



Diffusive fractionation of H₂O and CO₂ during magma degassing

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ABSTRACT

H₂O–CO₂ systematics of melt inclusions and obsidian pyroclasts has been used widely to explore the behaviour of fluids in magmatic systems under the assumption that a fluid–melt equilibrium is attained. However, fluid exsolution is a process involving the diffusive transfer of volatiles, and kinetic effects may control the composition of volatiles. In this study, single-step decompression experiments were carried out on H₂O–CO₂-bearing basaltic and rhyolitic melts to investigate the evolution of H₂O–CO₂ compositions during vesiculation. Microanalysis of the volatiles using Raman and infrared spectroscopy showed that CO₂ content decreased towards bubbles, while H₂O content was almost constant throughout the quenched glass samples. This resulted in higher CO₂/H₂O ratios than estimated from the equilibrium degassing, which is interpreted as a kinetic effect: the diffusivity of H₂O is higher than that of CO₂. A simple model for the diffusive degassing of ascending magma was developed to investigate the disequilibrium evolution of its H₂O–CO₂ content. CO₂/H₂O ratios were strongly dependent on the magma ascent velocity. The model was applied to melt inclusions with high CO₂/H₂O ratios from Etna and Stromboli volcanoes, and it was shown that the high ratios could not be explained by diffusive fractionation under a typical magma ascent velocity. Rather, these ratios are affected by other processes, such as CO₂ fluxing.

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1. Introduction

The exsolution and transport of fluids in magmatic systems are crucial processes in the control of volcanic eruptions because fluids constitute the primary driving force of magma ascent. One way to explore the behaviour of fluids in magma is to use the H₂O–CO₂ systematics of juvenile volcanic glasses such as melt inclusions and embayments (e.g., Anderson et al., 1989; Métrich and Wallace, 2008), as well as obsidian pyroclasts (e.g., Newman et al., 1988; Rust et al., 2004). Because the solubility of CO₂ in silicate melts is typically one order of magnitude lower than that of H₂O, CO₂ preferentially partitions into the fluid phase upon vesiculation, decreasing the CO₂/H₂O ratio of the residual melt. Based on this solubility behaviour and equilibrium fluid–melt fractionation models, petrological studies have discussed the degassing and fluid transport processes that occur in magma. If the H₂O–CO₂ content within glass samples produces a trend that can be reproduced via batch distillation, then the magma is considered to have experienced a closed-system degassing, in which the exsolved fluid continues to interact with the melt. If the H₂O–CO₂ trend can be reproduced by a Rayleigh distillation, then the magma is interpreted to have experienced an open-system degassing, in which the exsolved fluid is removed instantaneously. When the CO₂/H₂O ratio is significantly higher than is expected from the above degassing processes, either “CO₂ fluxing”, the addition of CO₂-rich fluids into a magma (Rust et al.,

2004; Spilliaert et al., 2006; Johnson et al., 2008, 2010; Vigouroux et al., 2008; Collins et al., 2009; Roberge et al., 2009; Bachmann et al., 2009; Blundy et al., 2010; Métrich et al., 2010; Oppenheimer et al., 2011; Mormone et al., 2011; Métrich et al., 2011; Yoshimura and Nakamura, 2011, 2013) or conduit convection and magma mixing (Witham, 2011a,b) are thought to be involved.

In contrast, some studies have focused on the disequilibrium nature of degassing, as exsolution of fluid involves the diffusion of volatiles in melt. Because the diffusivity of CO₂ is lower than that of H₂O, CO₂ tends to remain in the melt during degassing, resulting in a high CO₂/H₂O ratio. Such kinetic fractionation was first pointed out by Watson et al. (1982), and then it was incorporated into a degassing model (Gonnermann and Manga, 2005). Recent experimental studies have demonstrated that CO₂-rich melts are generated through this disequilibrium effect (Yoshimura and Nakamura, 2010; Pichavant et al., 2013). In order to use H₂O–CO₂ systematics in volcanology and igneous petrology, the extent to which diffusive fractionation may explain the high CO₂/H₂O ratio should be elucidated quantitatively.

In this paper, I present vesiculation experiments on H₂O–CO₂-bearing basaltic and rhyolitic melts, and demonstrate that diffusive fractionation takes place as a result of the difference in diffusivity of H₂O and CO₂. Vesiculation was caused by a single-step decompression: the melts were first equilibrated with an H₂O–CO₂ fluid at elevated pressure, and then the pressure was decreased instantaneously to induce bubble nucleation and growth. A microanalysis of the volatiles using Raman and infrared spectroscopy showed that CO₂ content decreased near the bubbles, while H₂O content was almost constant throughout the samples. This was a consequence of the diffusive

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fractionation of H₂O and CO₂. A simple diffusion model was then developed to show how H₂O and CO₂ contents evolve during the degassing of ascending magma. Finally, the model was applied to Etna and Stromboli melt inclusion data with high CO₂/H₂O ratios, and the results demonstrated that high ratios cannot be produced by diffusive fractionation alone. Rather, the high CO₂/H₂O ratios of these volcanoes require other processes, such as CO₂ fluxing.

2. Experimental and analytical method

2.1. Basaltic experiments

The starting material for the vesiculation experiments on basaltic melt was a basaltic glass synthesised from scoriae from the 1986 Izu-Oshima eruption. The scoriae were washed in distilled water ultrasonically, dried in an oven at 110 °C, and crushed into a fine powder. The powder was then placed in a platinum crucible and fused in a Siliconit furnace at 1450 °C for 6 h in a CO₂ atmosphere. After quenching, the glass ingot was recovered from the crucible, crushed again, ground in an agate mortar under ethanol, dried at 110 °C for 24 h, and sieved to a particle size of 63–126 μm. The glass composition was measured using a JEOL JXA-8600M wavelength-dispersive electron probe microanalyser at Yamagata University (Table 1). The resulting glass (volatile-free basalt, “VFB”) was chemically homogeneous and free of visible crystals in backscattered electron images.

Decompression experiments were carried out using a piston cylinder apparatus at Tohoku University (Table 2). The VFB powder was loaded into a 1.7-mm-diameter, 7-mm-height platinum-sleeved nickel capsule together with oxalic acid (COOH)₂. The amount of oxalic acid was in excess of the fluid saturation. The experimental run was carried out at 1200 °C and 10 kbar pressure for a period of 3 h. After fluid saturation, the pressure was decreased to 5 kbar in a single step by manually bleeding oil out of the piston ram. The decompression led to a decrease in the solubility of the volatiles and therefore induced bubble nucleation and growth. After 10 min, the sample was quenched by turning off the power. The recovered capsule was cut in half, mounted in epoxy, and polished to a mirror finish. As will be shown in the next section, the fluid in the capsule was not a binary mixture of H₂O and CO₂, but a CO- or CH₄-bearing H₂O–CO₂ fluid. The occurrence of such reduced species was unexpected because the oxygen fugacity in the piston-cylinder cell assembly was close to that controlled by a Ni–NiO reaction (Nakamura and Watson, 2001). The most likely explanation for the reduction is that the drying of the VFB powder after grinding in ethanol was insufficient (e.g., Fine and Stolper, 1985; Nakamura and Watson, 2001). However, I did not discard this run because the reduced species are practically insoluble in silicate melt (Holloway and Jakobsson,

1986; Pawley et al., 1992) and thus are unlikely to have any significant influence on the diffusion behaviour of CO₂ and H₂O.

The volatile composition of the vesiculated glass was analysed using a Thermo Scientific DXR laser Raman microscope at Yamagata University. This method enabled a high spatial resolution analysis of both H₂O and CO₂ (dissolved as CO₃²⁻) concentrations. The detailed procedure for the Raman calibration method is given in the Appendix A. The wavelength, power, and diameter of the incident laser beam were 523 nm, 10 mW, and 0.7 μm, respectively. A grating with 400 lines mm⁻¹ was used to obtain a wide range spectrum (50–6500 cm⁻¹) in a single analysis. The sample surface was focused through a ×100 objective lens. A 10-second acquisition was repeated ten times for a single analysis. The sample suffered no damage during the laser irradiation. The H₂O and CO₂ contents were measured along the radial direction around the bubbles using interval steps of 2 μm.

2.2. Rhyolitic experiments

The rhyolitic experiments presented here have already been reported by Yoshimura and Nakamura (2010). Therefore, the experimental procedure is described here in brief. A slab of rhyolitic obsidian with a WP3-24 composition (Table 1) was placed in a gold capsule together with oxalic acid dehydrate and a mixed Ni–NiO powder. The capsule was then placed in a René 41 reactor and kept at 800 °C at 1 kbar for a period of 96 h using a cold seal pressure vessel. After fluid saturation, the pressure was lowered to 0.5 kbar in a single step by manually controlling the pressure valve; this pressure was maintained for 5000 s. The sample was then quenched by blowing compressed air onto the pressure vessel. After recovery, a doubly polished wafer was prepared from the vesiculated glass, and the H₂O–CO₂ content in the glass was analysed using a Jasco MFT-2000 FT-IR at Tohoku University. The peak heights of absorption bands occurring at 4500 cm⁻¹ (hydroxyl groups), 5250 cm⁻¹ (H₂O molecules), and 2350 cm⁻¹ (CO₂ molecules) were measured. The concentration of volatiles was determined using Beer–Lambert’s Law and the molar absorption coefficients reported by Newman et al. (1986) and Behrens et al. (2004).

3. Results

Fig. 1 shows microscopic images of the vesiculated samples. Based on an image analysis, vesicularity was estimated at 2.1% and 7.4% for the basaltic and rhyolitic experiments, respectively. Figs. 2 and 3 show profiles of the volatile contents in the vesiculated glass samples. In most cases, the CO₂ content decreased towards the bubble–melt interface, which indicated that CO₂ was still diffusing into the bubbles. Profiles B1 and R1 exhibit a CO₂ plateau far from the bubbles (Figs. 2a and 3a), which represents the initial CO₂ concentration before decompression. In contrast, the H₂O content was almost constant throughout the sample. The difference in diffusivity suggests that these are likely the results of kinetic effects: the diffusivity of CO₂ is typically an order of magnitude lower than that of H₂O (e.g., Watson et al., 1982; Watson, 1991). Similar profiles in which the H₂O and CO₂ were decoupling were observed in obsidian pyroclasts (Watkins et al., 2012). Fig. 4 shows the H₂O and CO₂ contents at each analysed point on the profiles. Because the CO₂ content range was large and H₂O content was almost constant, the data produced a near-vertical trend in the H₂O–CO₂ diagram. The data points near the top of this near-vertical trend are those located far from the bubbles, while the points near to the bottom of this trend represent data points near to the bubbles.

To evaluate the effect of diffusive fractionation, the H₂O–CO₂ concentrations of the sample were compared with the equilibrium closed-system degassing path. The equilibrium degassing path was estimated as follows. Firstly, the final equilibrium concentration after decompression (referred as “new”) was estimated by assuming that the melt at the bubble–melt interface is in equilibrium with the fluid.

Table 1
Chemical compositions of starting materials.

	Basalt (VFB)	Rhyolite (WP3-24)
<i>wt% oxides</i>		
SiO ₂	54.39	77.81
TiO ₂	0.96	0.14
Al ₂ O ₃	15.13	12.65
FeO ^a	12.94	0.52
MnO	0.28	0.05
MgO	4.36	0.05
CaO	9.58	0.40
Na ₂ O	2.09	3.06
K ₂ O	0.26	4.65
H ₂ O ^b	0.00	0.66
CO ₂ ^b	0.00	0.00
Total ^c	100.00	100.00

^a Total Fe as FeO.

^b Measured by FT-IR analysis.

^c Normalised to 100%.

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