and Villemant, 2003). The SHRIMP data indicate a concentration of 63 ± 12 µg/g F in BIR-1a, which is indistinguishable from the values reported for BIR-1 (44-55 µg/g F; Michel and Villemant, 2003; Smith, 1998).

Relatively few data have previously been available for the international glass standards investigated, and the concentrations that have been reported for the NIST glasses vary by 400-600% (Table 2; Hinton, 1999; Hoskin, 1999; Jochum et al., 2006; Marks et al., 2017; Peate et al., 2012; Zhang et al., 2016). However, the values determined for the NIST glasses by SHRIMP in this study are within uncertainty of the GEOREM preferred values (Table 2). It should be noted that the random chips taken from the central portions of the NIST discs in this study had concentrations repeatable at the 2-4% level in a single SHRIMP session, and we avoided the edges of the NIST glass discs, the outermost ~100 microns of which have previously been shown to be depleted in F by up to ~80% (Hinton, 1999).

302 The SHRIMP results for F in BHVO-2G, BCR-2G and BIR-1G (as well as SRM 610
303 and 612) are higher than the EPMA values of Peate et al. (2012) and Zhang et al. (2016) and
304 values previously obtained by pyrohydrolysis and ion chromatography by Marks et al. (2017)
305 (Table 1). The coincidence of our F results for SRM 610 and 612 with GEOREM preferred
306 values; the good reproducibility of F in different SHRIMP sessions calibrated by different
307 methods (silicate glasses or Li-borate glasses); and the agreement of our analyses for diverse
308 rock standards (basalt to rhyolite) analysed as flux glasses with other techniques (Fig 1b);
309 suggests the differences between the SHRIMP, EPMA and pyrohydrolysis-IC results for the
310 glass standards cannot be attributed to SHRIMP matrix affects. Instead, we suggest that the
311 low F concentrations reported in the earlier studies of these glasses are the result of known
312 difficulties in the analysis of F by EPMA related to overlap with the Fe peak (Zhang et al.,
313 2016) and/or element mobility under the electron beam and incomplete F extraction during
314 pyrohydrolysis (Marks et al., 2017). Therefore we suggest that the F concentrations obtained
315 for the glasses analysed in this study are the most reliable yet available (Tables 1 and 2).

316 The SHRIMP results have an estimated accuracy of ~10 % for the USGS and NIST
317 glasses and a slightly lower accuracy of ~15% for the majority of rock standards analysed as
318 flux glasses. These estimates of accuracy are based on the reproducibility of results for NIST
319 and USGS glasses analysed in different SHRIMP sessions calibrated by different methods
320 (Table 1; Fig 1a; Kendrick et al., 2017), and the typical repeatability of the measurements in
321 the flux glass samples and calibration standards (Table 1).

322

323 **Chlorine**

324 The Cl concentrations determined for samples JR-1, BHVO-2, BCR-2, AGV-2, RGM-
325 2 and GSP-2 are all within 10% of either the GEOREM preferred values or the previously

reported upper limits on Cl concentration (Table 4; Fig 2a). The Cl concentrations of the standard glasses previously investigated by the noble gas method and other techniques also show good agreement with one another (Fig 2a; Marks et al., 2017). The good agreement between the Cl concentrations determined for the majority of international reference materials in this study and previous studies provides confidence in the overall reliability of our measurements (Fig 2a).

In contrast, we measured a concentration of 11 μg/g Cl in BIR-1a, which is twice the value of 5.6 ± 0.4 μg/g Cl reported in a single previous study of this sample (Sekimoto and Ebihara, 2017), although both studies agree that BIR-1a contains substantially less Cl than the range of 26-44 μg/g Cl reported for BIR-1 (Michel and Villemant, 2003). More seriously, the concentration of 407 μg/g Cl determined for a single aliquot of JB-2 is ~30% higher than the current GEOREM preferred value of 290 ± 12 μg/g Cl, which reflects a majority of previous studies (Table 4; Jochum et al., 2016). The reason for this discrepancy is unclear, however, as a single aliquot of this sample was irradiated, the repeatability of our result for this sample is untested (Table 3).

The long term reproducibility of Cl concentration measurements by the noble gas method is controlled by our ability to characterise the neutron flux in any given irradiation. The ^{40}Ar-^{39}Ar flux monitor Hb3Gr has K and Cl concentrations calibrated at the 1.5% level (Roddick, 1983) and flux gradients in RS#4 and RS#5 were monitored as 1.6-2 %. These uncertainties account for the reproducibility of JR-1 being ~2% between RS#4 and RS#5 compared to the repeatability of ~1% within a single irradiation (Table 3). The accuracy of the Cl measurements based on internal standardisation to K also depends on the previously reported K concentrations. The Cl concentrations determined by internal standardisation to Ca agree with those determined by internal standardisation to K at the ~10% level (Table 3), but the standardisation to K is preferred because it gives more repeatable results and is subject to

fewer data processing corrections (Kendrick, 2012). The Cl concentrations in the un-encapsulated aliquots of JR-1 and BHVO-2 included in RS#5, determined from the sample mass and noble gas abundance data are 3-5% lower than the concentrations based on internal standardisation to K (Table 3). This small discrepancy is of a similar magnitude to uncertainty in the mass spectrometer sensitivity and suggests an overall accuracy for Cl measurements of ~5%.

Bromine and Iodine

The Br concentrations determined for JR-1, BHVO-2, BCR-2, BIR-1a and GSP-2 are within uncertainty of the previously reported ranges and/or GEOREM preferred values (Table 4; Balcone-Boissard et al., 2009; Michel and Villemant, 2003; Sekimoto and Ebihara, 2017; Shinonaga et al., 1994). The concentration of 2004 ± 47 ng/g Br in RGM-2 is higher than the value of 1500 ± 200 ng/g reported for RGM-1 (Table 2; Michel and Villemant, 2003). Discrepancies exist for the Br concentrations of JB-2 and AGV-2, which we determined as approximately double the previously reported values (Fig 2b, Table 2; Balcone-Boissard et al., 2009; Michel and Villemant, 2003; Shinonaga et al., 1994).

The I concentrations determined for JB-2 and JR-1 are close to the values of Chai and Muramatsu (2007) and Ozaki and Ebihara (2007) (Table 4). The concentrations of I determined for JB-2, JR-1 and BHVO-2 are also within the large ranges of values reported by Balcone-Boissard et al. (2009) (Table 4). The concentrations of I determined for BCR-2 and GSP-2 are just within uncertainty of the lower precision values reported by Sekimoto and Ebihara (2017) (Table 4). However, in most cases the concentrations determined by radiochemical neutron activation analysis (Sekimoto and Ebihara, 2017) are higher than the values obtained by either the noble gas method in this study or by using ICPMS combined with

pyrohydrolysis (Table 4; Balcone-Boissard et al., 2009; Michel and Villemant, 2003). The good repeatability and reproducibility of the I measurements demonstrated here of 3-10% (Table 3) suggest that the wide ranges in concentration previously obtained for some of these samples (e.g. JR-1, JB-2 and BHVO-2; Table 4) are due to analytical issues rather than sample heterogeneity (cf. Balcone-Boissard et al., 2009).

The reproducibility's of 2-3% for Br and 3-10% for I measurements by the noble gas method are not as good as for Cl because they depend on the reproducibility of the Cl measurements and additional factors related to the reproducibility of Br/Cl (~3%) and I/Cl (~6%) in the scapolite mineral irradiation monitors (Kendrick et al., 2013). The accuracy of the Br and I measurements (estimated as ~10%) also depend on the experimentally determined neutron capture cross sections that underpin the reference values of Br/Cl and I/Cl in the scapolite mineral irradiation monitors (Kendrick et al., 2013). Nonetheless, we believe the Br and I measurements reported here are the most reliable available for the reference materials investigated.

Summary

SHRIMP has been used to measure F in silicate glass standards (NIST SRM 610 and 612, BHVO-2G, BCR-2G, BIR-1G) and whole rock sample powders prepared as Li-borate flux glasses (BHVO-2, BCR-2, BIR-1a, RGM-2, AGV-2, GSP-2, JB-2, JR-1), demonstrating the potential to measure whole rock F concentrations together with mineral concentrations in a single SHRIMP session. Matrix affects are estimated as less than ~10% for the samples analysed. The noble gas method has been applied to vacuum-encapsulated whole rock sample powders (BHVO-2, BCR-2, BIR-1a, RGM-2, AGV-2, GSP-2, JB-2, JR-1) to provide reliable and highly repeatable Cl, Br and I concentration measurements. Combined with the results of Marks et al. (2017), the dataset provides internally consistent and reliable reference values for

F, Cl, Br and I in a widely available suite of international reference materials (rock powders and glasses) that can help to cross check and/or calibrate a wide range of analytical techniques.

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Table 1. F concentrations (µg/g) of reference materials analysed as unknowns in four SHRIMP sessions

	Session 1 - 2015		Session 2 - 2016		Session 3 - 2017		Session 4 - 2018		Mean or preferred	RSD
Calibration standards	Silicate glasses		Li-B flux glasses (Fig 1a)		Li-B flux glasses		Li-B flux glasses			
	F µg/g	Repeats (n)	F µg/g	Repeats (n)	F µg/g	Repeats (n)	F µg/g	Repeats (n)	F µg/g	%
International glass standards (Silicate glasses)										
SRM 610	304 ± 2	5	270 ± 12	16	279 ± 1	2	296 ± 7	10	**287 ± 16**	**5**
SRM 612	50 ± 1	3	41.2 ± 0.2	2	--	--	47 ± 1	7	**46 ± 4**	**10**
BHVO-2G	412 ± 7	5	--	--	--	--	409 ± 13	7	**411 ± 7**	**2**
BCR-2G	469 ± 17	4	445 ± 7	6	428 ± 6	2	431 ± 44	8	**443 ± 19**	**4**
BIR-1G	38.4 ± 0.1	3	30 ± 1	9	--	--	35 ± 1	7	**34 ± 4**	**12**
International rock standards (Li-B flux glasses)										
JB-2 -a	--	--	86 ± 8	4	--	--	>60-80*	5	**99 ± 18**	**19**
-b	--	--	--	--	--	--	112 ± 4	5		
JR-1 -a	--	--	912 ± 35	6	--	--	>600*	5	**945 ± 40**	**4**
-b	--	--	--	--	--	--	984 ± 70	7		
-c	--	--	--	--	--	--	938 ± 92	6		
BHVO-2 –a	--	--	408 ± 23	4	--	--	435 ± 19	4	**420 ± 18**	**4**
-b	--	--	--	--	--	--	413 ± 64	2		
-c	--	--	--	--	--	--	425 ± 7	3		
BCR-2 –a	--	--	436 ± 55	4	--	--	476 ± 77	3	**475 ± 39**	**8**
-b	--	--	--	--	--	--	513 ± 54	3		
BIR-1a -a	--	--	49.4 ± 0.1	6	--	--	68*	1	**63 ± 12**	**20**
-b	--	--	--	--	--	--	73 ± 8	7		
RGM-2 -a	--	--	304 ± 8	4	289 ± 13	2	311 ± 6	3	**325 ± 30**	**9**
-b	--	--	319 ± 53	4	322 ± 10	4	--	--		
-c	--	--	--	--	363 ± 20	3	--	--		
-d	--	--	--	--	--	--	368 ± 20	5		
AGV-2 -a	--	--	382 ± 21	6	--	--	373 ± 20	4	**389 ± 24**	**6**
-b	--	--	--	--	--	--	413 ± 67	6		
GSP-2 -a	--	--	3030 ± 220	7	--	--	>2700*	3	**3260 ± 320**	**10**
-b	--	--	--	--	--	--	3482 ± 127	5		
Other										
Pist. Cyl. Glass		--	--	--	586 ± 46	4	--	--	**586 ± 46**	**8**
Li-B Flux glass (blank)		--	5.1 ± 0.3	4	--	--	--	--	**4.8 ± 0.2**	**5**

*The mean or preferred values and 1 standard deviation uncertainties have been calculated from the averages of each SHRIMP session, including uncertainties in the averages of each SHRIMP session. *Analyses of JB-2-a, JR-1-a and GSP-2-a in session 4 were influenced by sample mount charging effects and represent lower limits. A single analysis of BIR-1a-a was uninfluenced by this effect in session 4.*

Table 2. F concentrations (µg/g) of reference materials determined in this and previous studies

International rock standards	*Fluorine µg/g*			
	lower	upper	GEOREM preferred	**This Study**
JB-2	83 ± 5 [Sh]	99 [Im]	90 ± 7	**99 ± 18**
JR-1	945 ± 98 [W]	1034 ± 40 [BB]	n/a	**945 ± 40**
BHVO-2	370 [US]	409 ± 16 [W]	396 ± 43	**420 ± 18**
BCR-2	440 [US]	485 ± 19 [W]	470	**475 ± 39**
BIR-1a (BIR-1)*	(44 [US])*	(55 ± 4 [MV])*	(55)*	**63 ± 12**
RGM-2 (RGM-1)*	(280 ± 39 [MV])*	(340 ± 30 [US])*	n/a	**325 ± 30**
AGV-2	377 ± 8 [MV]	440 [US]	400	**389 ± 24**
GSP-2	3000 [US]	4100 ± 480 [US]	n/a	**3260 ± 320**
International glass standards				
	lower	upper	GEOREM preferred	**This Study**
SRM 610	150 ± 20 [M]	611 ± 11 [SL]	304	**287 ± 16**
SRM 612	20 ± 5 [M]	122 ± 17 [SL]	80 ± 89	**46 ± 4**
BHVO-2G	138 ± 16 [P]	300 ± 16 [M]	n/a	**411 ± 7**
BCR-2G	164 ± 36 [P]	317 ± 59 [Z]	n/a	**443 ± 19**
BIR-1G	<15 [M]	--	n/a	**34 ± 4**

*Literature values for rock standards (Balcone-Boissard et al., 2009; Imai et al., 1995; Peterman and Cloke, 2002; Michel and Villemant, 2003; Shimizu et al., 2006; Wang et al., 2014; Wang et al., 2010) and glasses (Guggino, 2012; Hoskin, 1999; Jochum et al., 2006; Marks et al., 2017; Peate et al., 2012; Zhang et al., 2016) are identified by superscript abbreviations. GEOREM preferred values downloaded from http://georem.mpch-mainz.gwdg.de/ Oct 2017. *Note that limited data are available for BIR-1a and RGM-2 and comparative values in brackets with asterix are for BIR-1 and RGM-1. Uncertainties represent one standard deviation.*

663 ***Table 3. Cl, Br and I concentrations of* rock standards determined by the noble gas method in this study**

Sample	Irradiation	Sample mass	CaO m/m % Reference	K_2O m/m % Reference	Cl_{Ca} µg/g	Cl_K µg/g	Br ng/g	I ng/g
JR-1 a	RS#4	8.9 mg	0.67	4.41	1086	1017	2240	90
JR-1 b	RS#4	8.6 mg	0.67	4.41	1039	1026	2222	92
JR-1 c	RS#4	8.9 mg	0.67	4.41	1304	1033	2183	88
JR-1 d	RS#5	14.8 mg	0.67	4.41	1112	1069	2267	89
JR-1 e	RS#5*	25.5 mg	0.67	4.41	1129	1058	2333	95
Av. ± 1 S.D.	(n = 5)					1041 ± 22	2249 ± 56	91 ± 3
JB-2	RS#4	10.0 mg	9.85	0.42	474	407	1417	71
BHVO-2 a	RS#4	7.5 mg	11.4	0.513	114	102	255	74
BHVO-2 b	RS#4	7.2 mg	11.4	0.513	114	101	257	67
BHVO-2 c	RS#5	17.3 mg	11.4	0.513	114	103	265	68
BHVO-2 d	RS#5*	24.7 mg	11.4	0.513	111	101	(225)*	(4)*
Av. ± 1 S.D.	(n= 4)*					102 ± 1	259 ± 5	70 ± 4
BCR-2 a	RS#4	10.0 mg	7.11	1.77	118	107	177	57
BCR-2 b	RS#4	10.7 mg	7.11	1.77	118	106	207	60
Av. ± 1 S.D.	(n = 2)					106.4 ± 0.3	192 ± 22	58 ± 2
BIR-1a	RS#4	10.2 mg	13.3	0.03	12	11	37	7
RGM-2 a	RS#4	7.1 mg	1.23	4.35	624	582	1944	49
RGM-2 b	RS#4	5.5 mg	1.23	4.35	708	576	2004	60
RGM-2 c	RS#5	14.1 mg	1.23	4.35	659	600	2060	49
RGM-2 d	RS#5	14.1 mg	1.23	4.35	656	598	2006	52
Av. ± 1 S.D..	(n = 4)					589 ± 12	2004 ± 47	52 ± 5
AGV-2	RS#4	8.4 mg	5.15	2.9	91	83	244	80
GSP-2 a	RS#4	7.4 mg	2.1	5.38	345	361	61	24
GSP-2 b	RS#4	11.5 mg	2.1	5.38	344	402	94	16
Av. ± 1 S.D.	(n = 2)					381 ± 29	77 ± 23	20 ± 6

664 *Note that the CaO and K_2O concentrations are literature values (USGS and GSJ recommended or GEOREM preferred values) used for internal standardisation*
665 *of Cl, denoted either Cl_K (standardised to K) or Cl_{Ca} (standardised to Ca) and that the Br and I concentrations are standardised to the preferred Cl_K values.*
666 **JR-1e and BHVO-2d were not encapsulated and the Br and I data for BHVO-2d are excluded from the averages (see text).*

667

Table 4. Cl, Br and I concentrations of rock standards determined in this and previous studies

International rock standards	*Chlorine µg/g*			
	lower	upper	GEOREM preferred	**This Study**
JB-2	262 ± 18 [BB]	321 ± 13 [Sh]	290 ± 12	**407**
JR-1	910 ± 60 [BB]	1042 ± 44 [OE]	n/a	**1041 ± 22**
BHVO-2	81 ± 11 [BB]	150 ± 21 [MV]	107 ± 94	**102 ± 1**
BCR-2	89 ± 6 [W]	112 ± 1 [SE]	96 ± 16	**106.4 ± 0.3**
BIR-1a (BIR-1)*	5.6 ± 0.4 [SE]	--	n/a	**11**
RGM-2 (RGM-1)*	536 [US]	--	n/a	**589 ± 12**
AGV-2	61 ± 3 [W]	75 ± 3 [MV]	68	**83**
GSP-2	363 ± 29 [SE]	400 ± 10 [US]	n/a	**381 ± 29**

International rock standards	*Bromine ng/g*			
	lower	upper	GEOREM preferred	**This Study**
JB-2	650 ± 100 [BB]	800 ±100 [Sh]	716	**1417**
JR-1	1680 ± 400 [BB]	2400 ± 100 [Sh]	n/a	**2249 ± 56**
BHVO-2	269-277 [MV]	290 ± 100 [BB]	300 ± 100	**259 ± 5**
BCR-2	144 ± 8 [SE]	157-175 [MV]	170	**192 ± 22**
BIR-1a	39 ± 12 [SE]	--	n/a	**37**
RGM-2 (RGM-1)*	(1500 ± 200 [MV])*	--	n/a	**2004 ± 47**
AGV-2	107 [MV]	145 [MV]	130	**244**
GSP-2	89 ± 7 [SE]	136 ± 10 [SE]	n/a	**77 ± 23**

International rock standards	*Iodine ng/g*			
	lower	upper	GEOREM preferred	**This Study**
JB-2	55 ± 25 (15-100) [BB]	63 ± 5 [CM]	61	**71**
JR-1	57 ± 31 (20-120) [BB]	104 ± 16 [OE]	n/a	**91 ± 3**
BHVO-2	20 ± 12 (12-100) [BB]	307 ± 50 [SE]	20	**70 ± 4**
BCR-2	17 ± 4 [MV]	82 ± 22 [SE]	17	**58 ± 2**
BIR-1a (BIR-1)*	--	41 ± 9 [SE]	n/a	**7**
RGM-2 (RGM-1)*	(24 ± 7 [MV])*	--	n/a	**52 ± 5**
AGV-2	7 ± 1 [MV]	197 ± 38 [SE]	7	**80**
GSP-2	363 ± 29 [SE]	400 ± 10 [US]	n/a	**381 ± 29**

*Literature values for rock standards (Balcone-Boissard et al., 2009; Chai and Muramatsu, 2007; Michel and Villemant, 2003; Ozaki and Ebihara, 2007; Sekimoto and Ebihara, 2017; Shinonaga et al., 1994; Wang et al., 2014; Wang et al., 2010) are identified by superscript abbreviations. GEOREM preferred values downloaded from http://georem.mpch-mainz.gwdg.de/ Oct 2017. *Note that limited data are available for BIR-1a and RGM-2 and comparative values in brackets with asterix are for BIR-1 and RGM-1. Uncertainties represent one standard deviation.*

Fig 1 (Kendrick et al., 2018)

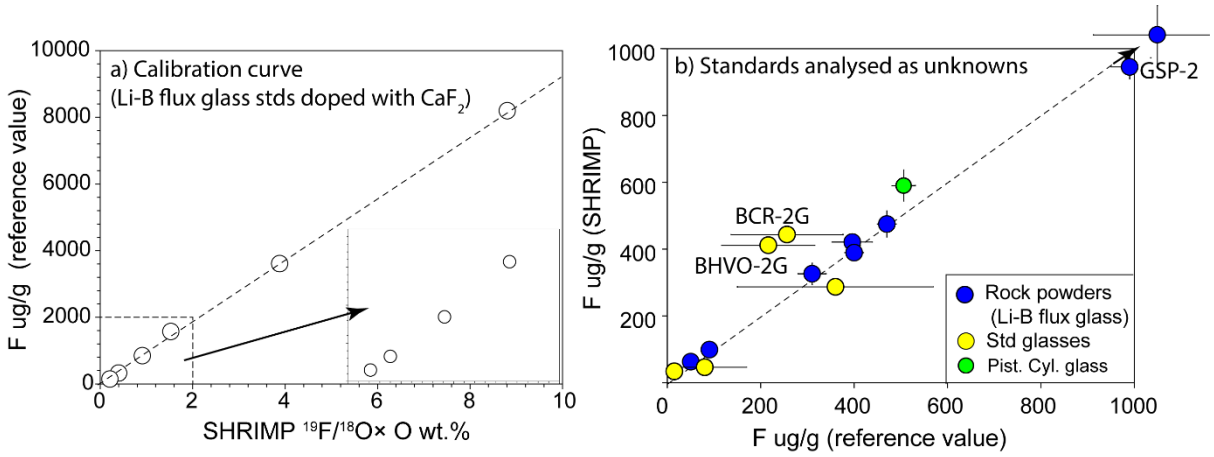

Fig 1. F data collected by SHRIMP. A) The calibration curve generated with CaF_2 doped synthetic MORB powders prepared as Li-borate flux glasses. B) Standards analysed as unknowns including powders of international rock standards prepared as Li-borate flux glasses, silicate glass standards (NIST SRM 610, 612, BCR-2G, BHVO-2G and BIR-1G) and a MORB-like glass prepared in the piston cylinder (Pist. Cyl. Glass). The uncertainties represent 1 standard deviation of sample repeats and either the GEOREM preferred values with 1 standard deviation uncertainty or the range of values reported in previous studies (Table 2). Note GSP-2 plots outside the field of view.

Fig 2 (Kendrick et al., 2018)

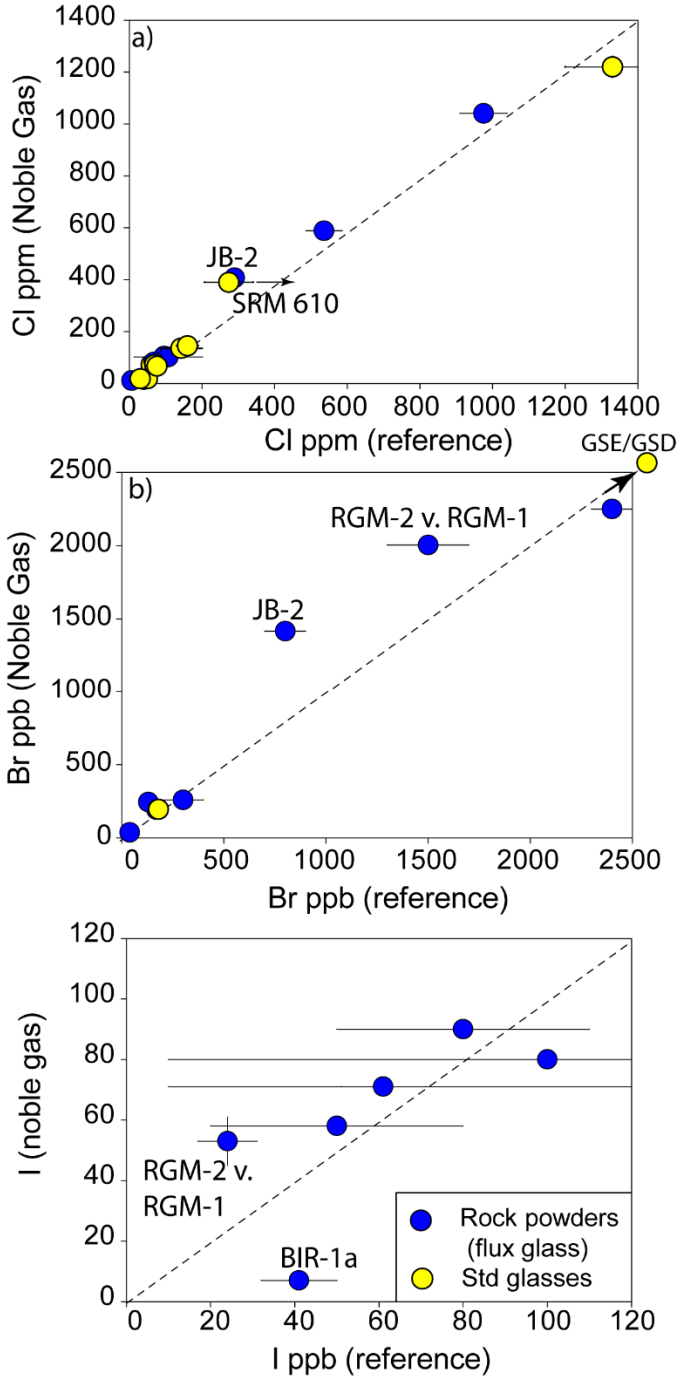

Fig 2. Comparison of Cl, Br and I data in reference materials analysed in this and previous studies (Marks et al., 2017; Table 4). The uncertainties represent 1 standard deviation of sample repeats and either the GEOREM preferred values with 1 standard deviation uncertainty or the range of values reported in previous studies (see Table 4). The GEOREM preferred value shown for Cl in SRM 610 is lower than previously compiled values shown by the arrow (GEOREM database). Data for standard glasses are from Marks et al. (2017).