In-situ measurements of magmatic volatile elements, F, S, and Cl, by electron microprobe, secondary ion mass spectrometry, and heavy ion elastic recoil detection analysis

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ABSTRACT

Electron probe and ion probe are the two most used instruments for in situ analysis of halogens in geological materials. The comparison of these two methods on widely distributed glass standards (example: MPI-DING glasses, Jochum et al., G-cubed, 2006) provides a basis for establishing laboratory method, independent geochemical data sets for these elements. We report analyses of F, S, and Cl concentrations in three geological glass samples (EPMA) and 10 referenced standards (EPMA and SIMS). Furthermore, F and Cl absolute abundances have been determined independently for three of the standards (KL2-G, ATHO-G, and KE12), via heavy ion elastic recoil detection analysis (HIERDA), to certify the accuracy of the cross-calibration EPMA-SIMS. The detection limits for EPMA are a 150 μ g·g⁻¹ for F, 20 μ g·g⁻¹ for S and Cl, and for SIMS < 48 μ g·g⁻¹ for F, <3 μ g·g⁻¹ for S, and <19 μ g·g⁻¹ for Cl. On SiO₂-rich glass-standards, F and Cl measurements by HIERDA highlight a weak matrix effect during SIMS analysis of F and Cl. With the HIERDA independently measured value, we therefore propose an alternative calibration function to empirically correct this matrix effect on the SIMS measurements of F, S, and Cl. **Keywords:** F, Cl, SIMS, EPMA, ERDA, melt inclusion; Halogens in Planetary Systems

INTRODUCTION

The behavior of trace volatile elements (magmatic volatile components other than H₂O and CO₂) in magmas has inspired many scientific contributions in the past decades (e.g., Baker et al. 2005; Wallace 2005; Behrens and Gaillard 2006; Fischer 2008; Aiuppa et al. 2009 and reference therein). There are several extensive reviews of the interest of halogens in earth sciences (Harlov and Aranovich 2018; Hanley and Koga 2018). Quantification of volatile elements recycling implies the knowledge of the magma volatile element composition prior to degassing. While lava erupting from arc volcanoes are at least partially degassed, olivine hosted-melt inclusions found in these lavas, are less affected by degassing because they are effectively shielded from interaction with their surrounding in the magma chamber and during magma ascent. This is especially true for halogens such as Cl and F, at pressure and temperature conditions of melt inclusion formation, they are less prone (1) to degassing (if at all) than H₂O (e.g., Carroll and Webster 1994; Métrich and Wallace 2008), (2) to diffusing through the host-olivine (e.g., Bucholz et al. 2013; Le Voyer et al. 2014; Lloyd et al. 2014). Halogen measurements in arc melt inclusions have proven to retain the

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information of magma genesis (Bucholz et al. 2013; Rose-Koga et al. 2012, 2014) along with other lithophile trace elements (such as REE; e.g., Cabral et al. 2014; Jackson et al. 2015; Rose-Koga et al. 2017; Narvaez et al. 2018). The subduction input/output mass balance calculations show that nearly 100% of Cl coming in subduction is incorporated in arc magmatism, compared to only about 50% of F (e.g., Straub and Layne 2003; Wallace 2005). Therefore Cl and F are ideal tracers to identify the fractionation process between the slab and the flux originating from it, especially since they are scarcely present in the mantle (F reservoirs, see, for example, Koga and Rose-Koga 2016, 2018). Moreover, recent experimental results have determined F and Cl partition coefficients between melt and crystals (Dalou et al. 2014) and put forward that the large variation of F/Cl in arc melt inclusions resulted from the composition, the amount of slab agent and the degree of melting (e.g., Narvaez et al. 2018).

Here we compare in situ analytical technics for F and Cl measurements because the smaller and smaller geological samples, today, that we are studying are requiring inter-calibration and comparison of analytical technics to make educated decisions on which one to use to achieve the goals we set. With recent advances of micro-analytical techniques and melt inclusion studies, there is a growing body of concentration measurements of relatively volatile, light-atomic-mass elements (H, B, C, F, S, Cl) in MORB glasses and primitive melts of subduction zone magmas (e.g., with SIMS: Sisson and Layne 1993; Métrich et

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al. 1999; Hauri et al. 2002; Wade et al. 2006; Le Voyer et al. 2008, 2010; Bouvier et al. 2008, 2010; Rose-Koga et al. 2012, 2014; see also references in Wallace 2005 and with NanoSIMS e.g., Bartoli et al. 2014; Créon et al. 2017, 2018; Carvalho et al. 2019). Other volatile elements, moderately heavier, such as Br, have also been successfully measured by secondary ion mass spectrometry (Cadoux et al. 2017).

Among the difficulties contributing to the limited comparison of the preexisting data, was, surprisingly, the lack of published comparison of S, Cl, and F measurements of standards between the two most used in situ analytical procedures: electron microprobe (EPMA) and the ion probe (SIMS). While recent precise rocks and glass analysis exist (e.g., Shimizu et al. 2015, 2017), in situ methods to measure halogens are rarely compared. Recently, an F, S, and Cl comparison between literature data obtained by EPMA and by SIMS (Le Voyer et al. 2019) concluded that inter-laboratory comparisons agreed within 10% for F and to a variable degree for S and Cl, and propose a quality controlled published-data summary table (Supplemental¹ Table S2 available through the EarthChem Library, http://dx.doi.org/10.1594/ IEDA/111195). Electron microprobes perform microanalysis of volatile elements, but the high detection limits of this technique (tens to hundreds of parts per million) place limitations on many volatile studies (cf. Devine et al. 1995 and references therein).

In this paper, we measure F, S, and Cl by SIMS on a set of six glasses from the WHOI standard-set (ALV519-4-1, ALV1654-3, ALV1649-3, GL03-D51-3, GL07-D52-5, EN113-46D-2) to create three working curves. We use our three SIMS working curves to compare our SIMS measured values of eight MPI DING glasses (ML3B-G, KL2-G, StHs6/80-G, GOR128-G, GOR132-G, ATHO-G, T1-G, KE12) and of two basaltic standards (VG2 and VG-A99) with our EPMA values. We also report independent, absolute F and Cl values from elastic recoil detection analysis (HIERDA) of three MPI DING glasses (KE12, ATHO-G, and KL2G) that independently anchors our calibration curves.

STANDARDS AND GLASS SAMPLES

All glasses and standards used have already been well documented elsewhere, and we summarize here the essential points. The set of six basalt samples used in this study for the SIMS analysis comes from several sources (Table 1). The ALV standards are fresh basaltic glasses sampled during Alvin dives over the Famous area (ALV519-4-1: Shimizu 1998; Michael and Cornell 1998) and over the Galapagos Spreading Center 85 °W (ALV1654-3 and ALV1649-3; Embley et al. 1988; Perfit et al. 1998). GL standards are fresh basalt glasses from the Salas y Gomez seamount area (GL03-D51-3 and GL07-D52-5; Simons et al. 2002). EN113-46D-2 is a fresh basaltic glass from the Endeavor spreading center (Simons et al. 2002).

For the other glass samples and standards, we used six basalts: KL2-G, from Kilauea volcano, Hawaii; ML3B-G from Mauna Loa Volcano, Hawaii; VG2, aka USNM 111240/52, from the Juan de Fuca Ridge (Jarosewich 2002); VG-A99, aka A99, USNM 113498/1, from Kilauea volcano, Hawaii (Jarosewich et al. 1979); Alvin 2746-15, from 9–10 °N East Pacific Rise (Bowles et al. 2006); Alvin 2390-5, from the Siqueiros Transform, (Sims et al. 2002), one andesite, (StHs6/80-G, Mt. St. Helens, U.S.A., Jochum

TABLE 1. F, S, Cl, and SiO₂ measurements in six basalt glasses with the corresponding analytical methods and references, which are the glass-standards used for the calibration on the WHOI SIMS

	5							
	F (ppm)	±	S (ppm)	±	Cl (ppm)	±	SiO2	Method;
							wt%	Reference
ALV519-4-1	90	30	950	95	45	23	48.9	EPMA; [1]
ALV1654-3	997	150	1562	78	2914	146	56.7	EPMA; [1], [2]
ALV1649-3	445	67	1640	82	1433	72	51.5	EPMA; [1], [2]
GL03-D51-3	299	45	1126	57	182	18	49.5	EPMA; [1], [3]
GL07-D52-5	431	65	1183	59	322	32	48.6	EPMA; [1]
EN113-46D-2	2 124	37	877	88	45	23	49.5	EPMA; [1], [3]

Notes: [1] Helo et al. 2011; [2] Michael & Cornell 1998; [3] Simons et al. 2002. Relative analytical error for F concentration >200 ppm is 15% and F<200 ppm is 30%. Relative analytical error for S concentration >1000 ppm is 5%, between 1 to 1000 ppm is 10% and <100 ppm is 50%. Relative analytical error for Cl concentration >400 ppm is 5%, between 50 and 400 ppm is 10%, and Cl <50 ppm is 50%. Errors of these standards are assessed on the long-term reproducibility. SiO₂ was measured by EPMA.

et al. 2000), two komatiites, (GOR128-G and GOR132-G both from Gorgona Island, Jochum et al. 2000), a rhyolite, (ATHO-G, from Iceland, Jochum et al. 2000), a quartz-diorite, (T1-G, from the Italian Alps, Jochum et al. 2000), two obsidians, (Sletta, from Iceland, courtesy from O. Sigmarsson; and KE12 from Eburru, Kenya; Malik and Bungard personnal communication; and a personal communication from 1974 that is cited in Devine et al. 1984).

ANALYTICAL PROCEDURES

EPMA analysis

Electron microprobe analyses were performed with a Cameca SX 100 equipped with four wavelength-dispersive spectrometers (WDS) at the Laboratoire Magmas et Volcans (Clermont-Ferrand). Major elements and volatiles were analyzed in separate analytical sessions with the following detailed conditions. Major elements in glasses were analyzed at an accelerating voltage of 15 kV, an 8 nA beam current, and a 20 µm defocused beam. These analytical conditions are well suited for glasses analyses; no geochemical instability (sodium loss principally) is detected even for silica-rich samples (e.g., Oladottir et al. 2011).

Chlorine, sulfur, and fluorine analyses were performed at 80 nA and with a 5 to 20 μ m defocused beam together with the trace element acquisition program proposed in the Cameca Peak Sight software. This quantification model takes into account the matrix composition of the glass to calculate the traces element concentration. ZAF data reduction was carried out by means of the X-PHI model. The analytical standards were: natural scapolite for the ClK α line, fluorite for FK α , and VG-2 glass for SK α . Sulfur concentration in VG-2 glass is 1340 µg·g⁻¹; this value corresponds to the average of a compilation of published data (Dixon et al. 1991; Thordarsson et al. 1996; Thornber et al. 2002).

Sulfur and chlorine. Because sulfur speciation (S^{6+} or S^{2-}) induces changes in the $SK\alpha$ spectral position (Carroll and Rutherford 1988), prior to sulfur concentration measurement and for every sample, the $SK\alpha$ peak maximum was first located by using the automated peak-scan routine of the Cameca SX 100 software. Then, if the measured peak position differs from the one of the standard, the new value is recorded in the analysis setup. The selection of the diffraction crystals is decided by the achievements of the highest peak counts to reach very low detection limits and by looking at the region of the spectrum with no interfering peaks. Thus, chlorine and sulfur were analyzed successively by using a large pentaerythritol (LPET) crystal.

Fluorine. The case of fluorine is more complex. This element can be measured either with a W/Si multilayer crystal (PC1) or with a thallium acid phthalate crystal (TAP). Multilayer crystal allows high precision and accuracy measurements, together with low detection limits. Unfortunately, for iron-bearing minerals or glasses, the FK α peak is strongly overlapped by the shoulder of a strong FeL α line. Different studies (Todd 1996; Witter and Kuehner 2004; Zhang et al. 2016) have proposed an electron microprobe method for analyzing F in Fe-bearing minerals and glasses using multilayer crystals that overcomes the spectral interference. This method is based on the linear relationship existing between the iron concentration of fluorine-free minerals (olivine and pyroxenes essentially) and the number of counts at the FK α peak position in the same fluorine-free minerals. Thus, the FeL α contribution (i.e., the background) can be easily deduced and quantified from the total iron concentration of the sample and subtracted from the bulk FK α peak counts. However, the calibration curve of this model is only found for the analysis of Fe²⁺-bearing minerals. In transition metals of the first row, the L-spectra exhibit peak position shifts as a function of the oxidation state (Fialin et al. 2001, 2004). The omission of the self-absorption induced shift of the $L\alpha$ peak between Fe²⁺ and Fe³⁺ could lead to the overestimation of the background counts at FK α peak position and thus to an underestimation of the fluorine content. The correction method established by Witter and Kuehner (2004) should be only applied for pure Fe²⁺-bearing minerals and glasses. To overcome this problem, we analyzed fluorine using TAP diffraction crystals although the detector is significantly less efficient than PC1. To improve its counting statistics (precision and detection limit), fluorine was measured simultaneously on three spectrometers according to the Cameca multi-spectrometers counting routine. On top of the choice of the detector, we tested CaF₂ and Durango apatite standards for F calibration and concluded that CaF₂ provides generally consistent results, most likely due to known F X-ray excitation issue of apatite (Stormer et al. 1993).

The challenge with traces of element analysis in glass is to find a compromise between low detection limit, i.e., the use of high beam current, long counting time, and limited beam damages. Volatile loss during the analysis is minimized through the use of a protocol derived from the CSIRO-trace routine (Robinson and Graham 1992). The total counting time (peak and background) for a single analysis is 40 s and is divided as follows: 10 s on peak and background) for chlorine and sulfur but 60 s on peak and background for chlorine and sulfur but 60 s on peak and background for fluorine (20 s per spectrometer). The low detection limit is achieved by increasing the number of analyses on the same point, thus improving the signal-to-noise ratio. After each analysis, the beam is shielded for 20 s allowing the sample to cool down. Total volatiles concentration is calculated from the sum of the counts from the successive iterations. With 15 kV accelerating voltage and 80 nA beam current, for a total Cl and S peak counting times of 100 and 600 s for F. Typical detection limits for F, Cl, and S were 150, 50, and 50 µg·g⁻¹, respectively.

SIMS analysis

Sample preparation for SIMS. The standards are mounted in high-purity indium metal (e.g., Hauri et al. 2002; Le Voyer et al. 2008) in a 1 inch diameter aluminum ring, washed in an ultrasonic bath with pure ethanol then with distilled water for 10 min each time. Indium is used because epoxy contains significant amounts of volatile molecules that can degass during the analysis, deteriorate the quality of vacuum, and increase the background signal. The mount is dried carefully in an oven overnight. The mount is finally gold coated before analysis

and kept overnight in high vacuum (low 10-8 torrs) until being introduced in the sample chamber.

Method. The measurements for the working curve calibrations were done on a set of 6 glass standards (Table 1), on the ion probe Cameca 1280 of Woods Hole Oceanographic Institution (Massachusetts, U.S.A.). We used a Kohler illumination with a primary beam current of 1.5 nA Cs⁺ primary positive beam, and negatively charged secondary ions were extracted through a nominal accelerating potential of 10 kV. Due to implantation of Cs⁺ ions and extraction of both negatively charged secondary ions and electrons, positive charging of the sample surface must be compensated with the use of an electron flood gun that delivers electrons to the sample surface. The isobaric interference was filtered by an energy slit opening at 50 eV and the contrast aperture at the cross over was large (400 µm). The entrance and exit slits are closed to achieve a mass resolution of $M/\Delta M = 5800$. With this resolution, the interfering signals were effectively separated for F, S, and Cl (Fig. 1).

We pre-sputter the sample's surface during 180 s while applying a raster of $30 \times 30 \ \mu\text{m}$. The field aperture (of 8000) corresponds to an area of $15 \times 15 \ \mu\text{m}$, is inserted into the image plane. This means that only the ions originating from the central 15 μ m square of the flat-bottomed sputtered-crater are admitted into the mass spectrometer. The elimination of stray ions sputtered from the crater walls and desorbed from the sample surface results in very low volatile backgrounds (routinely about 0.05–0.1 counts per second for the counting system at half mass positions with the primary beam and the electron gun on). We counted 8 s on ¹⁹F, 5 s on ³⁰Si, 5 s on ³²S, and 8 s on ³⁵Cl. One analysis was composed of 2 blocks of 10 cycles and took less than 15 min per spot. Intensities of ¹⁹F, ³²S, and ³⁵Cl were collected cyclically by an electron multiplier, processed through pulse-counting electronics and normalized to ³⁰Si for concentration calculations.

Calibration. Earlier studies that have involved Cs* beam were performed on small format SIMS (Cameca 6f, Hauri et al. 2002). However, hydride interferences, such as SH-, are difficult to effectively eliminate using the energy filtering technique (Shimizu et al. 1978) available on small format Cameca instruments (e.g., IMS 3f/4f/5f/6f/7f). The high mass resolution of the SIMS 1280 model is required to eliminate the ³⁴S¹H interference on ³⁵Cl (MRP > 5120) without giving up transmission significantly (Fig. 1c). The SIMS calibration curves for F, S, and Cl are shown in Figure 2. They are regressions of ion probe signals (x-axis) compared to known EPMA concentrations (y-axis). The former is the intensity ratio of two elements times the SiO₂ concentrations of each standard,



FIGURE 1. Secondary ion spectra at nominal masses, 19 (a), 32 (b), and 35 (c) for a basalt glass (ALV519-4-1) to illustrate the resolution of isobaric interferences at $M/\Delta M = 5800$ (10% definition). This basalt glass contains 90 µg·g⁻¹ F, 950 µg·g⁻¹ S, and 45 µg·g⁻¹ Cl (Helo et al. 2011; Table 1).

the numerator of the ratio being the element of interest and the denominator is a matrix element common to all samples (e.g., ¹⁹F/³⁰Si). Typically, here ¹⁹F, ³²S, and ³⁷Cl are normalized against ³⁰Si. This provides a robust analysis little influenced by primary beam fluctuations or by ionization efficiency changes owing to matrix effects (Shimizu and Hart 1982). In fact, the calibrations for F, S, and Cl are free of significant matrix effects. The calibration curve is determined at the beginning and at the end of each session to assure no significant drift has taken place.

Detection limit. With the calibration curves of the standards, we attributed the Y-intercept of the linear regression to the detection limit (e.g., Ihinger et al. 1994). We stress that this method is not accurate enough and depends on the uncertainties of the regressed data, and the leverage of the data for the higher concentrations being potentially unreasonable. Ideally, only the measurements of standards with F. S. and Cl concentrations lower than the expected background can give the detection limit (see Koga et al. 2003, for this procedure during low hydrogen concentration measurements by SIMS). It was not a simple task to verify sub-parts-per-million-level abundance, and we are not aware of any micro-analytical method that can independently verify sub-parts-per-million-level abundance of these elements. It should be noted that for the abundance of H2O, FTIR analyses were used for the blank verification. Therefore, we adapted the calibration without explicitly identifying zero point count rate as this method is less prone to inter-laboratory biases (Table 1). Some studies have used adapted "blank" material such as San Carlos olivine, synthetic forsterite, and high-purity quartz glass (Hauri et al. 2002; Le Voyer et al. 2017; Shimizu et al. 2017). With what was available to us, we calculated detection limits 48 μ g·g⁻¹ for F, 3 μ g·g⁻¹ for S, and 19 µg·g⁻¹ for Cl (Fig. 2). These values are effectively the zero intercept within the regression uncertainties. In addition, the linear regression of the calibration curve is equivalent to forcing the regression through zero. The slopes between forcing the linear regression through zero (red curve Fig. 2) and classic linear regression with a non-zero intercept (blue curve Fig. 2) is identical within error.

A detection limit of <1 μ g·g⁻¹ for F, S, and Cl was previously reported with a 6f ion probe (Hauri et al. 2002; <2 μ g·g⁻¹ for F; Guggino and Hervig 2010). With a 1280 ion probe detection limits down to 0.2 μ g·g⁻¹ for S and Cl, and 0.1 μ g·g⁻¹ for F can be achieved with "blank" standards (Le Voyer et al. 2019). Our analytical standard error (σ over the 20 cycles) was typically 0.6% for F, S, and Cl (1% Le Voyer et al. 2019) and the reproducibility on the standards (2RSD) was 6.3, 3.5 and 5.2%, respectively (n = 14, ALV519-4-1; comparable to 5.8, 7.6, and 10.8%, respectively, on in-run standard glass P1326-2, Helo et al. 2011; 7, 4, and 7%, respectively, on glass VG2, Le Voyer et al. 2019). This is to compare with the long term external reproducibility (2RSD) of standard ALV519-4-1 by EPMA was 55.3, 5.2, and 58.3% for F, S, and Cl, respectively.

Elastic recoil detection analysis (ERDA)

ERDA is an absolute measurement independent from the two previous methods (EPMA and SIMS). Absolute because it consists of a collision between the nuclei of 2 atoms and the radii of the two nuclei (i.e., collision cross-section, for example, ¹⁹F and 127I) are known with great precision, and therefore the ERDA method determines accurate statistical distributions of atoms in a substrate. Therefore, with a known oxygen abundance, fluorine concentration is calculated from a F/O ratio. ERDA has previously been used to measure hydrogen in geological materials (e.g., Mosbah et al. 1991; Bureau et al. 2009) or to intercalibrate with infrared spectroscopy measurements (e.g. Aubaud et al. 2009: Withers et al. 2012) The ERDA was conducted at ETH Zurich, in the Ion Beam Physics laboratory of the Paul Scherrer Institut. We used a primary ion beam of Heavy Ion 127I at 12 MeV; therefore the method is specifically called HIERDA (Döbeli et al. 2005). This iodine beam was produced by EN-tandem accelerator via cesium (Cs) sputtering of AgI. For lower projectile energies, Time of Flight-ERDA (ToF-ERDA) is a widely used technique. The analytical protocol is only briefly explained in the following; full details can be found in Kottler et al. 2006 (and reference therein) The beam hits the polished plane of the sample with a low angle and the scattered element of choice (F and Cl, here) are detected by the ToF-ERDA detector at the fixed angle of 36°. The recoil masses are identified by means of a coincident measurement of the particle velocity and total energy. The recoil energy for 19F is 3.5 MeV and that of 35Cl is 5.3 MeV. Here a gas ionization chamber (GIC) instead of silicon detectors has been used for energy measurements because silicon detectors suffer from considerable radiation damages. Such detector assured the resolution of energy spectra less than 1 MeV allowing the precise separation of different atoms. The mass resolving power is $M/\Delta M = 40$ for the mass range corresponding to F and Cl. The shape of the beam on the sample is a rectangle of 1 × 4 mm but only a small part of it was actually targeting the sample; the rest was hitting the surrounding indium. A classical ERDA graph displays a time of flight curve for each ion vs. energy (Kottler et al. 2006). These curves are processed to extract a spectrum for each element (Figs. 3a, 3b, and 3c). The detection limits were derived from off-peak baseline noise level.

RESULTS

There is a good general agreement on mafic standards for the measurements of F, S, and Cl between EPMA and SIMS above a certain treshold of concentrations, >150 $\mu g \cdot g^{-1}$ for F, and >20 $\mu g \cdot g^{-1}$ for S, and >20 $\mu g \cdot g^{-1}$ for Cl (Fig. 4). For F < 150 $\mu g \cdot g^{-1}$ SIMS can measure differences in F concentrations with a precision better than 10% relative when EPMA has a precision equal to the measured value (Fig. 4a). The performance of both EPMA and SIMS are in excellent agreement for Cl measurements down to 20 $\mu g \cdot g^{-1}$ (Fig. 4c). But for S measurements, SIMS can measure S concentrations below 10 $\mu g \cdot g^{-1}$ when EPMA will not measure the resolvable difference in standards with S<10 $\mu g \cdot g^{-1}$ (Fig. 4b).

The glass standards measured here have reported values that



FIGURE 2. SIMS calibration curves for abundances of (a) fluorine, (b) chlorine, and (c) sulfur in basalt glasses. The lines correspond to different fit. The red line is a weighted linear regression line forced through zero, and the blue line is a classic weighted linear regression line, the y-intercept giving the detection limit of the analyzed element. The gray field bounded by blue dashed lines indicates the 95% confidence interval. The uncertainties of fitted coefficients represent one standard deviation. Reduced $\chi^2 (\chi^2_v)$ values of fit are also reported. Because any of those fits are satisfactory within the error bar, we consider the calibrations are linear over the range in S, Cl, F concentrations. (Color online.)



FIGURE 3. Heavy Ion Elastic recoil detection analysis (HIERDA) spectra for oxygen ¹⁶O (**a**), fluorine ¹⁹F (**b**), and chloride ³⁵Cl (**c**). On the y-axis are reported the counts and on x-axis, the mass. This is the example of the measurements done on the standard MPI-DING glass KE12 (Jochum et al. 2006). (Color online.)

can vary up to a factor of 10 for certain elements (e.g., Cl in StHs6/80; Table 2). Nonetheless, overall we note that technical improvement of in situ instruments makes it possible to reach interlaboratory agreements. Our EPMA and SIMS measurements mostly agree within error with the reported values published since 2006 (e.g., Jochum et al. 2006), simply improving the precision in some cases. When they do not agree, we can invoke millimeter-scale heterogeneity of the standards. They have been reported for trace elements in the ATHO-G rhyolite (MPI-DING; Borisova et al. 2010) and caution must be applied when choosing the standards to perform micro-analysis. For example, it is clear



FIGURE 4. Concentrations of F (a), S (b), and Cl (c) measured by SIMS vs. that measured by EPMA (circles) and HIERDA (square, when applies) in a log-log plot. Standards are categorized according to their SiO₂ contents into mafic (blue), intermediate (gray), and acidic. The solid line is a one-to-one slope indicating perfect coherence of the fit. (Color online.)

from Table 2 that our ATHO-G piece is very different from the piece measured by SIMS in Jochum et al. (2006) and closer to the composition of that of Oskarsson et al. (1982). In any case, this disparity has nothing to do with the quality of the analysis. In this respect, ATHO-G and StHs6/80-G appear to be heterogenous for F, S, and Cl depending on the individual pieces that may be available in different labs. Also, the 2σ error that we report for our EPMA are, 9 times out of 10, better than previously reported,

demonstrating that the proposed settings for halogen measurements by EPMA are particularly well suited.

The ERDA results for F and Cl in ATHO-G, KE12, and KL2-G anchors independently the calibration curves for F and Cl. We note that the ERDA values for F and Cl of the two SiO₂-rich standards, are closer to the EPMA values than the SIMS values (Figs. 4a and 4c), and the ERDA measurement on the basalt standard KL2-G was difficult to assess because of the high detection limit of the ERDA.

DISCUSSION

Precision and accuracy

The lowest concentrations we measured were samples GOR-128 and GOR-132 for F and S and sample StHs for Cl (Table 2). While EPMA measurements tend to level out around 10 µg·g⁻¹ concentration for S (Fig. 4b), SIMS measurements are precise to $\mu g g^{-1}$ level for S and Cl (Figs. 4b and 4c). For F, S, and Cl, SIMS measurements always display smaller error bars (Figs. 4a, 4b, and 4c). Samples with a concentration in S, Cl >100 $\mu g \cdot g^{-1}$ are analyzed with similar precision with both methods. Measurements of F remains up to 5 times more precise with SIMS than EPMA on the basis of analytical precision based on counting statistics and for F concentration above 100 ug g^{-1} . Because many standard values are still tied to EPMA measured samples, it appears that the uncertainty of the slope and intercept (Fig. 2) contributes to the final uncertainty similar to EPMA values (Table 2). Therefore, it is strongly recommended to use SIMS when the interest of measurement is to detect variations of concentration among similar samples with high precision, while EPMA can certainly provide a rapid, good assessment of trace volatile abundances above a certain threshold.

Matrix effect

It is particularly notable that some measure values by SIMS (reported for ATHO-G and KE12; Table 2) significantly differ from those of EPMA and ERDA. Figure 4 also shows that higher SiO_2 glasses (e.g., ATHO and KE12) plot on the right side of the 1:1 line, indicating SIMS measurements are higher than EPMA and ERDA. While such offset is not present for mafic glasses, which have similar SiO_2 content as the calibration standards. This offset is present for measurements of F, S, and Cl. This systematic disparity related to the composition of material analyzed is called the matrix effect, in which the secondary ion emission is influenced by change either structural or compositional variation of the matrix.

The relative sensitivity factor (RSF) describes a bias of an elemental ratio introduced by SIMS:RSF = $(C_i/C_{ref})\times(I_{ref}/I_i)$, where C_i and C_{ref} are the known atomic concentration of mass i and mass ref, respectively, and *I* denotes the measured signal intensity. Essentially, the slope of the calibration function is a representative RSF of several calibration standards. It should be noted that RSF cannot distinguish bias of the signal of interest (e.g., I_F , I_S , and I_{Cl}) from the signal of reference (I_{Si}). Figure 5 shows the value of RSF calculated for the samples of Figure 4 as a function of SiO₂, excluding the EPMA data below the detection limit. It appears that RSF is slightly negatively correlated against SiO₂, consistent with a presence of matrix effect for the high SiO₂ samples. However, considering the scatter of RSF values, the ap-

parent negative correlation has only slight statistical significance. Unfortunately, the data acquired here is insufficient to discern the exact role of the "matrix effect." Because of such tendency, Van den Bleeken and Koga (2015) concluded from a similar analysis that as a first order, one should be able to determine the abundance of these elements without significant correction. A similar conclusion is also reached via measurements of rhyolitic glass with basaltic calibration standards (Shimizu et al. 2017). Alternatively, one should also note that H⁺ emission is shown to correlate with a molar mass of substrate suggesting that the matrix effect can be effectively corrected with glass compositions (King and Holloway 2002). According to the calibration, there is 40% relative change of H⁺ emission coefficient between a basalt and a rhyolite. With the data available today, we did not detect such a significant matrix effect for F, S, and Cl comparable to that for H⁺. Thus, the variation due to matrix-dependent emissions is expected to be small, and further investigations are certainly needed to identify the exact nature the matrix effect.

Choices of calibration method

Reference mass.Concentration analysis by SIMS requires a ratio of the element of interest (F, S, Cl here) over an element that constitutes the matrix. For silicate glasses, Si is commonly chosen (Shimizu and Hart 1982). Specifically, ³⁰Si is commonly selected for its low abundance permitting the use of an electron multiplier detector. However, depending on the SIMS facility, different reference mass is used. For example, ²⁸Si detected with Faraday cup can be used as the reference mass, as well as ¹⁸O⁻ or ¹⁶O⁻ providing stable, and high count rate. In general, emission of negative oxygen atom is approximately 10 times better than Si but this does not seem to result in a significantly more stable signal. While it will require further study to assess the advantages and disadvantages regarding the choices of the reference mass, a comparison results from different SIMS labs concluded that it would not influence the measurement significantly (in their electronic supplement, Van den Bleeken and Koga 2015).

Calibration curves. A linear function that converts a SIMS intensity ratio to a concentration can be expressed in the following two ways:

$$C_{\text{F,S,Cl}} = \alpha \times (I_{\text{F,S,Cl}}/I_{\text{Si}}) \times [\text{SiO}_2] + \beta$$
(1)

$$C_{\rm F,S,Cl} = \alpha \times (I_{\rm F,S,Cl}/I_{\rm Si}) + \beta \tag{2}$$

where C_i indicates the concentration of an element i, brackets indicates concentration, and I_x indicates SIMS intensity (i.e., count rate) of mass x. Slope and intercept of a regression correspond to α , and β , which are constants determined by fitting the linear function using known concentration standards. Among SIMS measurements reported, these two equations were commonly used. Equation 2 is sufficient for the measurement with a good match of sample and standard matrices (i.e., similar SiO₂ content). In the current study, we adapted Equation 1, which corrects for variable SiO₂ content (e.g., 50% basalt and 70% rhyolite), and produced acceptable results. However, it should be noted that Equation 1 does not correct for the matrix effect discussed above.

It should be noted that once a calibration is established either with Equation 1 or 2, the choice of the equation should not change the results, with an ideal set of standards, analyzing samples with

	F (ppm)	±	S (ppm)	±	Cl (ppm)	±	SiO ₂ wt%	Method; Reference
ML3B-G*	70	18	1.2	0.12	7.5	1.4	51.4	SIMS [1]
			100	100	110	33		EPMA [1]
			30	30	60	18		EPMA [1]
	64;57;69 71	30;20;30 29	5.2	0.2	36	2		EPMA; SIMS; PIGE [2] SIMS [WHOI this study]
	63	20	7.0	1.0	55	6		SIMS [Eq. 6]
	48	136	17	26	32	42	50.7	EPMA [LMV this study]
StHs6/80-G*	320	32	2.7	0.3	184	18	63.7	SIMS [1]
			40	40	210	42		EPMA [1]
					230	69		EPMA [1]
	139;122;155	2;2;2						EPMA; SIMS; PIGE [2]
	n.d.		4.3	0.2	27	1		SIMS; [WHOI this study]
			6.0	0.6	48	2.5		SIMS [Eq. 6]
	28	70	19	2	21	22		EPMA; [LMV this study]
T1-G*	321	32	2.6	0.3	113	14	58.6	SIMS [1]
			30	30	100	50		EPMA [1]
			0.00		130	65		
			0.92		119			
	107-04-110	6.6.9	1.94					
	37 /	79	6.0	0.2	175	15		SIMS [WHOI this study]
	2/4	56	7.6	1.4	157	52		
	154	47	20	8	158	7	57 5	FPMA [I MV this study]
GOR128-G*	25	3	43	04	117	1	46.1	SIMS [1]
0011120 0	25	5	30	30	50	35	10.1	FPMA [1]
			50	50	40	50		EPMA [1]
	n.d.		8.3	0.4	38	2		SIMS [WHOI this study]
			10	3	56	6		SIMS [Eq. 6]
	4	16	15	20	38	37	45.5	EPMA [LMV this study]
GOR132-G*	22	2	1.8	0.2	6.2	1	45.5	SIMS [1]
			50	50	30	30		EPMA [1]
					50	75		EPMA [1]
	n.d.		5.7	0.2	30	1		SIMS [WHOI this study]
			7.7	1.3	50	3		SIMS [Eq. 6]
	4	16	11	26	24	34	44.3	EPMA [LMV this study]
VG2*, aka	334	14					50.6	SIMS [4]
USNM 111240/52			1348	124	291	104		EPMA [5]
			1365	58	316	38		EPMA [5]
			1340	100				
			1303	155	270	90		
			1200	72	2/0	112		
			1500	12	505	112		EPMA [10]
	243	71	1440	110	325	30		SIMS [WHOI this study]
	224	49	1350	740	263	99		SIMS [Eq. 6]
	210	130	1343	46	306	26		EPMA [LMV this study]
VG-A99*, aka A99,			170	60				EPMA [6]
USNM 113498/1			135	100	229	80		EPMA [5]
	765	158	220	48	227	40		EPMA [5]
			177	42	212	62		EPMA [9]
			96	63				EPMA [7]
			200	100				EPMA [11]
	709	47					51.1	SIMS [4]
	976	8	175	110	205	<i>c</i> 0		EPMA [12]
	700	200	1/5	116	205	60		
	799	142	141	71	100	19		
	732 597	145	135	22	210	20		EPMA [I MV this study]
R6*	557	90	150	~~	3300	200	75 3	EPMA [LINV (IIIS SCUUY] EPMA [14]
Sletta	3306	340	28	18	2075	64	75.5	FPMA [I MV this study]
KI 2-G*	177	28	77	13	2075	45	50.3	
		20	90	54	40	32	5015	EPMA [1]
			320	320	60	18		EPMA [1]
	114;101;128	2;2;4						EPMA; SIMS; PIGE [2]
	114	40	9.1	0.5	45	2		SIMS [WHOI this study]
	105	27	10.7	3.0	61	8		SIMS [Eq. 6]
	99	310	23	30	51	40	50.5	EPMA [LMV this study]
	<71				<324			ERDA [Zurich this study]
ATHO-G*	770				530		74.5	EPMA [15]
	0.7	0.07	0.6	0.07	2430	0	75.6	SIMS [1]
			50	50	570	114		EPMA [1]
	000	000	200	140	510	102		EPMA [1]
	900	900	240	240	400	160		
	640	370	4.8	0.2	080	04 260		
	040	290	0.2	υ.ŏ	220	200		SIIVIS [EQ. 0]

TABLE 2. Report of F, Cl, S, and SiO₂ concentration measurements in 10 referenced materials* and three other basaltic glasses (±2 σ ; analytical methods and references are specified; in bold is the result of this study)

(Continued on next page)

TABLE 2.—CONTINUED

	F (ppm)	±	S (ppm)	±	Cl (ppm)	±	SiO₂ wt%	Method; Reference
ATHO-G*	670	400	17	24	453	44	74.1	EPMA [LMV this study]
	637	158			334	196		ERDA [Zurich this study]
KE12*	4338	1096						EPMA [16]
	4400							EPMA [16]
					3270	110	70.8	EPMA [17]
	4200				3300			EPMA [17]
	4000	240						Selective ion method [18]
					3225	160		EPMA [19]
					3200	800		EPMA [20]
	4513	88						EPMA [12]
	7540	1860	290	22	4670	450		SIMS [WHOI this study]
	3910	1430	210	150	3570	1640		SIMS [Eq. 6]
	4490	300	150	28	3410	110		EPMA [LMV this study]
	3848	230			3483	400		ERDA [Zurich this study]
Alvin 2390-5	300	70	1270	18	358	10	49	EPMA [LMV this study]
Alvin 2746-15	123	4	1449	30	890	18	50	EPMA [LMV this study]

Notes: [1] Jochum et al. 2006; [2] Guggino and Hervig 2010; [3] Wayne et al. 2006; [4] Straub and Layne 2003; [5] Thordarsson et al. 1996; [6] Dixon et al. 1991; [7] Thornber et al. 2002; [8] Coombs et al. 2004; [9] DeHoog et al. 2001; [10] Hall et al. 2006; [11] Fisk and Kelley 2002; [12] Witter and Kuehner 2004; [13] Streck and Wacaster 2006; [14] Tonarini et al. 2003; [15] Oskarsson et al. 1982; [16] Palais and Sigurdsson 1989; [17] Métrich and Rutherford, 1991; [18] Mosbah et al. 1991; [19] Marianelli et al. 1995; [20] Cioni et al. 1998.



FIGURE 5. RSF (the relative sensitivity factor) is plotted against SiO_2 concentration in glass samples. RSF is determined for individual analysis of known samples. (a) RSF of fluorine, (b) of sulfur, and (c) of chlorine is shown here. There exists a slight negative slope for all of the panels; however, due to the scattering of measurements, the trend is not statistically significant. There are fewer numbers of RSF values in **b** because many sulfur concentrations are below EPMA detection limit, and there was no independent way to verify their concentrations. (Color online.)

similar SiO₂ contents. Equation 1 may be considered applicable to a wider range of compositions as it can adjust for the abundance of SiO₂. On the contrary, if oxygen is used as referencing mass instead of Si, as the oxygen concentration in silicate varies much less than SiO₂, Equation 1 is unnecessary.

Alternative calibration curves. Recognizing the potential weak correlations between SiO_2 and RSF (Fig. 5), we have explored a potential modification of the working curve function in an aim to optimize the accommodation of SiO_2 variation in silicate glass. With an independent verification of the accuracy by ERDA for high silica samples, the new fitting procedure can be tested without the uncertainty of high concentration measurements. Furthermore, the revised fitting function should not introduce a bias if the true working curve is indeed linear. It is an attempt to empirically incorporate a simple matrix effect without changing what we have been doing so far.

In the following discussion, we take Cl as an example and derive the equations. From the definition of RSF, Equation 1 can be rearranged to show the relationship with RSF.

$$\frac{(C_{\rm Cl} - \beta)}{[\rm SiO_2]} \times k = \rm RSF \times \left(\frac{I_{\rm Cl}}{I_{\rm Si}}\right)$$
(1')

where *k* is a conversion factor for a concentration ratio to an atomic ratio, therefore $\alpha = \text{RSF}/k$. Inspecting Figure 5, we decided to explore two functional forms relating RSF and SiO₂.

$$RSF = a \times [SiO_2] + b \tag{3}$$

$$RSF = c \times [SiO_2] + b \tag{4}$$

Substituting Equation 3 or 4 into Equation 1', the working calibration curve will be in the following form:

$$C_{\rm Cl} = ak \left(\frac{I_{\rm Cl}}{I_{\rm Si}}\right) + bk \left(\frac{I_{\rm Cl}}{I_{\rm Si}}\right) [{\rm SiO}_2] + \beta$$
(5)

$$C_{\rm Cl} = dk \left(\frac{I_{\rm Cl}}{I_{\rm Si}}\right) [SiO_2] + ck \left(\frac{I_{\rm Cl}}{I_{\rm Si}}\right) [SiO_2]^2 + \beta$$
(6)

Table 3 shows the result of the regression with the above two equations. For the regression, in addition to six basaltic calibration standards, three high Si samples are added T1G, ATHO, and KE12. Inspecting the results of the regression, Equation 6 consistently produced a better fit, although slight, than Equation 5. On top of this, "ck" term is significantly smaller than "dk" term in Equation 6. This suggests that the role of an additional term

TABLE 3. Result of error weighted regression of Equations 5 and 6

				-			
	ak/dk	±	bk/ck	±	β	±	χ^2_v
F (Eq. 5)	660	100	-4	2	-46	17	0.55
F (Eq. 6)	18	2	-0.18	0.02	-44	17	0.53
S (Eq. 5)	218	15	9.03	0.03	-90	12	3.40
S (Eq. 6)	18	4	-0.10	0.09	-94	50	3.37
Cl (Eq. 5)	-120	150	14	3	42	5	0.87
Cl (Eq. 6)	10	3	0.03	0.05	43	5	0.87

Notes: χ^2_v is a reduced χ^2 statistics in which derived by a sum of square of difference between observation and prediction normalized by variance, then divided by the number of degree of freedom (i.e., the number of data minus 2).

in correcting the matrix-dependent calibration is minor. This conclusion is again consistent with the discussion above and that of Van den Bleeken and Koga (2015) in which authors concluded the use of Equation 1 is sufficient to determine trace halogen concentration in a wide range of silicate glasses.

While it remains a matter of debate whether to systematically adapt Equation 6 for the SIMS calibrations, we stress that the function is coherent with commonly used calibration curves. If RSF is constant, independent of SiO₂ content, the coefficients *a* (Eq. 5) and *c* (Eq.6) will be zero, resulting in the identical formula as Equation 1. For this ground, we think the new calibration function provides a convenient formulation and it is useful for a wide range of glass compositions. In reflection of this spirit, we reported the concentration values using Equation 6 in Table 2, indicated as SIMS (Eq. 6).

IMPLICATIONS

An inter-calibration of F, Cl, and S measurements between EPMA and SIMS is reported for 10 glass standards, some of them easily accessible to the scientific community (MPI-DING, Jochum et al. 2006). Both analytical methods are in excellent agreement for standards with concentrations in these volatiles elements above 150 µg·g⁻¹ for F and above 20 µg·g⁻¹ for S and Cl. However, SIMS has a lower detection limit and is preferable in the case of low concentration samples. The HIERDA measurements independently confirm and anchor our data. This study revealed a shift between acidic and mafic glass-standard on our HIERDA data, thus requiring (1) caution in the choice of standard materials, and (2) separate SIMS calibrations with standards covering the SiO₂ range of the samples. An alternative is to use Equation 6 that we propose to account for this matrix effect on the SIMS measurements of F, S, and Cl. In arc melt inclusions, F/Cl ratios of a series of inclusions from single volcanoes remains constant over a large range of H₂O concentrations, suggesting these halogens do not degas. From a broader point of view, halogens such as F and Cl (also Br and I), associated with radiogenic isotopes and trace element ratios, are promising new tracers of fluid and/or melt transport from their source regions and for degassing processes.

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