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Message in a bottle: Spontaneous phase separation of hydrous Vesuvius melt even at low decompression rates

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ABSTRACT

Violent explosive volcanic eruptions are destructive and threaten millions of people and infrastructure. Ejected ash, pumice and gases are end-products of volcanic factories sourced deep within magma chambers and conduits. The different production stages are not directly observable. However, experimental simulation reveals different stages of dynamic volcanic processes. The starting point of explosive volcanic eruptions is determined by the phase separation of an H_2O fluid from a supersaturated hydrous silicate melt. The number of formed H_2O fluid vesicles per unit volume of silicate melt (*VND*) is a basic property that controls the efficiency of fluid-melt separation, ascent velocity and finally explosive volcanism. We performed decompression experiments at superliquidus temperatures to simulate phase separation of a single phase hydrous silicate melt during ascent with AD79 Vesuvius white pumice composition using decompression rates of 0.024–1.7 MPa·s^{-1}. The white pumice buried Herculaneum and Pompeii and is representative of other catastrophic phonolitic and trachytic explosive eruptions like the violent 39 ka Campi Flegrei and the 1815 AD Tambora eruption. Here we report a high log *VND* of 5.2 (in mm^{-3}) that is independent from decompression rate within the investigated range. Even at a decompression rate of 0.024 MPa·s^{-1} the formation of a high *VND* inevitably causes rapid degassing due to short H_2O diffusion distances from the melt into fluid vesicles. A decompression rate meter based on nucleation theory, which is commonly used to estimate magma ascent velocity during volcanic eruptions using *VND* of volcanic ejecta, cannot be adapted to explain our experimentally determined decompression rate independent *VND*. Alternatively, decompression induced H_2O–silicate melt phase separation may be described by diffusion controlled spinodal decomposition where maximum supersaturation is reached. This process occurs spontaneously and free of activation energy if hydrous melt is driven into thermodynamic instability where the second derivative of free energy of mixing to the H_2O content is ≤ 0. However, the decompression rate independent *VND* has profound consequences for the dynamics of natural polyphase hydrous magma phase separation. Even at low ascent rates spontaneous hydrous melt phase separation facilitates rapid density decrease accompanied by sudden increase of magma buoyancy triggering explosive eruptions.

1. Introduction

Violent explosive volcanic eruptions that ejected in the past up to thousand km^3 magma, like Vesuvius (AD79; ~3 km^3; Cioni et al., 2008) Tambora (1815; 100 km^3) and Campi Flegrei (36 ka; 100–200 km^3) are extremely destructive (e.g. Miller and Wark, 2008). Actually, potentially explosive volcanic systems threaten millions of people and infrastructure. The ejecta composed of ash, pumice and gases are end-products of volcanic systems rooted deep within magma chambers and conduits. The dynamic processes in the Earth's interior prior and during eruptions are not directly observable. However, experimental simulation provides access to different stages of complex dynamic volcanic processes. During magma ascent the solubility of H_2O, the most important volatile component dissolved in magma, decreases with decreasing pressure (P) (e.g. Iacono-Marziano et al., 2007). Increasing supersaturation of hydrous silicate melt leads to phase separation of an H_2O fluid, an important prerequisite to initiate explosive volcanism (e.g. Gonnermann and Manga, 2007). The resulting vesicularity is described by the vesicle number density (number of vesicles per unit volume of silicate melt, *VND*) and porosity Φ. Previous experimental degassing studies of e.g. rhyolite (e.g. Hamada et al., 2010; Mourtada Bonnefoi and Laporte, 2004; Gardner et al., 1999) report a strong increase of *VND* with decompression rate (dP/dt). One order of magnitude increase in decompression rate causes an

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increase of *VND* by 1.6 log units, such that the *VND* of natural volcanic ejecta is commonly used to reconstruct the ascent velocity of a magma by using calculations based on nucleation theory (e.g. Toramaru, 2006).

First superliquidus decompression experiments with Vesuvius white pumice phonolite (VAD79) that buried Herculaneum and Pompeii, representative of other catastrophic phonolitic and trachytic explosive eruptions like the violent 39 ka Campi Flegrei (e.g. Mastrolorenzo et al., 2001) and the 1815 AD Tambora eruption (Foden, 1986), have been conducted by Iacono-Marziano et al. (2007). They have shown that the experimental investigation of hydrous melt phase separation at low decompression rates is limited by the capsule size due to diffusional loss of H_2O towards heterogeneously nucleated vesicles at the capsule–melt interface (fringe vesicles) early formed at low supersaturation during decompression. In the central part of the samples they observed a high $\log VND$ of ∼5.8 (*VND* in mm^{-3}) but no clear dependence of *VND* from decompression rate ranging from 1.7–4.6 $MPa{\cdot}s^{-1}$. Marxer et al. (2015) found a similarly high $\log VND$ of 5.4 for VAD79 melt towards higher decompression rates up to 10 $MPa{\cdot}s^{-1}$. Even at low decompression rates down to 0.17 and 0.024 $MPa{\cdot}s^{-1}$ Preuss et al. (2016) report a high $\log VND$ of ∼5 for VAD79 and Campanian Ignimbrite (Campi Flegrei) composition ensuring that supersaturation in the central part of the melt filled capsule was not affected by diffusional H_2O loss prior to vesicle formation.

To verify the decompression rate independency of *VND* in crystal free hydrous phonolitic melt which would be a new challenge for the interpretation of volcanic ejecta and dynamics, we extend within the frame of this study the dataset for single phase hydrous VAD79 melt with 5.3 wt% H_2O at superliquidus temperatures of 1323–1373 K to simulate phase separation during ascent using decompression rates of 0.024–1.7 $MPa{\cdot}s^{-1}$. The experimental results are essential to understand the initial step of phase separation generating fluid vesicles within silicate melt that is followed by vesicle growth, Ostwald ripening, coalescence, percolation and magma fragmentation. The *VND* controls the efficiency of diffusion controlled degassing of hydrous silicate melt. This is the basic production stage of the volcanic factory and a prerequisite to gain detailed insight into the degassing behavior of natural magma that usually is composed of hydrous silicate melt, crystals and possibly preexisting fluid vesicles prior to ascent and explosive volcanic eruptions. The understanding of homogeneous phase separation is one important part for computational modeling of volcanic activity and finally for risk assessment of potentially explosive volcanic systems.

2. Methods

2.1. Starting material and capsule preparation

A crystal free VAD79 glass was synthesized following the protocol of Marxer et al. (2015) with additional improvement of the final cooling step: The melt was air cooled from 1873 K to a temperature nearby the glass transition (T_g) within ∼1 min to inhibit crystallization. Then the supercooled melt was transferred into a furnace preheated to 833 K, whereupon the furnace was switched off to maintain a cooling rate of ∼5 $K{\cdot}min^{-1}$ to room temperature, which successfully minimized tension induced crack formation within the glass batch.

Cylinders with 5 mm diameter were drilled out of the glass, cut to 6.5 mm length and ground at the edges to prevent capsule damage during pressurization. One cylinder was embedded in epoxy resin and ground and polished for electron microprobe analysis (EMPA). Successful homogenization of the anhydrous glass was confirmed by the EMPA using measurement conditions as described in Preuss et al. (2016) (SiO_2: 57.24%; TiO_2: 0.29%; Al_2O_3: 21.08%; FeO: 2.71%; MnO: 0.15%; MgO: 0.39%; CaO: 3.19%; Na_2O: 5.38%; K_2O: 9.47%; P_2O_5: 0.1%). Porositiy of the glass cylinders that is caused by some air vesicles enclosed during synthesis was determined with a pycnometer to ensure values <6% prior to hydration (Preuss et al., 2016). Annealed Au80Pd20 capsules (13 mm initial tube length, OD: 5.4 mm, ID: 5.0 mm) were closed with Au80Pd20 lids at the bottom. For slightly H_2O undersaturated conditions prior to decompression (Iacono-Marziano et al., 2007), the glass cylinders were loaded together with 5.3 wt% H_2O into the capsules which were then crimped to a three-sided star at the top and welded shut. Possible leakage was checked by re-weighing of the bottle-shaped capsules after heating to 383 K and again after a pressure test at 100 MPa water pressure and room temperature.

2.2. Decompression experiments

Combined hydration and decompression experiments were conducted in an internally heated argon pressure vessel (IHPV) equipped with a rapid quench setup and a piezo-actuator driven high-pressure valve that facilitates continuous decompression (Nowak et al., 2011). The samples were equilibrated at 200 MPa and 1523 K for 96 h at an intrinsic oxygen fugacity close to $\Delta \log QFM = +3.5$ (Berndt et al., 2002). After hydration the run temperatures were reduced isobarically to 1373 and 1323 K, still above the liquidus and slightly H_2O undersaturated (Iacono-Marziano et al., 2007; Marxer et al., 2015), and held for 0.5 h to thermally equilibrate the samples before decompression. Then the hydrous melts were decompressed isothermally at decompression rates of 0.024–1.7 $MPa{\cdot}s^{-1}$ to induce H_2O supersaturation that is required for homogeneous phase separation at a supersaturation pressure ΔP_{hom}. At final pressures (P_{final}) of 110–70 MPa the samples were quenched isobarically with ∼150 $K{\cdot}s^{-1}$ (Berndt et al., 2002) to room temperature, extracted from the IHPV and re-weighed to test for possible leakage.

To ensure the absence of crystals after hydration prior to decompression, VAD79 samples from the study of Marxer et al. (2015) with 2.5 mm capsule diameter (Ref02–Ref08) that were hydrated at 1323 K, 200–75 MPa and quenched without decompression were re-examined with transmitted light microscopy (TLM, 1000x magnification). Compared to the 5 mm diameter samples from Preuss et al. (2016) that contain small objects of ∼1 µm in the glass, the 2.5 mm samples are free of objects down to the limit of optical resolution. This supports the assumption that the small objects in 5 mm samples are quench-crystals that have formed due to slightly slower cooling of larger samples and that the hydrous melt is crystal free prior to decompression (Preuss et al., 2016).

The air vesicles enclosed during glass synthesis and the air enclosed in the free volume of the capsules after preparation completely dissolves in the melt during hydration at slightly H_2O undersaturated conditions (for details see Preuss et al., 2016). Thus, the phase separation of the hydrous melt starts from a single phase.

2.3. Sample preparation

The decompressed sample capsules were cut along the cylinder axis. One half was prepared for SEM. The other half was prepared to a double-sided polished cantilever thin section (100–250 µm thickness) for FTIR spectroscopy and TLM analysis.

2.4. FTIR spectroscopy

Total H_2O contents (c_{H_2O}) of the decompressed samples were analyzed with a Bruker Vertex v80 FTIR-spectrometer connected to a Hyperion 3000 IR-microscope in the near infrared (NIR) using a CaF_2 beam splitter, a tungsten light source and an InSb