Diffusion of Halogens (F, Cl, Br, I) in silicic melt

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Abstract

Chemical diffusion of the halogens F, Cl, Br, and I in silica-rich natural melts was experimentally investigated by the diffusion couple technique. Experiments were conducted under anhydrous conditions at atmospheric pressure and hydrous conditions (\~1.5 wt.\% H\textsubscript{2}O) at 160 MPa, over a temperature range of 750–1000 °C and 1000–1200 °C, respectively. Quenched trachytic melt samples were analyzed using an electron microprobe (EPMA) and secondary ion mass spectrometry (SIMS).

All halogens exhibit Arrhenian behavior during diffusion in the investigated melt compositions with F always diffusing fastest. The other halogens show progressively slower diffusion (F > Cl > Br > I) correlated to their ionic radii. In anhydrous melt a diffusivity range of 3–4 orders of magnitude is covered among the halogens with D\textsubscript{F}(1000 °C) \~5\times10\textsuperscript{-13} m\textsuperscript{2}s\textsuperscript{-1} and D\textsubscript{I}(1000 °C) \~1\times10\textsuperscript{-16} m\textsuperscript{2}s\textsuperscript{-1}. The diffusivities of all halogens increase in hydrous melt yielding for example D\textsubscript{F}(1000 °C) \~3\times10\textsuperscript{-12} m\textsuperscript{2}s\textsuperscript{-1}. However, the largest increase is observed for the slowest-diffusing halogens, resulting in a narrower overall diffusive range of only 1–2 orders of magnitude with iodine diffusivity yielding D\textsubscript{I}(1000 °C) \~9\times10\textsuperscript{-15} m\textsuperscript{2}s\textsuperscript{-1}. Activation energies (E\textsubscript{A}) of all halogens consistently range from \~200–290 kJ mol\textsuperscript{-1} in anhydrous melts.
In hydrous melt $E_A$ generally decreases, with the highest decrease determined for F (~131 kJ mol$^{-1}$) and only slight changes for the other halogens (~201–222 kJ mol$^{-1}$).

Our diffusivity data of the anhydrous series exhibit a pronounced correlation of diffusivity with the ionic radii, suggesting that halogen diffusion in highly polymerized melt is closely related to the melt's ionic porosity. The correlation between diffusivity and ionic radius is only weakly observed in the hydrous experiments indicating that the ionic porosity is sufficiently large to weaken the rate-limiting effect of the ionic radius due to the more depolymerized melt structure in the hydrous case. In hydrous experiments, the process of ionic detachment becomes more important as a rate-limiting diffusion mechanism, comparable to the case of diffusion of divalent/trivalent cations or halogen diffusion in basaltic melt.

The results of this study provide the first consistent diffusion dataset including all halogens under naturally relevant magmatic conditions and highlight the pronounced compositional effect of both, major element and dissolved H$_2$O on halogen diffusion. These data emphasize the potential of diffusive fractionation among the halogens, especially in a melt of low water content, which may be applied as a monitoring tool for volcanic unrest on actively degassing volcanoes.

**Keywords:** halogens (F, Cl, Br, I); diffusion couple; ionic porosity; iodine; silicate melt

### 1. Introduction

Volatile are among the most influential constituents of natural silicate magmas. They affect various chemical and rheological melt parameters, which in turn have crucial implications for individual volcanic eruption behavior. Typically, volcanic volatiles are dominated by water (H$_2$O) and carbon dioxide (CO$_2$), however, sulfur-species (e.g., SO$_2$) and halogens, mainly F and Cl, can reach significant concentrations (up to few wt.%) in
silicic melts and volcanic gases (e.g., Aiuppa et al., 2009; Dolejš and Zajacz, 2018). Halogens are known to exert strong effects on the physico-chemical properties of silicate melts such as melt viscosity or phase equilibria (e.g., Manning, 1981; Mysen and Virgo, 1985; Webster et al., 2018). For example, F is known to reduce the viscosity of silicic melts to a similar degree as added H$_2$O (Dingwell et al., 1985; Dingwell and Hess, 1998; Zimova and Webb, 2007; Giordano et al., 2008; Baasner et al., 2013), and can depress the isobaric liquidus temperature in basalt (e.g., Filiberto et al., 2012) and felsic melts (e.g., Dolejš and Baker, 2007b; Dolejš and Baker, 2007a). Even though more complex, substantial effects on the liquidus temperature have also been reported for Cl-bearing natural melts of both basaltic (e.g., Filiberto et al., 2014; Farcy et al., 2016) and silicic systems (Feisel et al., 2022). The physico-chemical effects of added Br and I to a melt are, by contrast, far less understood. Concentrations of Br and I are typically lower than those of F and Cl, consistent with an increasing fluid-melt partition coefficient with increasing ionic radius of Cl, Br and I (181, 196 and 220 pm, respectively; Bureau et al., 2000). F (133 pm) instead has an ionic radius very similar to O$^2-$ and OH$^-$ (140 and 137 pm; Shannon, 1976) and can therefore easily substitute for these components which promotes its solubility and compatibility in the melt (Balcone-Boissard et al., 2010).

Volcanic halogen degassing can have significant impacts on the environment and Earth’s climate, for example by the depletion of stratospheric ozone by Cl and Br (Bobrowski et al., 2003; Bobrowski et al., 2007; von Glasow et al., 2009; Surl et al., 2015; Roberts, 2018). The degassing of F and Cl into isolated pores of slowly cooling magma was shown to cause etching of silica and re-precipitation of vapor-phase cristobalite (e.g., Horwell et al., 2010; Schipper et al., 2020). Due to the high impacts that halogens can have on volcanological and environmental processes, they have received increasing attention in recent years and are routinely
measured in volcanic plumes. Halogen exsolution was shown to occur at relatively shallow depths compared to the release of H₂O or CO₂ (e.g., Spilliaert et al., 2006; Schipper et al., 2019) and may therefore help to characterize volcanic degassing. Due to the large differences in diffusivity between water and the halogens, as well as amongst halogens themselves, diffusive fractionation is expected to occur during melt inclusion entrapment or bubble and crystal growth (e.g., Alletti et al., 2007). Relative halogen (or halogen ratios) measurements in volcanic gases and plumes could therefore be applied to track diffusive fractionation processes in order to monitor volcanic activity at depth.

Even though halogen diffusion has been investigated since the 1980s our knowledge is still far from complete. It was shown that halogen diffusion is independent of its concentration and follows Arrhenian behavior in silicate melts. A weak pressure-dependence on diffusivities was reported by some authors (e.g., Dingwell and Scarfe, 1984; Bai and Koster van Groos, 1994), however, most recent studies have found only minor pressure effects (e.g., Alletti et al., 2007; Balcone-Boissard et al., 2020). Many studies focused on simplified model systems (Dingwell and Scarfe, 1984; Dingwell and Scarfe, 1985; Bai and Koster van Groos, 1994) and most investigated F and/or Cl only (Balcone-Boissard et al., 2009; Böhm and Schmidt, 2013; Fortin et al., 2017; Yoshimura, 2018; Feisel et al., 2019). To date only two studies include Br diffusion (Alletti et al., 2007; Balcone-Boissard et al., 2020) and, to our knowledge, no study has addressed iodine diffusion.

In this study we applied the diffusion couple technique on three different homogeneous melts synthesized from natural silicic pumice and lava to determine the diffusivity of all halogens (F, Cl, Br, I) over a temperature range relevant to the studied magmatic systems. Concentration profiles of F and Cl were measured by electron microprobe (EPMA) and additional profiles were acquired by secondary ion mass spectrometry (SIMS) covering
all halogens. We report data for both anhydrous and hydrous (≈1.5 wt.% H₂O) conditions and this is — to our knowledge — the first study to report iodine diffusion data in natural silicate melts. These results highly improve our understanding of magmatic halogen transport mechanisms at crustal conditions and expand the database of halogen diffusion to advance a thorough understanding of volcanic processes.

2. Methods

2.1 Experimental procedure

Two different starting materials were used in this study comprising glass synthesized from tephra of the Hekla (Iceland) H3 eruption (e.g., Thordarson and Larsen, 2007; Weber and Castro, 2017), and glass synthesized from natural obsidian lava of the 2011 Cordón Caulle eruption, Chile (e.g., Castro et al. 2013, 2016; Schipper et al. 2013, 2019; Alloway et al. 2015). Synthesis and experimental methods utilizing the Hekla material (“HX” series – “Hekla experiments”) are described in detail in the study of Feisel et al. (2019). Synthesis of starting glass derived from Cordón Caulle obsidian lava (“CCX” series – “Cordón Caulle experiments”) is described in detail in Feisel et al. (2022). The general approach used for both melts is briefly described below.

The initial sample synthesis was carried out in the laboratories of the Earth Science department of the LMU Munich. Natural obsidian was crushed, synthesized and homogenized at high temperature (1400–1550 °C) for ~2 days to produce almost completely volatile-free glass. After the first synthesis, the batch was crushed and split. One half was enriched with halogen-bearing Na-salts (NaF, NaCl, NaBr, NaI) so that each halogen would account for approximately 1 wt.% of the whole batch after mixing. The halogen-depleted split was in turn enriched with a certain amount of Na₂CO₃ to account for the sodium enrichment in the halogen-bearing glass, due to the use of aforementioned
Na-salts to add halogens. Each aliquot was again synthesized and homogenized at high T before preparation of ca. 2 mm thick polished glass discs (4.6 mm diameter) and crushed glass powder to be used in anhydrous and hydrous diffusion experiments, respectively.

2.1.1 Anhydrous diffusion experiments

Diffusion couples were constructed using 5 mm platinum tube with a wall thickness of 0.2 mm. The bottom of the capsule was closed with a Pt lid which was pressed onto and welded to the tube using an arc-welder. Afterwards the bottom of the capsule was tamped into a cylindrical shape. One halogen-enriched glass disc was loaded into the bottom of the capsule and a disc of the equivalent halogen-depleted glass was loaded on top of it, resulting in both pieces touching at their polished surfaces. Each capsule was closed by welding a second lid to the top of the capsule, which ensured closed-system conditions. The diffusion experiments were carried out in a vertical tube furnace at atmospheric pressure. Each capsule was first weighed and then loaded into an alumina tube that is closed on the bottom end, making sure the halogen-depleted half was facing upwards. After the furnace equilibrated at the target temperature the alumina tube was inserted vertically into the furnace through a small opening in the top, ensuring that the capsule was sitting upright on the closed bottom of the alumina tube in the hot zone of the furnace. The temperature was monitored by the internal thermocouple and an external K-type thermocouple being in direct contact with the experimental capsule. Additionally, most experiments were monitored using a second external K-type thermocouple interfaced with an Arduino microprocessor to read the temperature remotely and store the $P$-$T$-$t$ data to a computer. Temperatures are estimated to be accurate to ±2 °C based on the manufacturer's (Omega) reported accuracy of the thermocouple device. The experimental durations ranged from ~20 hours to 35 days depending on the temperature
investigated. The time needed for the capsule to heat to the target temperature ranged between 3 and 5 minutes. The experiments were quenched by sliding the alumina tube out of the hot furnace and letting it cool in air at room temperature in an upright position. Typical cooling times to a temperature of 200 °C as indicated by the external thermocouple were in the range of 3 to 4 minutes. After each experiment the samples were weighed again to confirm closed-system conditions were maintained during the experiment.

2.1.2 H₂O-bearing diffusion experiments

Hydrous experiments were carried out using CCX starting material only and are denoted by “CCX-H”. The capsule preparation followed the procedure described in Feisel et al. (2022) using powdered starting glass and Pt-tube with a diameter of 4 mm and a wall thickness of 0.2 mm as capsule material. After welding the capsule shut on the bottom and tamping into a cylindrical shape using a tight-fitting rod, ground glass powder of the halogen-enriched samples was introduced until the capsule was filled about halfway. During filling the powder was slightly tamped several times to avoid entrapment of air and ensure a flat diffusion interface. The exact amount of added sample powder was weighed using an analytical balance of 5-digit precision and the equivalent amount of 1.5 wt.% H₂O was added to the capsule using a microsyringe. The procedure was repeated using the halogen-depleted powder and again the equivalent amount of 1.5 wt.% H₂O for the top part of the capsule. Finally, the capsule was closed by welding a tight-fitting lid to the open end and tamped into cylindrical shape with a pressure of ~750 kg using a hydraulic press. Before an experiment, the capsules were repeatedly heated to ~120 °C and weighed to confirm no weight loss. Capsules with significant weight loss were discarded.
Experiments were performed in a *Deltech* vertical tube furnace fitted with a gas-pressurized TZM (Tungsten Zirconium Molybdenum) cold-seal pressure vessel assembly. The sample capsule is loaded into the cold-seal assembly which is connected to a stainless-steel high-pressure tubing using Argon gas as a pressure medium. To mitigate water-loss from inside the capsule to the Ar-atmosphere ca. 0.3 MPa of CH$_4$ was inserted to the pressure system before pressurizing with Ar (e.g., Sisson and Grove, 1993; Szramek et al., 2006; Shea and Hammer, 2013). The cold-seal assembly consists of an inner autoclave made of TZM (~30 mm outer, ~6.5 mm inner diameter) and an outer sheath made of Inconel (~50 mm diameter, 5 mm wall thickness), both attached to a water-cooled base on the bottom. The outer sheath slides over the inner autoclave leaving ~5 mm between the two. This space is constantly purged with Ar during the experiment to provide a non-reactive atmosphere for the inner pressurized autoclave. The inner autoclave is tightened against a steel cylinder via a doubly coned and sealed small Beryllium-bronze cylinder (“football”-shape) between the two. A second, lower vessel made of stainless steel is attached to the bottom of the water-cooled coupling base and is connected to the pressure line on the bottom with a high-pressure fitting. The sample capsule sits in a small cup which in turn is attached to an Inconel rod which is inserted into the bottom of the steel cylinder. A magnet at the bottom of the rod allows for the control of the position of the sample capsule in the assembly from the outside using a neodymium ring-magnet that slides over the lower steel cylinder. The whole assembly including the experimental capsule is inserted into the vertical tube furnace from the bottom before it is brought up to the target temperature and pressure. The pressure is generated by an HIP GB-60 gas booster device operated with compressed air and conveying Ar gas as a pressurizing medium.
During the time of heating, the capsule remains in the water-cooled part of the assembly (rapid-quench coupler) which is outside the furnace and constantly flushed with water (~15 l/min). When the target $P$-$T$ conditions are reached and equilibrated, the experiment is started by upward movement of the sample holder using the outer magnet. In this way, the capsule is — within seconds — brought into the top part of the TZM autoclave, which is in the hot zone of the furnace. Quenching is done the opposite way by sliding the magnet down to bring the capsule back into the water-cooled zone of the assembly, resulting in an almost immediate quench. During the experiments, temperature is monitored using the internal thermocouple of the furnace and an external K-type thermocouple which is inserted into a small bore in the sheath of the TZM assembly and touching the top of the internal autoclave, which is the position closest to the capsule. The pressure is monitored with a factory-calibrated Bourdon-tube gauge and a digital pressure transducer. Considering the small thermal volume of the capsule relative to the massive TZM autoclave we expect no significant thermal gradient within the diffusion couple capsule.

Upon the start of the experiment while inserting the rod with the sample capsule into the hot zone of the autoclave, a pressure drop of up to 20 MPa over ca. 10 s is commonly observed. We interpret this to occur due to the displacement and concomitant cooling of a large amount of the hot gas from the autoclave to the cooler parts of the pressure system during to insertion of the rod. The rod is cold relative to the hot atmosphere in the autoclave and upon heating causes the pressure to increase again slowly by typically about 10 MPa over the duration of ca. 50 s. The opposite process is observed upon quench of the experiment, resulting in an up to 20 MPa overpressure during quench, which decreases to ca. 10 MPa overpressure in about 50 s at the end of an experiment. These processes are accounted for by slight over-pressurization before the start of the
experiment. The pressure increase at the end of the experiment also ensures that bubbles do not form during the quench. Additionally, it was shown that halogen diffusion is mostly insensitive to pressure variations (e.g., Baker and Balcone-Boissard, 2009). Therefore, we consider these short-lived pressure fluctuations to be insignificant for the results of the diffusion experiments.

2.2 Analytical methods

Before preparation for further analyses all samples were weighed individually to ensure no weight loss or gain occurred during the experiment. Diffusion couple capsules were embedded in epoxy and cut open along the center of the capsule and parallel to the diffusion direction (i.e., parallel to the cylindrical capsules rotation axis) using a Buehler IsoMet precision saw. All samples were polished using a series of diamond embedded disks to an ultimate grain size of 1 µm while taking care that the polished surface remained parallel to the diffusion direction.

2.2.1 Electron probe micro analysis (EPMA)

Major element and halogen concentration analyses of experimental glasses were conducted at the Department of Geoscience of the University of Mainz, and using a JEOL JXA8200 electron microprobe. Analyses employed an acceleration voltage of 15 kV, a beam current of 12 nA, and a beam diameter of 10 µm. Dwell times for F and Cl were 120 s and 30 s, respectively, yielding a detection limit of 60 ppm (1 σ). Analysis dwell times of each major element was: Si 25 s, Al 40 s, Na 20 s, K 30 s, Ca 30 s, Fe 60 s, Mg 30 s, Mn 50 s, and Ti 30 s. The device was calibrated before a measurement using the following reference materials: SrF₂ (F), tugtupite (Ca, Na), VG-2 (Ca, Mg), VG-A99 (Fe, Si), MnTi (Mn, Ti), and orthoclase (Al, K). Proper calibration was assessed by analyzing standards VG-2,
VG-A99, VG-568 and a natural obsidian standard (~74 wt.% SiO$_2$) repeatedly during each analytical session. The data was corrected using the ZAF method. Concentration vs. distance profiles were acquired using line-scans with a fixed step-width of 5–250 µm depending on the sample (i.e., the anticipated diffusive speeds and therefore profile distances) and the position of the analyzed points relative to the diffusion interface. Points in the transition zone between the two diffusion couple halves were analyzed using a smaller step-width while the profile ends were covered by a larger step-width. This way it was possible to achieve a high spatial resolution of data, in turn facilitating good resolution of slow diffusion patterns while covering a large range of diffusion widths and keeping analysis time low. Profiles were acquired along traverses away from the capsule edges to avoid analyzing inhomogeneities that could distort diffusion profile data (e.g., devitrification, Feisel et al. 2019).

### 2.2.2 Secondary Ion Mass Spectrometry (SIMS)

As the concentration of Br and I in the samples is too low to be analyzed by EPMA, experimental samples were further analyzed on the SIMS. The analyses of all HX samples and of CCX1 and CCX4 were carried out during two analytical sessions in October 2018 and January 2019 at the University of Lausanne, Switzerland. The other samples (CCX3, CCX5 and all CCX-H) were analyzed at Heidelberg University, Germany, in two sessions in May 2021 and April 2022. Both facilities feature a CAMECA IMS 1280HR ion microprobe. The analytical parameters for all SIMS analyses (halogens and H$_2$O) in both labs are summarized in Table S1 of the supplementary material.

Analyses carried out at the University of Lausanne were referenced internally on each sample in an area far outside of the region of diffusion where the constant Si-content was
known from EPMA analyses. These data included the less abundant Si-isotope $^{30}\text{Si}$ for calculation of ratios with Br and I which are of low concentration in our samples compared to F and Cl. $^{28}\text{Si}$ and $^{19}\text{F}$ intensities were detected using a Faraday-Cup. The other halogens ($^{35}\text{Cl},^{79/81}\text{Br},^{127}\text{I}$) and $^{30}\text{Si}$ were analyzed using electron multipliers. The SIMS analyses of halogens in Heidelberg were calibrated using an obsidian glass (JV1, Pichavant, 1987) for F and Cl and the GSE-1G glass for Br and I (Marks et al., 2017a; Marks et al., 2017b; Wiedenbeck, 2017). The accuracy of these analyses is limited by the poor homogeneity of halogens in GSE-1G and the fact that JV1 is not an established reference material with multiple independent determinations of the concentrations. The halogen concentrations determined by SIMS must therefore be interpreted as semi-quantitative with an estimated accuracy of $\leq 50$% (relative error).

For each water-bearing sample (CCX-H), $\text{H}_2\text{O}$ concentration profiles were acquired next to the halogen profiles using a CAMECA IMS3f ion microprobe at Heidelberg University. The $\text{H}_2\text{O}$ background caused by in-situ contamination was reduced by using a LN$_2$-cooled metal plate in the sample chamber. The apparent $\text{H}_2\text{O}$ concentration caused by in-situ contamination was monitored by analyzing San Carlos olivine and was $< 0.01$ wt.%. $\text{H}_2\text{O}$ analyses were calibrated using JV1 as reference material. Accuracy is estimated to be $< 20$% relative error.

3. Results

3.1 Chemical composition of starting materials

The major element compositions of the different starting materials as determined by microprobe analyses are compiled in Table 1. The synthesized samples reveal a similar composition, both plotting in the field of Trachyte in a TAS diagram, very close to the
borders to rhyolite and dacite. However, the CCX melt is slightly enriched in alkalies (Na$_2$O, K$_2$O) compared to the HX melt. All samples were analyzed using line scans on the microprobe not only to measure F and Cl gradients but also to validate major element homogeneity over the diffusion couple (Fig. 1). Maximum absolute concentrations of F are around 0.5–0.6 wt.% in the HX samples, and about 0.8–1 wt.% in the CCX samples. Cl concentrations are about 0.2–0.3 wt.% in the HX samples and about 0.3–0.4 wt.% in the CCX samples. Absolute Br and I concentrations were only measured for the CCX samples using the SIMS at Heidelberg University. The maximum Br and I concentrations in the halogen-enriched glasses of the CC melts are ~2500 ppm and ~300 ppm, respectively.

3.2 Post-experimental diffusion couple textures

During data acquisition, all diffusion couples were assessed for textural homogeneity by means of backscattered electron images. Most samples comprised a clean and straight diffusion interface between two homogeneous glassy areas which were particularly prominent in the anhydrous samples. Some samples and mainly those of the hydrous series contained minor cracks in the glass, which were interpreted to stem from the relatively fast quenching rates (Fig. 2a). However, the cracks were not found to influence the acquired diffusion data. Few samples underwent deformation during the experiments caused by bubble formation or the onset of convection. Both phenomena were mostly recognized in experiments of the water-bearing series in which the melt viscosity was reduced due to the presence of water (e.g., Giordano et al. 2008) which enhanced convection. These effects resulted in distorted diffusion couple geometry, and according samples were discarded from further analysis. Small amounts of oxide phases (<100µm; <<1 vol.%) were recognized in the halogen-bearing parts of some experiments utilizing the CCX melt. These were analyzed qualitatively using EDS which showed they are
tungsten-oxides. This was interpreted to stem from a slight contamination of the sample powder caused by using a tungsten-carbide mill for sample preparation. However, these oxides are not thought to affect halogen diffusion in our experiments.

3.3 Halogen diffusion coefficients

Most concentration profiles comprise a smooth and symmetric transition between the high and low halogen concentration portions of the charge, indicating that no other processes than diffusion (e.g., convection) were involved (Fig. 1). Smooth and symmetric profiles are recognized especially for experiments run at high temperatures. Diffusion profiles of Br and I are in general shorter than those of F and Cl. However, all concentration vs. distance profiles presented here yielded good results during fitting and are treated as effective binary diffusion of each halogen element in the melt matrix (e.g., Zhang 2010).

Diffusion coefficients for each acquired concentration vs. distance profile were calculated by fitting the respective data to the equation for constant one-dimensional diffusivity between two semi-infinite media (Crank, 1975):

\[ C(x, t) = \frac{C_{low} + C_{high}}{2} + \frac{C_{low} - C_{high}}{2} \text{erf}\left(\frac{x - x_0}{2\sqrt{D t}}\right) \]  

The parameter \( C(x,t) \) describes the concentration at distance \( x \) (m) after the experimental time \( t \) (s). \( C_{low} \) (ppm) is the concentration of the halogen-poor, and \( C_{high} \) (ppm) the concentration of the halogen-rich half-space. The term erf indicates the error function. \( x_0 \) (m) describes the position of the diffusion interface and is in this case determined mathematically. The term \( D \) (m\(^2\) s\(^{-1}\)) is the diffusion coefficient.

Data fitting was performed using the nonlinear least-squares method implemented in a \textit{MatLab} script, specifically programmed for easy use with diffusion profile data. The
results obtained by this script were regularly validated by comparing to the results calculated by the commercially available curve-fitting software *CurveExpertPro*. As equation (1) is independent of absolute concentrations it was used with both, concentration data determined by EPMA and SIMS and ratios of halogen- over silica-concentration (e.g., F/Si) as determined by SIMS to calculate diffusion coefficients. All parameters of equation (1) except x and t were calculated based on the fitting algorithm. In some cases, parameters $C_{low}$ and $C_{high}$ were set manually to facilitate proper fitting calculations, for example where the analyzed profiles did not cover the whole length of diffusion for that particular profile. Additionally, some profiles suffered from slight distortion, caused, for example, by deformation of the capsule during quench, and resulting in asymmetrical profiles which was mainly prominent in the longest profiles of F diffusion. Where profiles were asymmetrical, each half of the diffusion profile was fitted individually using equation (1) and the results were compared to those of the complete profile. Those profiles of which the individually fitted halves yielded different diffusion coefficients larger than 0.6 orders of magnitude were discarded. F diffusion coefficients calculated on profiles where this method was applied are indicated by “*” in Table 2. Typical concentration vs. distance profiles of sample CCH-X-42 fitted with equation (1) are illustrated in Figure 2b. All measured diffusion profiles with their respective fit curves are provided in Figures S1-S4 of the supplementary material.

### 3.3.1 Anhydrous HX

Of the nine HX experiments presented in Feisel et al. (2019), six samples were analyzed by SIMS for the scope of this study. One concentration vs. distance profile was acquired for each of the samples, covering lengths of ~500–1000 µm. Diffusivities of F and Cl determined here agree well with the results of microprobe analyses indicating that F is
generally faster than Cl by up to 2 orders of magnitude in the investigated temperature range. \( D \) values are on the order of \( 10^{-15} \) to \( 10^{-13} \) m\(^2\) s\(^{-1}\) for fluorine and \( 10^{-17} \) to \( 10^{-15} \) m\(^2\) s\(^{-1}\) for chlorine, of which the lower and higher values each correspond to temperatures of 750 °C (HX9) and 950 °C (HX8), respectively (Table 2). Bromine and iodine diffusivities are generally lower than those of chlorine, with Br consistently being faster than I. \( D_{\text{Br}} \) ranges from \( 10^{-18} \) to \( 10^{-15} \) m\(^2\) s\(^{-1}\) while \( D_{\text{I}} \) values are about half an order of magnitude smaller at the corresponding temperatures, ranging from ca. \( 10^{-18} \) to \( 10^{-16} \) m\(^2\) s\(^{-1}\) (Table 2).

### 3.3.2 Anhydrous CCX

Out of seven anhydrous experiments performed using CCX melt and analyzed by EPMA, three were discarded due to textural features indicating compromised geometry. The remaining four experiments were additionally analyzed by SIMS. Diffusivities of all halogens in samples using the CCX melt are similar to those obtained for the HX melt. However, the difference between F and Cl diffusion is less pronounced in this melt composition compared to HX. Diffusion coefficients of F (\( D_{\text{F}} \)) range from \(~10^{-14} \) to \( 10^{-13} \) m\(^2\) s\(^{-1}\) in the temperature range of 850 °C (CCX3) to 1000 °C (CCX5). Cl diffusion is up to two orders of magnitude slower with \(~10^{-17} \) to \( 10^{-14} \) m\(^2\) s\(^{-1}\) at these temperatures. For these two halogens, results of EPMA and SIMS analyses agree well within statistical errors (Table 2). Diffusion of Br is slower than that of Cl by \(~0.5–1.5\) orders of magnitude and I is even slower than Br by \(~1\) order of magnitude with diffusivities in the range of \(~10^{-16–10^{-14}} \) and \(~10^{-16–10^{-15}} \) m\(^2\) s\(^{-1}\), respectively.

### 3.3.3 Hydrous CCX-H
All diffusion couple experiments of the hydrous series performed in the TZM assembly were analyzed both by EPMA (F, Cl) and by SIMS (F, Cl, Br, I). In general, diffusivities are higher than those obtained for the anhydrous CCX series with $D_F$ ranging from $\sim 10^{-12}$ to $\sim 10^{-11}$ m$^2$s$^{-1}$ from 1000–1200 °C. Cl diffusion is 0.5 to 1 orders of magnitude slower than F, and Br and I are even slower. However, diffusivities of Cl, Br and I are all within less than one order of magnitude of each other at the respective experimental temperatures (Table 2). This results in a total diffusivity range of only 1–2 orders of magnitude among all halogens which is significantly less than observed for the anhydrous series of CCX melt which spans a range of 3–4 orders of magnitude among all halogens (Table 2).

### 3.4 Temperature dependence of halogen diffusion

All diffusion coefficients determined in this study increase with increasing temperature for each of the used melt compositions. As shown in various previous studies, diffusivity follows Arrhenian behavior (e.g., Baker and Balcone-Boissard 2009), which is also confirmed by our data. Plotted in a diagram of log(D) vs. inverse temperature (Fig. 3), the data clearly shows this Arrhenian trend and can be described by the following equation:

$$D = D_0 * e^{-\frac{E_A}{R*T}}$$

(2)

where $D$ is the diffusion coefficient (m$^2$s$^{-1}$), $D_0$ is the pre-exponential factor, $E_A$ the activation energy (J/mol), $R$ the universal gas constant (8.3145 J mol$^{-1}$ K$^{-1}$), and $T$ is the temperature (K). The characteristic parameters describing the diffusive behavior of each halogen in a specific melt composition are $D_0$ and $E_A$ which are mathematically represented by the y-axis intersect and the slope of the trendline in the Arrhenius diagram, respectively. For the calculation of the characteristic Arrhenius parameters, equation (2) was linearized to the form
\[
\log(D) = -\frac{E_A}{\ln(10) \ast R \ast T} + \log(D_0)
\]  

and fitted to all available data (EPMA + SIMS) of each starting material using the nonlinear least-squares method implemented with Matlab. Where multiple profiles were measured on one sample and with the same method, the resulting diffusion coefficients were averaged to avoid a weighing effect during the Arrhenius fitting calculations. The results of all fits are illustrated in Fig. 3 and listed in Table 3. Fitted with the data of the two anhydrous series, the results of the HX and CCX starting materials are similar, yielding activation energies in the range of \(\sim 200–290 \text{ kJ/mol}\) for all halogens. However, diffusion in HX melt generally comprises slightly higher activation energies than in CCX melt. The similarity is further represented by the parallel fit curves in the Arrhenius diagrams (Fig. 3). However, in the HX series it is apparent that F is significantly faster than all other halogens which is represented by a gap of 1.5–2 orders of magnitude between the fit lines of F and Cl, while Cl, Br and I are all within about 1.5 orders of magnitude. In comparison, the data of the CCX series shows more equally spaced Arrhenius fits of the halogens spanning an overall similar range of diffusivities compared to the HX experiments. The data of the hydrous series shows the same ordering of diffusive speeds, with F being the fastest and I being the slowest, but spanning a narrower range of diffusivities among all halogens. In the Arrhenius diagram this is represented by the more closely spaced fit curves compared to the anhydrous data. Activation energies are similar to the anhydrous series, except for F whose \(E_A\) is only 131 \text{ kJ/mol}\) in the hydrous case compared to 198–213 \text{ kJ/mol}\) in the anhydrous experiments (Table 3).

**3.5 \(H_2O\) content in CCX-H experiments**
The experimental products of the CCX-H series show a range of 1.5–2 wt.% H$_2$O (Table 2). Most of the hydrous experiments suffered from water loss to some extent, which was indicated by increasing totals towards one end of the diffusion profile recognized in the EPMA results (Fig. 1) and confirmed by SIMS analyses (Fig. 2; Fig. S1 of the supplementary material). The use of CH$_4$ in the pressure medium helped to reduce this issue but did not resolve it completely. Interestingly, water was only lost on the halogen-depleted side of the diffusion couple leading to a weak, mostly linear H$_2$O-concentration gradient over the length of the diffusion couple. Experiments comprising significant water loss were discarded, however, small losses were considered negligible with regard to diffusivity. This is particularly true considering that the transition between high and low halogen concentration in most cases is relatively narrow, especially relative to the short diffusion lengths of the slower diffusing halogens. Over this narrow range the H$_2$O concentration can be considered to be constant within error. Due to this issue, we have calculated the average H$_2$O-concentration over the length of the transition zone of each hydrous diffusion profile and reported it with other relevant data in Table 2.

4. Discussion

4.1 Halogen diffusion mechanisms

Diffusivity and the mechanism of halogen diffusion are both strongly dependent on the composition and internal structure of the host glass. In the case of aluminosilicate melts a vast range of compositions are present in nature and structural melt parameters such as the degree of polymerization show an accordingly wide range. Arrhenius parameters of halogen diffusion have been determined for a range of different melt compositions and illustrate the strong compositional dependence of halogen diffusion (Watson and Bender,
1980; Dingwell and Scarfe, 1984; Dingwell and Scarfe, 1985; Bai and Koster van Groos, 1994; Alletti et al., 2007; Balcone-Boissard et al., 2009; Böhm and Schmidt, 2013; Fortin et al., 2017; Yoshimura, 2018; Balcone-Boissard et al., 2020). Most of these studies studied F and Cl diffusion and only few have investigated Br diffusion. However, none of the available studies provide I diffusivity data. Hence the present study is the first to our knowledge.

One major compositional parameter defining the behavior of silicate melts is the degree of polymerization, which itself is a function of, for example, the amounts of SiO₂, volatiles or network modifying cations. Typically, the degree of polymerization in a melt is characterized by the parameter of NBO/T, i.e., the ratio of non-bridging oxygen atoms over tetrahedally coordinated ions (Mysen, 1988). The melts of the present study exhibit NBO/T values in the range of ~ 0.08–0.11, calculated using the method of (Mysen, 1988) and splitting FeOtot equally between Fe₂O₃ and FeO (Giordano et al., 2008). The NBO/T values are reported together with the bulk rock chemistry in Table 1.

The bond strength of an ionic species dissolved in melt generally increases with the charge of that species (Zhang et al., 2010). Halogens in the combined state (e.g., as a halide) typically have an univalent charge of -1 and are therefore comparably weakly bonded to other atoms, despite being very reactive. This means that halogens are relatively easily detached from their original site by breakage of the ionic bonds around a previously coordinated halogen ion before moving to a new site (Zhang et al., 2010). Additionally, even though the halogen group elements have the highest electronegativity of all elements in their respective periods, the significant within group variation in this parameter means that the bond strength should also vary accordingly. For example, F, being the most electronegative, should foster the highest bond strength of the halogens.
Within this simplified chemical framework the diffusive “jump” can be envisioned to proceed by passing through an aperture formed by neighboring ions. The size and stiffness of the aperture should generally be structurally controlled and relate to the polymerization of the melt, while the detachment rate should be controlled by ionic charge (Zhang et al., 2010). The size and number of the apertures are determined by the ions present in the melt and the resulting “free space” formed which is called the ionic porosity. Naturally, smaller ions such as F diffuse faster, because they can pass through apertures of various sizes and are therefore less sensitive to ionic porosity. Larger ions can only pass large apertures and their diffusion rate is therefore structurally controlled and, hence, more sensitive to ionic porosity. This is typically the case for noble gases and monovalent ions (e.g., Henderson et al., 1985; Lux, 1987; Alletti et al., 2007) and was also confirmed for halogens by recent studies which showed that diffusion is negatively correlated with the ionic radius of the halogen in low NBO/T melts, i.e., in melts with a high degree of polymerization (Rhyodacite/Trachyte, NBO/T: ~0.08, Feisel et al., 2019; Na- and K-Phonolite, NBO/T: ~0.08, Balcone-Boissard et al., 2020). In melts with higher NBO/T (lower degree of polymerization) halogen diffusion typically comprises only weak correlation with the ionic radius. Alletti et al. (2007) suggested that halogen diffusion in a basaltic melt (NBO/T ~0.5) is mostly independent of “free space” in the melt structure but instead occurs by exchange mechanisms that are predominantly controlled by the preservation of local charge balance, similar to the diffusion of divalent and trivalent cations (Henderson et al., 1985). This means that in this kind of melt movement of halogens is mainly rate-limited by the charge-controlled detachment process.

The present study complements the data of Feisel et al. (2019) by including all new SIMS analyses which also cover Br and I in two different highly polymerized melts (HX: NBO/T...
~0.08; CCX: NBO/T ~0.08–0.11). Figure 4 illustrates the diffusivity of the halogens in different melt compositions relative to their ionic radii (Shannon, 1976) at 1250 °C. The data of Alletti et al. (2007) are included as a reference of a weakly polymerized melt and the data of studies performed at lower temperatures were calculated based on the published Arrhenius parameters. The results of the present study and especially those of Br and I confirm the strong influence of the ionic radius on diffusivity in polymerized anhydrous melts. The difference between F and Cl is particularly pronounced for most anhydrous studies, yielding a significant negative slope between the two in the diagram (Fig. 4). However, the slope between Cl and Br defines a discordance to the trend between F and Cl in most studies. For the anhydrous CCX melt the slope increases from Cl to Br and this trend is continued to I. For the anhydrous HX melt, however, the slope decreases from Cl to Br and I. This stepwise correlation of ionic radius and diffusivity is recognized for all polymerized melts that were analyzed for Br (and I). We interpret this behavior to show that the ionic porosity of the melt is limited to distinct aperture sizes dictated by the melt structure. The fact that Cl and Br seem to have a similar diffusivity in anhydrous phonolite (Balcone-Boissard et al., 2009) regardless of their different ionic radii suggests that Cl and Br move through similarly sized apertures in this melt. By contrast, in the HX and especially CCX melt, Br cannot move through the same apertures as Cl due to its size, resulting in its lower diffusivity. Likewise, the I ion is too large to pass these aperture sizes and can diffuse only in the vicinity of ions that allow the formation of larger openings between sites. F, being the fastest diffuser among all of the halogens, can move through both small openings and all the larger apertures that are used by Cl, Br, and I in a polymerized anhydrous melt.

4.2 The effect of H₂O on diffusion
The hydrous experiments (~1.5 wt.% H₂O) generally yield high diffusivities which span a range of only 1–2 orders of magnitude among the different halogens (Fig. 3). This restricted range of diffusivities contrasts those of the anhydrous CCX melt which displays 3–4 orders of magnitude variation. For better comparison to the anhydrous results, the Arrhenius parameters of the anhydrous CCX series were used to calculate hypothetical anhydrous diffusivities in the temperature range of the hydrous experiments and plotted in an Arrhenius diagram together with the hydrous Arrhenius fits (Fig. 5). The calculated anhydrous values are consistently lower than the hydrous data. While the difference for F is only ~0.2 log units at high T (1200 °C) and ~0.8 log units at low T (1000 °C), the difference for the slower diffusing halogens is more pronounced. Cl is ~1 log unit, Br ~0.5–1.5 log units and I ~2 log units faster in hydrous compared to dry melt. These results highlight the strong influence of H₂O on halogen diffusivity in the high silica melts of this study. These findings are in contrast to the those of Balcone-Boissard et al., (2020), who showed that the addition of up to 2.65 wt.% H₂O exerts only minor influence on Br diffusion in phonolitic melts; a fact which further underlines the strong compositional dependence of halogen diffusion.

The increase in diffusivity in the melts of this study indicates a change in the diffusion mechanism that is likely caused by the modification of the melt structure due to the addition of H₂O. This effect can also be observed in Figure 4, where the strong correlation of diffusivity with the ionic radii observed in the anhydrous melts is highly attenuated for the hydrous case. Indeed, the hydrous data is more similar to those of basalt confirming that water effectively lowers the degree of polymerization of the melt. In doing so, the rate-limiting influence of melt structural apertures is reduced which makes the process of detachment more relevant as a diffusion-rate-limiting factor. Interestingly, the slope
between Cl and Br increases in the hydrous melt similar to the behavior in the anhydrous CCX melt. At the relatively low water contents of ~1.5 wt.% used in the present study, the majority of the added H₂O is expected to be dissociated to form hydroxyl (OH) in the melt (e.g., Silver et al., 1990; Ihinger et al., 1999). The experimental results indirectly show that hydroxyl effectively depolymerizes the melt and allows for faster halogen diffusion. However, even in the hydrated melt, halogen diffusion is still somewhat correlated with the ionic radii. This may indicate that for the given added water content (~1.5 wt.%) the melt structure is still polymerized enough to assert some control on the aperture-limited jumping processes, mainly affecting larger ions. We speculate that diffusivities will increase even more and may become more equal among the halogen species with increased water content. Indeed, our own preliminary results using 3.5 wt.% of H₂O added to the same CCX melt and in the same experimental setup (e.g., 1000 °C / 160 MPa) yield still higher diffusivities that span over an even smaller range among all the halogens (Fig. 5). This strongly implies that the rate at which a halogen ion jumps into a new site grows as the melt becomes increasingly depolymerized.

Another notable distinction between anhydrous and hydrous melt is the change in the activation energy, $E_A$, of F diffusion, which is lowered from 198 to 131 kJ mol⁻¹, while the $E_A$ of the other halogens are only weakly affected (Table 3). That is, F diffusion becomes less sensitive to temperature in hydrous melts, which is apparent in the comparably shallow slope of the F Arrhenius fit in Figures 3c and 5. As already concluded from the observation that F diffusion is less strongly enhanced in the hydrous melt, compared to the other halogens, F diffusion appears only weakly sensitive to the melt structure and is more strongly controlled by the detachment process. F is known to substitute for bridging oxygen in Si-O-Si units (e.g., Mysen and Virgo, 1985) and preferably coordinates with Si
or Al (e.g., Zeng and Stebbins, 2000; Liu and Nekvasil, 2002), while Cl and Br prefer to coordinate in larger sites (Cassidy et al., in press). Similarly, OH⁻ typically replaces oxygen bonds of the Si-O network (Mysen et al., 1980). Consequently, the addition of H₂O and the concomitant formation of OH⁻ in the melt must influence the preferred bonding environment of F in the silicate network. Here, we interpret the change in activation energy of F to reflect that the rate of detachment from its site is enhanced by the replacement of F with OH⁻. This way more F is available for diffusion compared to the anhydrous case, which in turn suggests that F diffusion becomes less sensitive to temperature (i.e., lower activation energy) under hydrous conditions. Consequently, we speculate that the introduction of water has a two-fold effect on the halogen diffusion mechanism: 1) The resulting decrease in the degree of polymerization generally promotes halogen diffusivities by increasing the ionic porosity; 2) The strong effect on the activation energy of F is interpreted to be due to OH⁻ directly affecting the bonding environment of F. Clearly, these explanations are qualitative, and therefore meant to suggest possible microscale chemical processes that might explain our macroscopic observations. Testing these ideas could benefit from appropriate imaging experiments (e.g., Schaller et al., 1992; Zeng and Stebbins, 2000; Mysen et al., 2004) that may isolate the relevant coordination and bonding environments of the halogens, with implications for their bond strengths in natural silicate melt.

### 4.3 Halogen diffusion and viscosity

Oxygen self-diffusion is commonly seen as a solid estimate of the structurally defined lower limit of diffusion rates in silicate melts (Oishi et al., 1975; Shimizu and Kushiro, 1984; Dingwell, 1990; Lesher, 2010; Zhang and Ni, 2010) and appears closely related to anhydrous melt viscosity via the Eyring equation (Glasstone et al., 1941; Dingwell, 1990;
Zhang and Ni, 2010). Calculated oxygen self-diffusivity of our anhydrous samples using viscosity data derived from the model of Giordano et al. (2008) are included in Figure 3. Diffusion of all four halogens in the dry melt is at least 1 order of magnitude faster than the calculated oxygen self-diffusion (Fig. 3), indicating that the silicate network behaves as in quasi-static structural sites relative to the diffusing halogen ion; therefore, diffusion may only be affected weakly by self-diffusion of the silicate network. Notably, iodine diffusion is the slowest of the halogens and thus closest to the calculated Eyring diffusion. The steeper slope of the Eyring diffusivity compared to the slope of the halogen fits in the Arrhenius diagrams (Fig. 3) suggests that with increasing temperature the jump frequency of iodine may approach that of the Si-O bonds in the silicate structure and the network surrounding iodine may no longer be viewed as quasi-static. With increasing temperature, iodine diffusion might therefore be enhanced by the cooperative rearrangement of the local silicate structure as oxygen diffuses. The activation energy of diffusion, i.e., the slopes of the Arrhenius fits of the other halogens (Fig. 3) likewise indicate that all fits will meet the lower limit of oxygen self-diffusion at higher temperatures. Consequently, at sufficiently high temperatures (i.e., sufficiently low viscosity), all halogens will move with the same frequency as the silicate network, hence, diffusion will be the same for all halogens, being determined by the jump frequency of the structural movement of the Si-O bonds, broadly consistent with the conclusions of Dingwell (1990).

The indicated oxygen self-diffusivities in Figure 3 are considered to represent the lower limit of possible values as they are based on the halogen-depleted melt compositions. In F-bearing melts, like those of the enriched diffusion couple halves, the viscosity can be significantly reduced due to the depolymerizing effect of F (e.g., Dingwell et al., 1985; Giordano et al., 2008), which will in turn yield higher calculated oxygen self-diffusivities.
For the melts used in this study, the F-bearing melts yield Eyring diffusivities of up to 1 order of magnitude higher than the F-depleted melts, approaching the derived diffusivities of iodine at the highest of the experimental temperatures. Therefore, during the experiments, the melt structural lower limit of halogen diffusion is expected to change upon diffusion of F. In the resulting F enriched melts, the halogen diffusivities might approach the Si-O jump frequency already at lower temperatures compared to the F-depleted case. Expanding on this idea, we speculate that when F diffusivity and the F-depleted Eyring diffusivity are within ~1 order of magnitude in Arrhenius space (i.e., at sufficiently high temperatures), diffusion of F into the depleted melt will enhance F diffusivity by decreasing the degree of polymerization. This would in turn result in a concentration dependent F diffusivity comparable to the case of H$_2$O (e.g., Behrens et al., 2004). However, it is unclear if the Eyring equation is valid for the case of F-enriched polymerized melts.

In case of the hydrous melt, the Eyring equation was shown to be inapplicable as it underestimates oxygen-diffusion by 3–4 orders of magnitude in rhyolitic melt (Behrens et al., 2007). In this case, oxygen no longer moves solely by self-diffusion but is mainly transported by the diffusion of molecular H$_2$O in the melt (Behrens et al., 2007; Zhang and Ni, 2010) which shows that the structural limit of diffusion rates in hydrous melt can no longer be described by the self-diffusion of oxygen.

In an attempt to define a lower limit of diffusion rates in the hydrous melt of the present study, calculated oxygen self-diffusivities of rhyolite and dacite (Tables 4 and 5 of Zhang and Ni, 2010) have been included in Figure 3c. However, these predicted self-diffusivities are faster than the experimentally constrained diffusivities of Br and I over a large range of the investigated temperatures. This is interpreted to indicate that in a
slightly depolymerized melt of sufficiently large ionic porosity, the jumps of Si-O bonds no longer define the lower limit of transport rates but that the diffusive characteristics may be mostly determined by the ionic charge and radius.

5. Conclusions

The diffusion characteristics of four halogens in silicic melts were determined experimentally under anhydrous and hydrous conditions and over a temperature range relevant for magmatic processes (750–1200 °C). The results are consistent in that F is the fastest diffusing halogen and diffusivity decreases with increasing ionic radius indicating that diffusivity is highly dependent on the melt structure and therefore melt composition. Halogen diffusion covers a range of 3–4 orders of magnitude in silica-rich anhydrous melt, but diffusivities increase dramatically when water is added. The diffusivity increase due to the addition of water is most pronounced for the largest of the halogens and thus, the slowest diffusing halogen iodine. The effect of added water is weaker for the smaller halogens, leading to an overall diffusive range of only 1–2 orders of magnitude among all halogens. While the temperature dependence in terms of activation energies of Cl, Br and I diffusion is similar in the dry and wet case (~200–290 kJ/mol), $E_A$ of F is reduced by about 35% in hydrous (~131 kJ/mol) compared to anhydrous melt (~200 kJ/mol). This is interpreted to indicate that F diffusion is more strongly dependent on the ionic detachment during diffusion and is therefore less sensitive to ionic porosity, especially in hydrous melt.

This study represents a significant contribution to the experimental database of halogen diffusion in natural silicate melts, and to our knowledge, is the first to include coherent results on iodine diffusion. The new data are highly relevant for the better understanding of halogen mobility in magmatic processes. Our results suggest that diffusive
fractionation of faster diffusing components such as H$_2$O and the halogens, could occur during bubble formation in a weakly water-enriched magma during slow magma ascent (e.g., Watson, 2017). Modeling of different magma ascent and bubble growth scenarios using the proposed diffusion parameters may help to characterize possible halogen fractionation trends during volcanic unrest.

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### Table 1: Major element composition of the synthesized starting glasses as determined by EPMA and SIMS analysis. All values represent units of wt.% unless otherwise stated. All data are corrected for Na-loss during EPMA analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>HX&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CCX</th>
<th></th>
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</thead>
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<tr>
<td></td>
<td>enriched (n = 15)</td>
<td>depleted (n = 14)</td>
<td>enriched (n = 6)</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>68.3 (3)</td>
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<td>0.46 (2)</td>
<td>0.66 (3)</td>
</tr>
<tr>
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<td>14.57 (8)</td>
<td>14.49 (4)</td>
</tr>
<tr>
<td>FeO</td>
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<td>4.76 (6)</td>
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<tr>
<td>I</td>
<td>nd</td>
<td>nd</td>
<td>~ 290 ppm</td>
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<td>100.05</td>
<td>99.82</td>
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<tr>
<td>NBO/T&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.08</td>
<td>0.08</td>
<td>0.09</td>
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</table>

<sup>a</sup> Data from Feisel et al. (2019)

<sup>b</sup> Absolute values of Br and I estimated based on SIMS analyses and only available for CCX melts.

<sup>c</sup> NBO/T is calculated after (Mysen, 1988) and Giordano et al. (2008).
Table 2: Conditions and results of all experiments. Experiments of the anhydrous series (HX and CCX) were carried out at $P = 1$ bar. Hydrous experiments were done at $P = 160$ MPa. All diffusivities in $m^2 \, s^{-1}$.

<table>
<thead>
<tr>
<th>sample</th>
<th>$T \ [°C]$</th>
<th>$t \ [s]$</th>
<th>H$_2$O [wt.%]</th>
<th>#</th>
<th>$D_F$</th>
<th>s.d.</th>
<th>$D_{Cl}$</th>
<th>s.d.</th>
<th>$D_{Br}$</th>
<th>s.d.</th>
<th>$D_I$</th>
<th>s.d.</th>
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<td>3023535</td>
<td>-</td>
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<td>$8.4 \times 10^{-18}$</td>
<td>2$^b$</td>
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<td>587235</td>
<td>-</td>
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<td>$1.6 \times 10^{-16}$</td>
<td>$4.9 \times 10^{-17}$</td>
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<td>$5.0 \times 10^{-15}$</td>
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<td>$2.0 \times 10^{-16}$</td>
<td>2$^a$</td>
<td>$1.9 \times 10^{-14}$</td>
<td>$5.9 \times 10^{-15}$</td>
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<td>154560</td>
<td>-</td>
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<td>2$^a$</td>
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<td>$1.1 \times 10^{-13}$</td>
<td>$1.4 \times 10^{-14}$</td>
<td>$1.5 \times 10^{-15}$</td>
</tr>
</tbody>
</table>

$a$ Results from EPMA analyses. EPMA data of HX series from Feisel et al. (2019)

$b$ Results from SIMS analyses

*Asymmetric profiles were first fitted each half at a time to confirm reliability of the fit of the complete profile (see text for further discussion)
<table>
<thead>
<tr>
<th>sample</th>
<th>$T$ [°C]</th>
<th>$t$ [s]</th>
<th>H$_2$O [wt.%]</th>
<th>#</th>
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Table 3: Arrhenius parameters of all halogens and oxygen self-diffusion in all investigated melt compositions. \( D_0 \) is given in \( m^2 \text{ s}^{-1} \) and \( E_A \) is given in \( kJ \text{ mol}^{-1} \). Calculation of Eyring diffusivities is described in the text.

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Fig. 1: Concentration vs. distance diagrams of one sample of each investigated melt composition acquired by EPMA and SIMS analyses. In the upper row, data of SiO₂ and totals refer to the secondary y-axis. EPMA data represents absolute values whereas the SIMS data was normalized to the average of the 4 outermost datapoints of each respective halogen in the enriched diffusion couple half. This way it is possible to visualize all halogens of a sample in one diagram.
Fig. 2: Backscattered image and diffusion profiles of sample CCX-H-42. a) Backscattered image of the center part of sample CCX-H-42 showing minor cracks likely caused during rapid quench (few seconds). b) Concentration vs. distance profiles of F, Cl, Br, I and H$_2$O as acquired by SIMS. The halogen data are plotted together with their respective fit curves calculated using equation 1. Diagrams of the other CCX-H samples are provided in the supplementary material.
**Fig. 3:** Arrhenius diagrams of all investigated melt compositions illustrating the individual diffusion coefficients and the corresponding Arrhenius fits of all halogens. 

- **a)** anhydrous HX melt.
- **b)** anhydrous CCX melt.
- **c)** hydrous CCX melt (~1.5 wt.% H$_2$O). The bold black lines indicate the self-diffusivity of oxygen calculated with the Eyring-equation and based on the calculated viscosities of the anhydrous melt compositions (Giordano et al., 2008). The dashed lines in c) indicate calculated oxygen self-diffusion in Rhyolite (dash-dot) and Dacite (dashed) from (Zhang and Ni, 2010). Open symbols represent data based on EPMA analyses.
**Fig. 4:** Halogen diffusivity at 1250 °C of the melts of this and other published studies plotted relative to the ionic radius of the respective halogen. All data are for anhydrous compositions except the hydrous data of the present study. Diffusivities at 1250 °C were calculated from the respective Arrhenius parameters of each composition and halogen. Data from: 1 Alletti et al., (2007); 2 Balcone-Boissard et al., (2009) and Balcone-Boissard et al., (2020); 3 Böhm and Schmidt, (2013).

**Fig. 5:** Comparative Arrhenius diagram of halogen diffusion in anhydrous and hydrous (1.5 wt.% H₂O) trachytic melt determined in this study. Solid lines represent diffusion in anhydrous melt and dotted lines indicate extrapolation to higher temperatures. Long-dashed lines represent diffusion in hydrous melt. Solid symbols show preliminary results of halogen diffusion in melt containing 3.5 wt.% H₂O. Note that the diffusivity of all halogens is even more enhanced in the more strongly hydrated melt.