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Lithium concentration gradients in feldspar and quartz record the final minutes of magma ascent in an explosive supereruption

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ABSTRACT

Pre- and syn-eruptive time-scales of magmatic processes in large-scale explosive eruptions can be quantified from compositional gradients established between (and within) crystals and their host melt using models of diffusive relaxation. The faster the elemental diffusion rate, the shorter the time periods that are measurable. Here we document Li compositional gradients from crystals in the rhyolitic magma of the ~27 ka Oruanui supereruption (Taupo, New Zealand). In plagioclase feldspar and quartz from pumices in the first-erupted material, and loose feldspar crystals from late-erupted ignimbrite, the crystal rims display a ~50% increase in Li concentration over equilibrium values in the crystal cores. At appropriate magmatic temperatures, these gradients represent time-scales of 125 to 720 s, equivalent to decompression rates of 30–180 kPa/s and rise rates of frothy magma of 4–21 m/s. We infer that these short time-scales reflect changes in lithium partitioning behaviour during decompression, and cannot be due to changes in Li concentration accompanying degassing and the growth of bubbles (which act in the opposite sense). The Li partitioning changes are due to the breakdown of the liquid–vapour equilibrium at the critical pressure of 22 MPa, where the vapour phase transitions from a supercritical to a subcritical state. This breakdown causes Li to partition from melt into crystals, inducing a short-lived increase in effective Li activity of about 50%. The system is then quenched rapidly by cooling in air or water on eruption. These results capture syn-eruptive processes on unprecedentedly short time-scales in a type and size of eruption where information concerning such late-stage processes has never before been obtainable.

1. Introduction

An enduring challenge in volcanology is measuring the time-scales of processes involved in the final ascent, foaming and fragmentation of silicic magma during explosive eruptions, especially those extremely large examples termed supereruptions ($>10^{15}$ kg magma: e.g., Miller and Wark, 2008). Quantifying these processes and time-scales from past events is important in understanding eruption dynamics, and in assessing the likelihood of different eruption styles (e.g., fall activity versus production of pyroclastic density currents) and the associated hazards from future outbreaks (e.g., Cioni et al., 2008; Dellino et al., 2010). Direct measurements of the final stages of magma rise and eruption are not possible. Rather, inferences about the immediately pre- and syn-eruptive behaviour of magma rely on proxy data from experiments (e.g., Austin-Erickson et al., 2008; Kremers et al., 2010), measurements on erupted fragmentary material (e.g., Klug et al., 2002; Shea et al., 2010), or remote measurements from geophysical techniques (e.g., Brenguier et al., 2008; Di Grazia et al., 2009).

Linking these different approaches, so that rates of syn-eruptive processes can be inferred from the characteristics of materials discharged during past eruptions, especially those of great size or explosivity, requires exploitation of non-equilibrium processes that are quenched in on rapid cooling (e.g., Wilding et al., 1995; Zhang et al., 2000). Measurements of compositional gradients in minerals and glasses have been widely used to quantify the growth and development of silicic magma bodies over periods of 10^0 to $>10^5$ years (e.g., Costa et al., 2008; Zhang and Cherniak, 2010, for reviews). However, use of diffusive processes to quantify the short time-scales associated with processes during the explosive eruptions themselves has not yet been fully explored. Gradients generated by elemental or isotopic diffusion during shortly pre- and syn-eruptive processes can capture information on a variety of time-scales, depending on the element(s) and phases (minerals and/or glass) involved. Of the solid elements, lithium is particularly mobile and knowledge of the diffusion coefficients at magmatic temperatures (Giletti and Shanahan, 1997; Richter et al., 2003) suggests that preservation of Li concentration gradients that deviate from equilibrium mineral-melt partitioning values

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must represent exceptionally short-lived processes, operating over timings of hours or less. Here, we use micro-scale Li analyses on single crystals from the deposits of a well-documented explosive supereruption to show how the latest-stage syn-eruptive processes associated with large-scale, prehistoric explosive activity can be quantified over unusually short time-scales.

The ~27 ka Oruanui eruption, New Zealand, is the youngest supereruption on Earth (Wilson, 2001; Wilson et al., 2006). About 530 km^3 of moderate- to high-silica rhyolite magma with between 4 and 13 wt.% crystals were discharged to generate sub-equal volumes of (a) widespread fall deposits, (b) non-welded ignimbrite and (c) intra-caldera fill in an episodic, complex eruption (Wilson, 2001). Entrapment pressures recorded by melt (glass) inclusions in quartz crystals, inferred to have been at the gas saturation pressure with respect to a H_2O–CO_2-dominated fluid phase (Wallace et al., 1995), are between ~100 and 200 MPa, equivalent to pre-eruptive storage depths of c. 4 to 8 km (Liu et al., 2006). Similar pre-eruptive storage depths (within uncertainties) are also reflected in apparent pressures derived from amphibole compositions (Wilson et al., 2011, using methods of Ridolfi et al., 2010).

Concentration gradients of water and CO_2 in melt pockets in Oruanui quartz crystals have previously been interpreted to reflect magma decompression rates of 1–7 kPa/s, equivalent to magma ascent rates of 5–35 cm/s under litho- (or magma-) static pressures (Liu et al., 2007). These decompression/rise rates are capturing syn-eruptive processes that occurred over periods of tens of minutes to hours, as the magma ascended as a coherent but expanding foam from its storage pressures towards and into the conduit. The final processes of vesiculation and fragmentation, however, operated at rates too fast to be captured by H_2O and CO_2 diffusion. Because Li has a diffusion coefficient about 2–3 times faster than H_2O (Richter et al., 2003; Zhang and Behrens, 2000), it has the potential to respond to changes in conditions on even shorter time scales. Here, we report Li measurements in Oruanui plagioclase feldspar and quartz crystals by Secondary Ion Mass Spectrometry (SIMS). We couple these measurements with diffusion modelling to determine rise rates of the Oruanui magma during the dynamic processes of volatile exsolution and bubble growth to the point of fragmentation and quenching upon eruption. We use the plagioclase data in the first instance because it has an established diffusion coefficient (Giletti and Shanahan, 1997), then compare our quartz data against the feldspar data to arrive at a first-order estimate for the diffusion coefficient of Li in quartz. We have adopted this approach because published diffusivity values for Li^+ uncoupled diffusion in quartz (Verhoogen, 1952) are calibrated at temperatures significantly different to the magmatic temperature, and extrapolation may be invalid.

1.1. Samples and analytical methods

1.1.1. Samples

For this work we sampled material at two stratigraphic levels in the Oruanui deposits.

(a) A single pumice (sample P1961) was collected from within 10 cm of the base of the initial pumice lapilli-rich fall unit of phase 1 at a location at NZ metric (NZMS260) 100 m grid reference U18/708739. Here the fall deposit is 2.2 m thick and evenly graded so that the height at which samples are collected can be related to a first order to the elapsed proportions of magma erupted in that phase. We thus infer that clast P1961 was erupted as part of the first ~0.001 km^3 of the whole ~530 km^3 magma volume in the eruption (Wilson, 2001). The clast was gently crushed and plagioclase feldspar and quartz crystals with adhering glass selvedges were handpicked from a 250 μm to 1 mm sieve fraction.

(b) Plagioclase feldspar grains with distinctive blue-grey cloudy cores and adhering glass selvedges were hand-picked from the 1–2 mm sieve fraction of a bulk sample of the phase 9 ignimbrite from a location at U18/890739. Additional examples of the feldspars from this sample were used in the study by Charlier et al. (2008).

1.1.2. Methods

SIMS analyses were carried out using the Sensitive High Resolution Ion Microprobe–Reverse Geometry (SHRIMP–RG) instrument at the joint U.S. Geological Survey–Stanford ion microprobe facility in the School of Earth Sciences, Stanford University. Quartz and feldspar grains were mounted in 25 mm diameter epoxy discs, then ground and polished to provide a cross section through the approximate mid-section of each grain. Mounted samples were inspected with transmitted and reflected light on a petrographic microscope, then imaged via cathodoluminescence (CL) and back-scattered electron (BSE) imagery. The epoxy mounts were cleaned with soapy water and thoroughly rinsed with distilled water, dried in a vacuum oven, then a ~100 nm thick Au coating was applied before loading into the ion microprobe. A primary beam of 1 to 2 nA O_2^-, yielding a spot diameter of 12–15 μm at the sample surface, was used to sputter secondary ions from a series of points along transects within the grains and into the adhering glass selvedge whenever possible.

We used a mass resolution of 6000 at 10% peak height, which eliminated any interference at the mass positions used for all elements. Data were collected in three sessions over nine months. The basic run table included for the purposes of this paper ^7Li, ^{30}Si, $^{23}Na^{16}O$ and $^{27}Al^{16}O$, and counting times at each mass varied from 2 to 10 s as necessary to produce sufficient counting statistics. Because of unfavourable counting statistics, we did not try to systematically measure $^6Li/^7Li$ ratios. Two or three scans through the run table were used for each point, giving a total analysis time for each spot of ~7 min. Background counts for all isotopes measured were insignificant. In the absence of a matrix-matched standard, data were reduced by determining average counts per second for each isotope and calculating a ratio with respect to ^{30}Si. The external reproducibility of the $^7Li/^{30}Si$ count ratios is estimated at ±0.8%, 2 S.D., from repeated analysis of NIST 610 and 612, and natural rhyolite glasses RLS-37, -132, -140, -158, 76–75 and Macusani (Macdonald et al., 1992).

Following SIMS analysis, the analysed grains were imaged again using light microscopy to determine the precise analysis pit locations relative to the crystal margins (e.g., Fig. 1a). The major element compositions of the feldspar grains along transects parallel to the SIMS traverses were then determined using the Cameca SX-100 electron microprobe at the Open University (e.g., Fig. 1b,c). Where possible, the anorthite compositions were taken directly in this manner; for some spots, however, SIMS spots had their anorthite compositions determined by calibrating the BSE response in and around the SIMS analysis spot in the manner of Ginibre et al. (2002).

2. Results

2.1. Plagioclase feldspar

For the feldspar crystals, analytical data can be divided into two groups. First, within the crystal interiors there is a linear relationship between Li concentration and major element composition (e.g., Fig. 1d). Second, towards the crystal margins there is observed an increase in the $^7Li/^{30}Si$ ratio, apparently independent of major element composition, and the highest values of $^7Li/^{30}Si$ ratios are found at the crystal rims (Fig. 1e).

Prior to interpreting these data, there are several factors that need to be taken into account which influence the final values used in this paper. First, the raw Li and Si count rates vary according to sputter rate, and are further fractionated by the difference in ionisation efficiency. This is why we report the $^7Li/^{30}Si$ ratio, rather than an absolute Li concentration. However, in a plagioclase crystal, the Si