Halogen diffusion in dry rhyodacitic melt

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1. Introduction

Volatiles in magmas are the main driving force controlling the style of volcanic eruptions. Halogens influence magma properties *(e.g. Dingwell et al. 1985)* and phase equilibria *(e.g. Manning 1981)* and can also have an impact on atmospheric and environmental processes *(e.g. Bobrowski et al. 2007)*. Even though the halogens, in particular F and Cl, are amongst the most important constituents of magmamtic volatiles *(e.g. Symonds et al. 1994, Aiuppa et al. 2009)* our knowledge of their characteristic properties during degassing, such as diffusion and solubility as a function of composition and *P-T* conditions, is still poor. Recent advances showed that F and Cl are exsolved from the ascending magma at relatively shallow depths in basaltic systems *(Spilliaert et al. 2006)*. Monitoring may therefore help to identify pre- or syn-eruptive degassing and magma ascent *(Alletti et al. 2007)*. Studies investigating F and Cl (and Br) diffusion in melts were carried out on basaltic *(Alletti et al. 2007)* or phonolitic *(Balcone-Boissard et al. 2009, Böhm & Schmidt 2013)* melts only. However, the most F-rich melts are generally those of rhyodacitic to rhyolitic composition which also commonly produce the most hazardous eruptions. While few diffusion data for Cl is available on those systems *(e.g. Bai & Koster Van Groos 1994, Yoshimura 2018)*, data for F, Br and I are still mostly lacking.

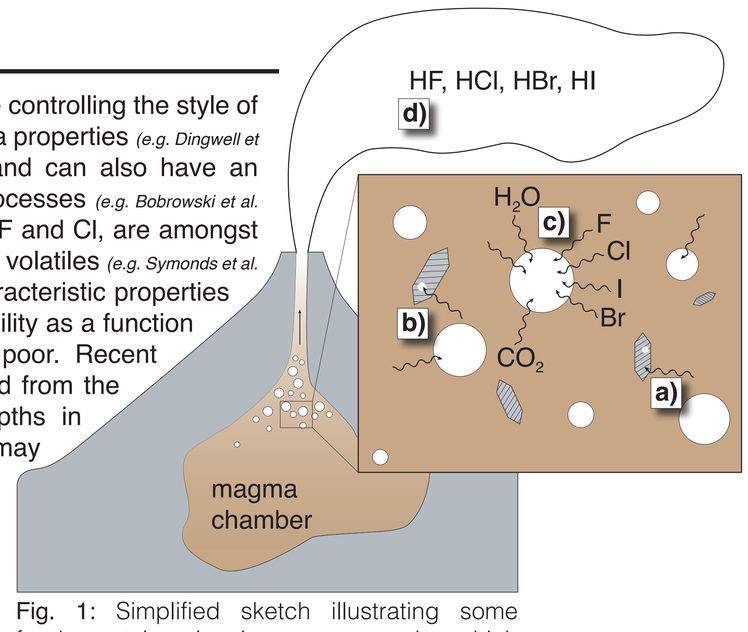


Fig. 1: Simplified sketch illustrating some fundamental volcanic processes in which halogens are involved. a) Crystal growth b) melt inclusion entrapment c) bubble growth d) atmospheric volatile injection. Modified after *Aiuppa et al. 2009.*

2. Objective

Characterize halogen diffusion in anhydrous rhyodacitic melt at temperatures relevant for natural systems.

3. Methods

Diffusion couple experiments

T = 750 - 950 °C
P = 1 atm (+1 @ 100 MPa)
t = 1 - 35 days

Homogenised anhydr. rhyodacitic glass (~ 69 wt.% SiO_2)
Synth. from nat. Hekla H3 pumice

Vertical tube furnace

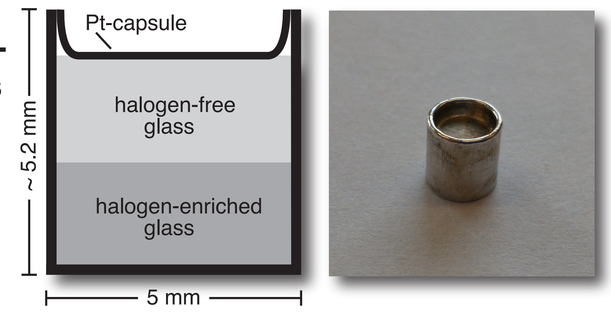


Fig. 2: Sketch showing the capsule geometry of each diffusion couple (left). Finished capsule before the experiment (right).

Quantitative (points + lines) and qualitative (maps) analyses

EPMA (F, Cl)
SIMS (F, Cl, Br, I)

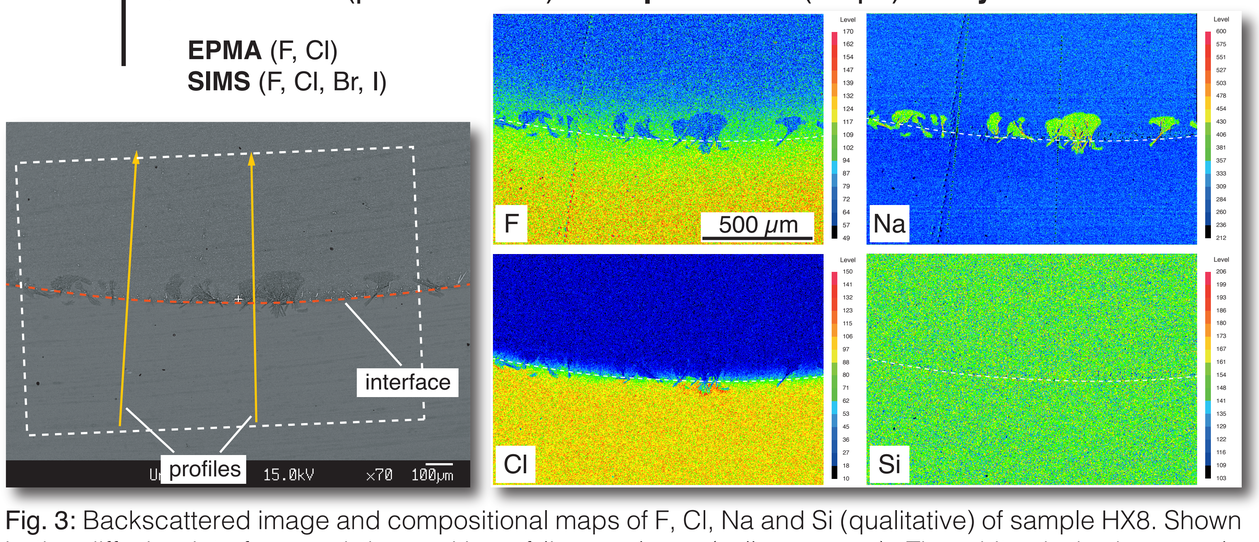


Fig. 3: Backscattered image and compositional maps of F, Cl, Na and Si (qualitative) of sample HX8. Shown is the diffusion interface and the position of line analyses (yellow arrows). The white dashed rectangle represents the area of the maps. Irregular patches of Na-enrichment and F-depletion were avoided for concentration profile analyses.

4. Results

Concentration data obtained by EPMA and SIMS are fitted to the equation for constant one-dimensional diffusivity between two semi-infinite media in a cartesian coordinate system *(Crank, 1975)*:

$$C(x,t) = \frac{C_{low} + C_{high}}{2} + \frac{C_{low} - C_{high}}{2} * \mathrm{erf}\left(\frac{x - x_0}{2\sqrt{\mathbf{D}t}}\right)$$

Diffusion coefficient

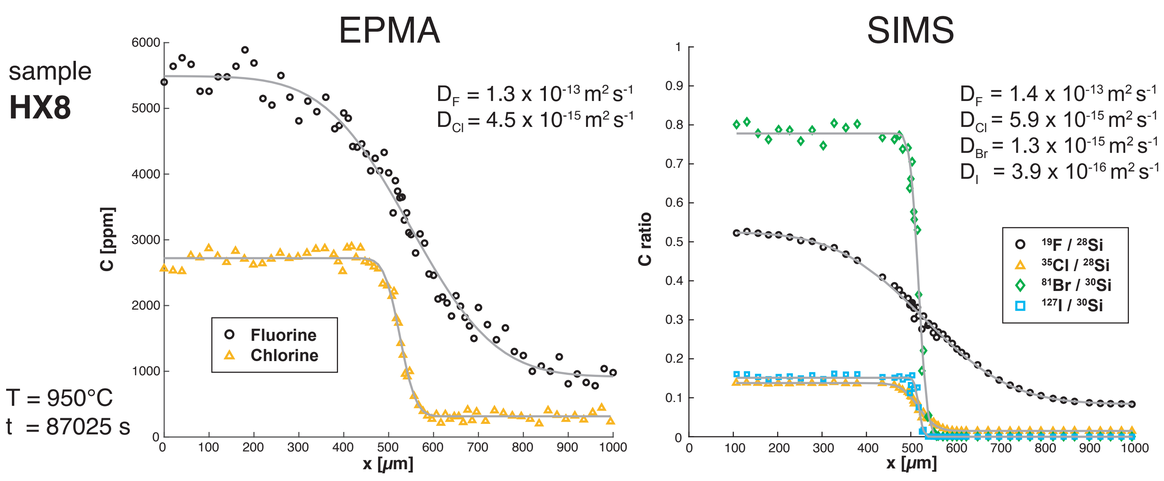
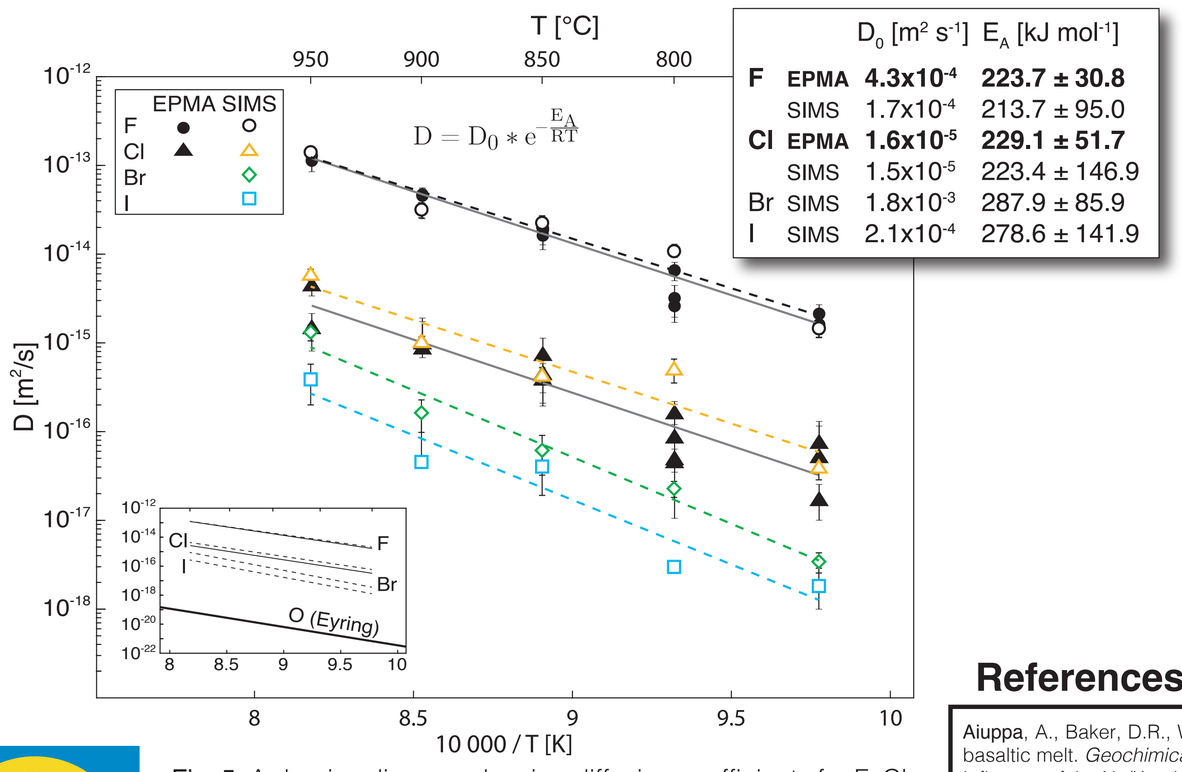


Fig. 4: Concentration vs. distance (EPMA) and concentration ratio vs. distance (SIMS) diagrams of the highest temperature sample (HX8 - 950°C). Grey curves represent fitted functions. D_F and D_{Cl} agree well between the different analytical techniques.



		D_0 [m² s⁻¹]	E_A [kJ mol⁻¹]
F	**EPMA**	**4.3×10^{-4}**	**223.7 ± 30.8**
	SIMS	1.7×10^{-4}	213.7 ± 95.0
Cl	**EPMA**	**1.6×10^{-5}**	**229.1 ± 51.7**
	SIMS	1.5×10^{-5}	223.4 ± 146.9
Br	SIMS	1.8×10^{-3}	287.9 ± 85.9
I	SIMS	2.1×10^{-4}	278.6 ± 141.9

Fig. 5: Arrhenius diagram showing diffusion coefficients for F, Cl, Br and I calculated from fitted diffusion profiles. Solid symbols and corresponding solid grey lines represent D values and respective fits obtained by EPMA while open symbols and dashed lines represent SIMS data. Inlet shows calculated Eyring diffusion of oxygen, based on measured viscosities (at 690, 720 and 750 °C) of the sample material used.

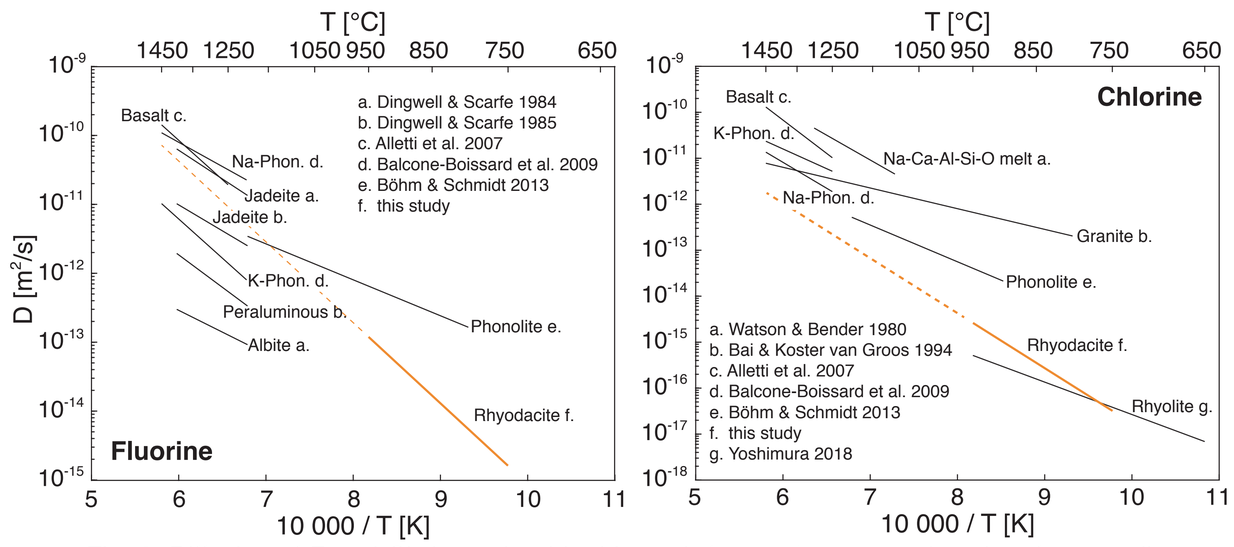
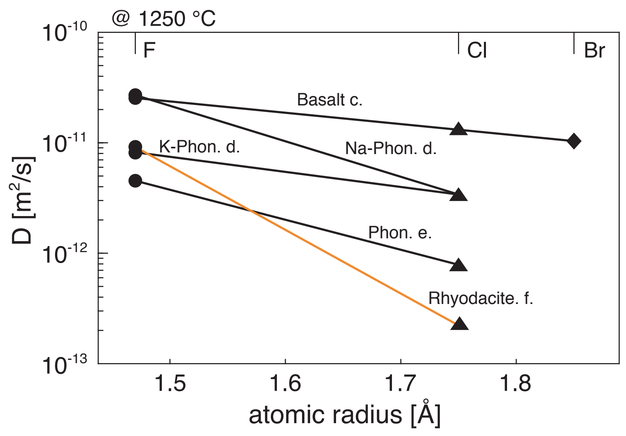


Fig. 6: Diffusion of F and Cl determined in this work (orange) compared to data from studies on other melt compositions. Dashed lines indicate data at higher temperatures, extrapolated using Arrhenius parameters D_0 and E_A.

Fig. 7: Atomic radius vs. diffusivity of F and Cl (and Br) determined in different melt compositions at 1250 °C. Diffusivities of Phonolite (e) and Rhyodacite (f, this study, orange) were calculated from the Arrhenius parameters D_0 and E_A. Different correlations of radius and D among different melt compositions suggest that diffusivity and the diffusion mechanism is dependent on the melt structure.



5. Conclusions & Outlook

- Halogen diffusion in rhyodacite is slow in the relevant temperature range
- Correlation of diffusivity and atomic radius most pronounced in rhyodacite
- Diffusivity and diffusion mechanism dependent on melt structure
- Fractionation may occur under conditions of magma ascent and bubble growth

Next steps:
- Collect more SIMS data
- Hydrous experiments with different H_2O contents
- Model fractionation during degassing and validate in the field

References

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Photography encouraged