



Fluorine and chlorine diffusion in phonolitic melt

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ABSTRACT

The chemical diffusion of fluorine and chlorine in a Na-rich phonolitic melt of Montaña Blanca, Tenerife, was investigated experimentally at 1 kbar in the temperature range of 800 to 1200 °C, for anhydrous conditions and water contents of 2.1 to 2.4 wt.%. Diffusion couple experiments were performed in rapid quench cold-seal pressure vessels and in an internally heated pressure vessel. Experimental durations were 3–24 h for fluorine diffusion and 4–48 h for chlorine diffusion. After the experiments, concentration profiles were measured by electron microprobe along the direction of diffusion and the diffusion coefficients were determined by assuming concentration independent diffusion.

Fluorine and chlorine diffusion increases with increasing temperature and shows Arrhenian behaviour. In the temperature range 900–1200 °C $\log D_{\text{fluorine}}$ ranges from about -12.3 to -11.4 m^2/s and $\log D_{\text{chlorine}}$ from about -13.7 to -12.3 m^2/s . Thus, fluorine diffusion is faster by about one order of magnitude than chlorine diffusion. Dissolving about 2 wt.% water in the melt leads to a diffusivity increase by a factor of ~ 3 for fluorine (2.1 ± 0.1 wt.% H_2O) and by a factor of ~ 7 for chlorine (2.4 ± 0.3 wt.% H_2O). The activation energies for F and Cl diffusion are quite similar in dry and hydrous (2.1–2.4 wt.% water) melts and were determined to be about 100 ± 10 and 155 ± 15 kJ/mol, respectively.

These results present the first data on halogen diffusion in phonolitic melts below 1200 °C. The applied experimental conditions are directly relevant for magmatic processes of phonolite erupting volcanoes and the diffusivities do not need to be extrapolated from high temperatures.

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1. Introduction

Volatiles are important components in volcanic magmas due to their influence on transport properties (diffusion and viscosity) and phase relations. In particular, the volatile content of a magma can control its eruptive style. When saturation levels are reached, volatiles exsolve from the melt to form vesicles, which can expand during magma ascent and can lead to explosive eruptions. The bubble growth in the erupting magma is caused by volatile diffusion from the supersaturated melt and by the expansion of existing fluid within the vesicles upon decompression. Therefore, the knowledge of diffusion properties of volatile components is important to understand and to model eruptive behaviour. Although water and carbon dioxide are the most abundant volatiles in magmatic systems, halogens can reach the percent level in highly evolved magmas such as phonolites (Aiuppa et al., 2009). Furthermore, halogens have become routinely measured during monitoring of volcanic activity and may have some potential for the prediction of volcanic eruptions (Aiuppa, 2009).

Despite the important role of transport properties of volatiles in magmatic degassing, the diffusion of fluorine and chlorine has only

been investigated in relatively few studies. Up to date F-diffusion was studied only at high temperatures above 1200 °C for some model systems such as albite, jadeite or a peraluminous Na-aluminosilicate melt (Dingwell and Scarfe, 1984, 1985) and more recently for basaltic (Alletti et al., 2007) and phonolitic compositions (Balcone-Boissard et al., 2009). All available literature data span a range of about 3 orders of magnitude, highlighting a strong compositional dependence of F-diffusion in silicate melts. The data for jadeite melt (Dingwell and Scarfe, 1984, 1985) may suggest a (strong) pressure dependence of about 0.7 log units between 1 atm and 1–1.5 GPa.

Chlorine diffusion was studied so far for basaltic and phonolitic melts at high temperatures between 1250 and 1450 °C (Alletti et al., 2007; Balcone-Boissard et al., 2009), soda lime melt (1100–1300 °C, Watson and Bender, 1980) and to lower temperatures (650–1450 °C) for rhyolitic compositions (Watson, 1991; Bai and Koster van Groos, 1994). All data span a range of about 1.5 to 2 orders of magnitude in the Cl diffusion coefficient, thus indicating a smaller compositional dependence of chlorine compared to fluorine.

However it is obvious that the majority of diffusion data for fluorine and chlorine were obtained in a temperature range, which exceeds the eruption temperatures of highly evolved, halogen rich magmas by several hundreds °C. The aim of this study was to provide chemical diffusion data (i.e. diffusion along a chemical gradient) for a highly evolved Na-phonolitic melt composition of Montaña Blanca, Tenerife, Spain in the pressure and temperature range that is directly relevant for storage

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and eruption of such phonolitic magma (P up to 3000 bars, T between 800 and 1000 °C; e.g. Ablay et al., 1995; Berndt et al., 2001; Harms et al., 2004; Andújar et al., 2008, 2010; Scaillet et al., 2008).

2. Experimental and analytical techniques

2.1. Starting material

As starting material for our study we used a glass with the composition of the Montaña Blanca phonolite (MBP) (Table 1). This composition was already used by Carroll and Blank (1997) and Schmidt and Behrens (2008) for the determination of water solubilities, by Signorelli and Carroll (2000) for measuring Cl solubilities while saturating the melt with a 2-phase H₂O–NaCl fluid and in our group for determining water diffusivity (Schmidt et al., unpublished).

The dry halogen-free starting glass was synthesized from a mixture of oxides and carbonates. The mixture was placed into a platinum crucible and was first decarbonated at 1000 °C and then melted at 1600 °C in a 1 atm oven for half an hour and quenched to a glass by dipping the bottom of the crucible into water. To obtain a better homogenisation the mixture was melted 3 times overall, between each melting process the glass was ground in an automatic mortar. The short melting time of 30 min each should avoid Na loss. Since the halogen free 1 atm glass contained numerous air bubbles, the glass was ground to a powder, densely packed into Au₇₅Pd₂₅ capsules (6 mm outer diameter, 0.2 mm wall thickness, 30 mm length) that were welded shut. These samples were melted at 1200 °C, 1 kbar for 1 day in an internally heated pressure vessel (IHPV) to produce bubble free glass cylinders suitable for diffusion experiments.

Halogen enriched glasses for the diffusion experiments with about 1 wt.% F and 0.4 wt.% Cl were prepared under pressure in sealed capsules. The Cl-enriched glass was produced by mixing AlCl₃ to the MBP glass powder. For the F-enriched glass NaF was mixed with a separately produced glass which had the composition of the MBP glass except for depletion in Na, such that after adding NaF the composition was consistent with MBP. These mixtures were welded into Au₇₅Pd₂₅ capsules (6 mm outer diameter, 0.2 mm wall thickness, 30 mm length) and were melted at 1200 °C, 1 kbar for 3 days in an IHPV.

To compare F and Cl diffusivity between anhydrous and hydrous conditions, halogen free and halogen bearing starting glasses with about 2 wt.% water were prepared by adding 2 wt.% distilled water to the MBP glass powder or glass–NaF/AlCl₃ mixture. These mixtures were also welded into Au₇₅Pd₂₅ capsules (6 mm outer diameter, 0.2 mm wall thickness, 30 mm length) and were melted in the IHPV at the same conditions (1 kbar, 1200 °C, 1–3 days) and procedures as the water free samples. All starting samples for diffusion experiments were quenched to bubble free glasses by switching off the power of the IHPV furnace. Using this procedure cooling to room temperature took about 10 min and yielded crystal free glass bodies with no or only few stress fractures (rapid quench with these large capsules generally leads to more stress fractures in the glass, which

makes preparation of diffusion experiments more difficult). After the high pressure experiments, the glass cylinders were unwrapped from the Au₇₅Pd₂₅ capsules and were subsequently ground and polished to long glass blocks of about 20×4×1.8 mm. These blocks were then cut by a diamond saw into smaller blocks of 1.5×1.8×4 mm, which were used for the diffusion experiments.

The water contents of the hydrous glasses were determined by near infrared (NIR) Fourier transform (FT) spectroscopy using a Perkin Elmer 2000 FTIR spectrometer with attached IR microscope (Dept. of Applied Geology, University Göttingen). NIR spectra were obtained in 100 scans using a tungsten white light source and a CaF₂ beamsplitter. 3 to 5 spectra were acquired for each sample, the size of the analysed spot was 100 μm in diameter. Water concentration were determined from the peak heights of the absorption band at about 5200 and 4500 cm⁻¹, which are due to molecular H₂O and structurally bonded OH groups, respectively. Linear extinction coefficients for MBP composition glasses were previously determined to be ε₅₂₀₀ = 1.282 ± 0.022 L·mol⁻¹·cm⁻¹ and ε₄₅₀₀ = 1.117 ± 0.052 L·mol⁻¹·cm⁻¹ (Schmidt et al., unpublished). The water contents of the halogen free and the F-bearing starting glass were 2.1 ± 0.1 wt.% and 2.6 ± 0.1 wt.% for the Cl-bearing starting glass, resulting in diffusion couples with average water contents of 2.1 ± 0.1 and 2.4 ± 0.3 wt.% for fluorine and chlorine, respectively. The higher water content in the Cl-bearing glasses originates most likely from the use of highly hygroscopic AlCl₃ as Cl source.

2.2. Diffusion experiments

The diffusion experiments were performed using the diffusion couple technique. The F- or Cl- enriched glass blocks were assembled with F- or Cl-poor glass blocks and were wrapped in Au- or Pt-foil (0.05 mm thickness) according to the experimental temperature. This wrapping ensured a good contact of the polished 1.5×1.8 flats between the two glass blocks. Subsequently these packages were placed into Pt-capsules (3 mm outer diameter, 0.15 mm wall thickness, 15 mm length) and were welded shut.

The diffusion experiments were performed in 2 types of pressure vessels. Experiments between 800 and 950 °C were performed in rapid-quench (RQ) cold-seal pressure vessels (CSPV) made of Inconel IN713LC alloys and were pressurised with water. These vessels were used in vertical operation and were inserted from the bottom into tube furnaces. The vessel design is similar to that described in Matthews et al. (2003). The sample capsules were placed in the hot top part of the vessels and were kept in position by a Ni-filler rod sitting on top of a 1.5 mm diameter stainless steel rod, which was levitated by an external ring magnet fitting over the stainless steel extension to the pressure vessel. Pressure was measured by a pressure sensor and is accurate to ±50 bars. The temperature was measured with a K-type thermocouple located in an external borehole in the top part of the vessel. The sample temperature was determined by calibration of the temperature difference between the temperature in the top bore of the vessel and internal thermocouples at pressure. The temperature accuracy is considered to be ±10 °C and temperature gradients in the hot zone of the vessels (measured by 2 internal thermocouples) are smaller than 10 °C/cm. The vessel design allowed a very rapid heating as well as quenching of the sample. At the beginning of an experiment, the sample was located in the cold, water-cooled part of the connection between the vessel and the stainless steel extension, while the vessel itself was located in the tube furnace and was slowly temperature equilibrated. When the desired temperature was reached, the sample was quickly lifted by the external magnet and the inner stainless steel rod into the top hot part of the vessel. Quenching worked the opposite way and occurred by lowering the magnet to the base of the stainless steel extension, which moved the sample capsule from the hot top part of the vessel back into the water cooled part of the connection between vessel and extension tube. The heating and quench rates were estimated to be

Table 1
Chemical composition of the MBP starting glass from EMP analysis.

	wt.%	stdev
SiO ₂	58.52	±0.23
TiO ₂	0.68	±0.04
Al ₂ O ₃	19.87	±0.14
Fe ₂ O ₃	3.92	±0.09
MnO	0.21	±0.02
MgO	0.36	±0.01
CaO	0.75	±0.04
Na ₂ O	9.90	±0.12
K ₂ O	5.67	±0.04
Total	99.88	
(Na + K)/Al	1.13	

Notes: MBP is similar to sample T2-182 from Carroll and Blank (1997).

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