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Distribution of dissolved water in magmatic glass records growth and resorption of bubbles

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ABSTRACT

Volcanic eruptions are driven by the growth of gas bubbles in magma. Bubbles grow when dissolved volatile species, principally water, diffuse through the silicate melt and exsolve at the bubble wall. On rapid cooling, the melt quenches to glass, preserving the spatial distribution of water concentration around the bubbles (now vesicles), offering a window into pre-eruptive conditions. We measure the water distribution around vesicles in experimentally-vesiculated samples, with high spatial resolution. We find that, contrary to expectation, water concentration increases towards vesicles, indicating that water is resorbed from bubbles during cooling; textural evidence suggests that resorption occurs largely before the melt solidifies. Speciation data indicate that the molecular water distribution records resorption, whilst the hydroxyl distribution records earlier decompressive growth. Our results challenge the emerging paradigm that resorption indicates fluctuating pressure conditions, and lay the foundations for a new tool for reconstructing the eruptive history of natural volcanic products.

1. Introduction

Bubbles nucleate when magmatic volatiles (species such as water, CO_2 and SO_2, that are only weakly soluble in the silicate melt) exsolve from a supersaturated melt. Water is the most important volatile because it is usually the most abundant and because it strongly affects melt viscosity (Hess and Dingwell, 1996). It is dissolved in the melt as two principal species: molecular water, H_2O_m, and hydroxyl groups, OH. As magma ascends, bubbles grow through decompressive expansion and continuing exsolution of volatiles from the melt (Sparks, 1978). Together these processes control the bubble growth rate which, in turn, controls or influences almost every aspect of magma ascent and eruption, including: magma vesicularity, buoyancy, rheology and permeability; the pressure gradient that drives the eruption; and the onset of magma fragmentation. Understanding and quantifying bubble growth is, therefore, one of the most fundamental challenges in physical volcanology.

Water exsolves from the melt, into a bubble, when its solubility in the melt decreases, and resorbs into the melt when its solubility increases. The resulting change in the water concentration at the bubble wall creates a chemical potential gradient in the melt, which drives diffusion towards a growing bubble and away from a shrinking bubble (Fig. 1). The water concentration profile may be preserved when the melt quenches to glass, offering the tantalising prospect of reconstructing the bubble's history of growth and resorption. We quantify the spatial distribution of dissolved water and its species in experimentally-vesiculated magmatic glasses, using secondary ion mass spectrometry (SIMS)-calibrated backscatter

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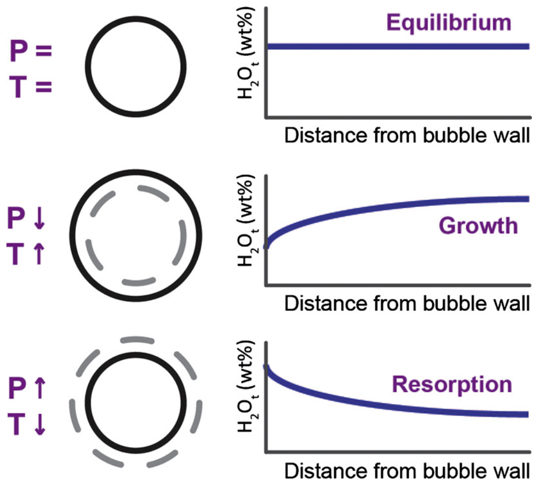

Fig. 1. Bubble growth and resorption. Schematic figure to show the pressure and temperature (P, T) conditions required for a bubble to remain in equilibrium, to grow, or to resorb, with example H_2O_t concentration profiles that result. Solid black lines indicate current bubble size; dashed grey lines indicate previous bubble size, hence whether bubble is growing or resorbing.

scanning electron microscope (BSEM) images (Humphreys et al., 2008) and Fourier-transform infra-red (FTIR) imaging (e.g. Nichols and Wysoczanski, 2007), in order to test this hypothesis.

Two recent studies apply a similar conceptual framework to draw significant conclusions about conduit processes. Watkins et al. (2012) analyse volatile distributions around vesicles in obsidian clasts and find water concentration profiles consistent with bubble resorption (cf. Fig. 1). They infer a pressure increase in the volcanic conduit prior to eruption. Carey et al. (2013) study vesicle distributions in basaltic pyroclasts and find indirect evidence of resorption of bubbles prior to eruption, which they also interpret as evidence of a pressure increase in the conduit. Based on our data, we propose that bubble resorption may occur during the quench from melt to glass as H_2O solubility increases with decreasing temperature, and present an alternative interpretation of these findings in Section 4.4.

Other workers have used textural evidence from experimentally-vesiculated magma samples to investigate interactions between bubbles (Castro et al., 2012). They observe dimpled and sinuous glass films between vesicles, which they interpret as preserved evidence of incipient coalescence of growing bubbles. We analyse water distribution in the same samples and offer an alternative interpretation for their observations, which is consistent with our conceptual model (Section 4.3).

1.1. *Water in silicate melts*

Interpretation of water distributions in glass relies on quantitative models for water solubility and diffusivity. Experimental studies of various magma compositions show that, for crustal pressures relevant to magmatic degassing, solubility increases with increasing pressure and decreasing temperature (Baker and Alletti, 2012; Newman and Lowenstern, 2002) while diffusivity (D) increases with increasing temperature, decreasing pressure, and increasing water concentration (Ni and Zhang, 2008) (Fig. 2). Temperature exerts a dominant control on water diffusivity and, to a lesser extent, on solubility; however, there remains a gap in data between ambient and magmatic temperatures, which includes the transition between melt and glass.

The two species of water present in glass (H_2O_m and OH) interconvert via the equilibrium reaction

$$H_2O_{m(melt)} + O^o_{(melt)} \rightleftharpoons 2OH_{(melt)}, \qquad (1)$$

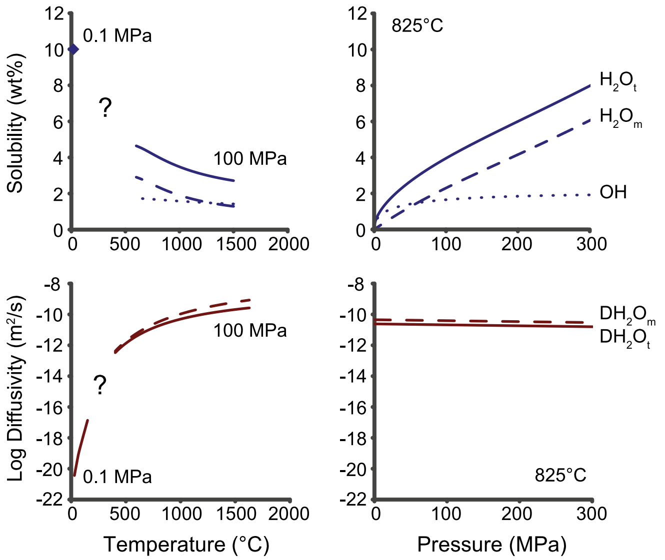

Fig. 2. Controls on diffusivity and solubility of water. Variation in water solubility (upper) and diffusivity (lower) with pressure and temperature for rhyolite composition. A data gap exists between magmatic and ambient temperatures. High-T solubility model is from Newman and Lowenstern (2002) showing proportion of H_2O_m and OH at equilibrium speciation; diffusivity data are from Ni and Zhang (2008) assuming 4 wt% H_2O_t with both H_2O_t and H_2O_m diffusivity shown. Low temperature solubility (diamond) is taken from Anovitz et al. (1999); low temperature diffusivity data (for 0.1 MPa) are from Anovitz et al. (2006).

in which molecular water reacts with bridging oxygens (O^o) in the melt to produce hydroxyl groups that are bound to the silicate polymer framework (Stolper, 1982a). The 'total water' (H_2O_t) content of a melt or glass is the sum of the contributions from H_2O_m and OH. The position of the equilibrium of Eq. (1) (the 'equilibrium speciation') changes with pressure, temperature, H_2O_t concentration and melt composition (Hui et al., 2008; Silver et al., 1990; Stolper, 1989, 1982a) (Fig. 2). The bound OH groups are effectively immobile and H_2O_m is the diffusing species; consequently, OH concentration gradients form indirectly by diffusion of H_2O_m and subsequent readjustment towards equilibrium speciation via Eq. (1) (Zhang et al., 1991). For identical conditions, $D_{H_2O_m}$ is therefore higher than $D_{H_2O_t}$ (Fig. 2). At experimental (or magmatic) temperatures the rate of the species interconversion reaction is sufficiently fast that, following a perturbation to the system, equilibrium speciation is re-established over timescales of milliseconds. As a result of the strong temperature-dependence of the reaction rate however, the time taken to achieve equilibrium speciation becomes much longer as temperature decreases, taking minutes to hours at ∼600 °C and days at ∼400 °C (Zhang et al., 1995, 1991).

2. Materials and methods

Samples are obtained from pre-existing experimental suites, and were manufactured under controlled conditions of pressure (P) and temperature (T). P and T conditions are given in Table 1, along with references to the original studies; sample compositions are given in Table S1 in the Supplementary Information. The experiments were all designed to produce bubble populations with either equilibrium profiles (solubility experiments) or bubble growth profiles (decompression experiments) (Fig. 1).

2.1. *Sample production*

All samples were synthesised at high pressure (P_{syn}) and temperature (T_{exp}, constant throughout experiment) with excess water to form a starting melt that was water-saturated and fully equili-