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Chlorine diffusion in rhyolite under low-H_2O conditions

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ABSTRACT

The chlorine diffusivity in rhyolitic melts containing < 1.2 wt% H_2O was determined at 650 °C–950 °C and 1.5–11.8 MPa. Diffusion experiments were carried out by reacting rhyolitic obsidian with four types of chlorine sources including a pure Cl_2 fluid, $Cl_2 + H_2O$ fluid mixture, molten NaCl, and NaCl aqueous solution. In the pure Cl_2 experiments, the chlorine diffusivity ranged from 7.7×10^{-18} m^2/s (650 °C) to 8.2×10^{-16} m^2/s (950 °C); it is much lower than previously reported values for rhyolitic melt. The $Cl_2 + H_2O$ fluid mixture experiments revealed that the chlorine diffusivity strongly depends on the water content: it increased by 1–2 orders as the water content of the melt increased to ~1 wt%. In the molten NaCl experiments, sodium infiltrated into the melt while potassium diffused out. The chlorine diffusivity was higher than that in the pure Cl_2 experiments by a factor of 4–10. A single experiment using NaCl solution as a chlorine source resulted in the highest Cl diffusivity, probably due to the high H_2O and sodium contents. The activation energy of chlorine diffusion was 135–202 kJ/mol, and it is comparable to the activation energy in more mafic melts. Because the diffusivity of chlorine is much smaller than that of H_2O and CO_2, a strong diffusive fractionation is expected to occur during magma vesiculation and degassing. Calcium diffusion was observed as a by-product of chlorine diffusion under anhydrous conditions. In the pure Cl_2 experiments, calcium diffusivity ranged from 6.2×10^{-17} m^2/s (650 °C) to 3.9×10^{-14} m^2/s (950 °C), and the activation energy was 177 ± 15 kJ/mol. In molten NaCl experiments, the calcium diffusivity was higher by one order of magnitude, and the activation energy was similar to that for the pure Cl_2 experiments.

1. Introduction

Vesiculation and degassing of magma are the primary factors controlling the driving force and style of silicic volcanic eruptions (e.g., Sparks et al., 1994; Cashman and Mangan, 1994). The mechanisms and history of degassing during magma ascent have been widely investigated based on analyses of volatiles in volcanic glass samples (e.g., Blundy et al., 2010). Since H_2O and CO_2 are major volatile components in magma, many studies have used H_2O–CO_2 systematics as a primary tool to understand degassing processes in the conduit and magma chamber (e.g., Newman et al., 1988; Rust et al., 2004; Rust and Cashman, 2007). Although chlorine is less abundant than H_2O and CO_2 ($H_2O = 70–98\%$, $CO_2 = 0.3 - 49\%$, $HCl = 0.1 - 1.7\%$ in volcanic gas; Aiuppa et al., 2009), degassing processes can be tracked through its exsolution behaviour. This is especially true for shallower zones where CO_2 has already been degassed due to low solubility (e.g., Dunbar and Kyle, 1992; Villemant and Boudon, 1998, 1999; Villemant et al., 2008; Balcone-Boissard et al., 2008, 2010). These studies have traditionally assumed that the gas and melt are always in chemical equilibrium. However, it is increasingly recognised that disequilibrium degassing may also play a crucial role in controlling the composition of volatiles because the diffusivities of volatile components may differ significantly. For H_2O–CO_2 components, disequilibrium degassing is considered to be a common process as the diffusivity of CO_2 is one order of magnitude lower than that of H_2O (Watson, 1991; Gonnermann and Manga, 2005; Yoshimura and Nakamura, 2010; Pichavant et al., 2013; Yoshimura, 2015; Le Gall and Pichavant, 2016a, 2016b). This effect is especially strong for rhyolitic magma where the temperature is low (Yoshimura, 2015). For chlorine, however, although some studies have noted the possibility of disequilibrium degassing (Balcone-Boissard et al., 2008; Barnes et al., 2014), the extent of this has not been quantified. Chlorine diffusivity should be determined accurately before using it as a tracer for shallow-zone degassing.

Previous studies have investigated chlorine diffusion in silicate melts across a broad range of compositions including rhyolitic, phonolitic, and basaltic (Watson, 1991; Bai and Koster van Groos, 1994; Alletti et al., 2007; Baker and Balcone-Boissard, 2009; Balcone-Boissard et al., 2009; Böhm and Schmidt, 2013). For rhyolitic melts, Watson (1991) first reported four data points for the chlorine tracer diffusivity under hydrous conditions by using a ^{36}Cl radiotracer technique. Bai and Koster van Groos (1994) carried out chemical diffusion experiments using NaCl as the source for chlorine under both dry and hydrous

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conditions. However, chlorine diffusivity data for rhyolite under low-H_2O conditions, which corresponds to the shallow-zone of a volcanic conduit or lava dome, are still insufficient to accurately understand degassing processes.

In this paper, I report new results with respect to the chlorine diffusivity in rhyolitic melts containing < 1.2 wt% H_2O at 650 °C–950 °C. Natural rhyolitic obsidian was reacted with four types of chlorine sources including pure Cl_2 fluid, $Cl_2 + H_2O$ fluid mixture, molten NaCl liquid, and aqueous NaCl solution. The experiments revealed that under anhydrous conditions the chlorine diffusivity is much lower than that previously expected for rhyolite. It increases dramatically with increasing water content. The results indicate that the chlorine degassing may occur in a disequilibrium manner, especially when the ascent of magma is rapid. In some experiments, calcium diffusion towards the surrounding fluid was observed. In these cases, the Ca diffusivity was determined as a by-product of chlorine diffusion experiments.

2. Experimental and analytical procedures

2.1. Starting material

Two types of naturally-occurring rhyolitic obsidian with a similar composition (Table 1) were used for the chlorine diffusion experiments. Natural obsidian was used because large, homogeneous rhyolitic glass cannot be readily synthesised in our experimental laboratory. One sample was pale-brown, transparent rhyolitic obsidian collected from a quarry at the Wada-Pass (WP) in Central Japan. This obsidian occurs at a marginal section of a cylindrical volcanic conduit or near the base of a lava flow (Yamazaki et al., 1976). The total water content of this obsidian is 0.56 wt%. Multiple-point analysis using EPMA and FT-IR showed that WP obsidian is homogeneous throughout the sample a few tens of centimetres thick (Table 1). Because of the relatively high water content, WP obsidian vesiculates to a foam when heated above 700 °C under atmospheric pressure. Therefore, this obsidian was used for experiments with a high total pressure (> 1.5 MPa). Another type of obsidian is ST obsidian from Shirataki in Hokkaido, Japan. This obsidian constitutes an outer part of a thick rhyolite lava flow (Sano et al., 2015; Sano and Toramaru, 2017). This obsidian is black and less transparent than WP obsidian as ST obsidian contains magnetite crystallites. The presence of magnetite crystallites is considered to have no major effect on chlorine diffusion because of its small abundance of < 0.3 vol% as estimated from analysing a backscattered electron image. The interstitial glass is colourless and transparent. The H_2O content of ST obsidian is 0.16 wt% (Table 1). Multiple-point analysis showed that ST obsidian has a homogeneous glass composition (Table 1). Because of the low H_2O content, ST obsidian does not vesiculate when heated to > 1000 °C, even under a vacuum. Therefore, ST obsidian was used for molten NaCl experiments (Section 2.4), where the sample chamber is close to a vacuum. Both WP and ST obsidian contain no detectable CO_2 (less than a few ppm, analysed with FT-IR), sulphur (< 0.1 wt%, analysed with EPMA), or fluorine (< 0.1 wt%, analysed with EPMA).

Table 1
Chemical composition of starting obsidian.

Oxides (wt%)	WP[a]	ST[a]	Lake County[b]	LGB[c]
SiO_2	76.92 (0.11)	76.52 (1.03)	76.37	77.86
TiO_2	0.09 (0.04)	0.02 (0.03)	0.15	0.07
Al_2O_3	12.30 (0.06)	12.40 (0.16)	13.35	12.64
FeO^t	0.54 (0.04)	1.49 (1.18)	0.79	0.80
MnO	0.05 (0.05)	0.04 (0.04)	0.06	0.04
MgO	0.04 (0.01)	0.01 (0.01)	0.07	0.06
CaO	0.51 (0.02)	0.53 (0.04)	0.51	0.62
Na_2O	3.87 (0.06)	3.84 (0.15)	4.31	3.88
K_2O	5.01 (0.10)	4.89 (0.12)	4.67	4.03
Cl	0.12 (0.01)	0.09 (0.02)	na	na
H_2O	0.56 (0.05)[d]	0.16 (0.05)[d]	na	2.6 ppm
Total	100.00[e]	100.00[e]	100.28	100.00

[a] Parenthesis indicates a standard 1σ deviation for multiple point analysis in a single obsidian chunk.
[b] Obsidian used in Watson (1991).
[c] Obsidian used in Bai and Koster van Groos (1994).
[d] Total H_2O (OH + H_2O molecule). Measured with FT-IR.
[e] Normalised to 100%.

2.2. Pure Cl_2 experiments

The starting material for the pure Cl_2 experiments was WP obsidian. A slab with dimensions of 1.5 mm × 1.5 mm × 8 mm was prepared from a chunk of WP obsidian, ultrasonically cleaned in acetone, and kept in a desiccator until use. A quartz glass pressure vessel (Speed and Filice, 1964) was used for the experiments. The obsidian slab was put in a 20 cm long thick-wall quartz glass tube, one end of which had been presealed with an oxygen torch. The inner and outer diameter of the tube was 2.5 and 6 mm or 1.5 and 4.5 mm, respectively. The 2.5–6 mm type was used in the earlier stage of this study. The larger type was replaced with a 4.5–1.5 mm type to improve pressure resistance after some experiments failed due to explosion during heating. The pressure resistance did not seem to improve, however. The tube containing the obsidian slab was connected to a chlorine purification line and air was evacuated. A known amount of nearly pure chlorine gas (Cl_2) was then introduced (see Appendix A for the detailed technique) and the tube was closed with an oxygen torch at a distance of ~10 cm from the bottom. Because the thickness of the obsidian slab was sufficiently small compared with the inner diameter of the tube, the entire surface of the slab was securely placed in direct contact with the chlorine fluid. The quartz glass vessel (Fig. 1) was placed in an electric furnace and was kept at 650 °C–950 °C for 23–216 h. Upon heating, the chlorine becomes a single gas or supercritical fluid phase under the experimental pressure and temperature conditions (critical temperature and pressure are 416.956 K and 7.99 MPa, respectively; Angus et al., 1985). The pressure within the quartz glass vessel was 1.5–11.8 MPa, estimated

Fig. 1. Quartz glass pressure vessels for pure Cl_2 experiments. A rectangular WP obsidian slab is immersed in liquid Cl_2. The space above the liquid is filled with Cl_2 gas. A similar experimental setup was used for other experimental series.