

The density and the compressibility model of hydrous silicate melts at crustal and upper mantle conditions

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The density of hydrous melt is the primary control of various igneous processes, such as the rates of melt separation and upwards migration, and the efficiency of the crystal fractionation and the magma mixing. Despite these importances, the density of hydrous melt is poorly constrained, especially at the pressure range corresponds to crust to wedge mantle (~5GPa). Recently, new precise experimental determined relationship between density and pressure of hydrous silicate melt have been determined using X-ray absorption method (e.g., Sakamaki et al., 2009). In this study, we compile and calibrate the volumetric parameters of dry and hydrous basaltic-rhyolitic melts and construct the density model that describes the density of the silicate melt as a function of T, P, H₂O content and the and composition of the melt.

The Birch-Murnaghan equation is used for the equation of state of the silicate melt. The partial molar volume and the bulk modulus of the dry silicate melt are calculated based on the parameters provided by Lange and Carmichael (1990). K' (the pressure derivative of bulk modulus) is newly parameterized as a function of SiO₂ content. A set of the partial molar volume, compressibility, and K' of the H₂O component in the silicate melt are newly compiled and calibrated based on the results of high pressure experiments that have been reported in previous literature.

The combination of the Birch-Murnaghan equation and the set of parameters well reproduces the experimentally determined pressure-density relations of various dry and hydrous melts such as komatiite, phonolite, andesite and rhyolite between the pressure range of 0-5 GPa. The model covers the pressure, H₂O content and compositional ranges of the entire melting region of the subduction zone. The model and the parameter set will be useful for the calculations of density contrasts between hydrous melt and minerals/wall rock, prediction of physical and chemical state of subduction zone mantle and crust based on inversion of geophysical observations, and the construction of a thermodynamic model for the calculation of phase relations of hydrous melt bearing system. Volume and compressibility of the hydrous melt is well reproduced assuming linear combinations between volumes and compressibility's of dry melt and H₂O component in the melt, indicating H₂O component in silicate melt shows an ideal mixing behavior in terms of volume during dissolution into silicate melt along the entire pressure range tested. This result will be a strong constraint during constructing a thermodynamic model for the calculation of phase relation of the hydrous melt.

Keywords: magma, density, hydrous

Effect of the bonding and the speciation of water on the polymerization and the viscosity of silicate melts

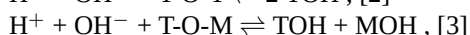
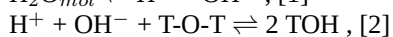
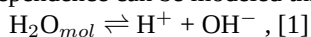
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Degassing of water during the ascent of hydrous magma in a volcanic edifice produces dramatic changes in the magma density and viscosity. This can profoundly affect the dynamics of volcanic eruptions. The water exsolution history, in turn, in part is driven by the water solubility and solution mechanisms in the silicate melt and in part by the decompression history of the magmatic liquid. Previous studies pointed to dissolved water in silicate melts as molecules (H_2O_{mol} species) and hydroxyl groups, OH. The later are commonly considered bonded to Si^{4+} , but may form different bonding, such as with alkali or alkaline-earth cations. Those various bonding mechanisms influence the structure of hydrous melts in different ways, and therefore, the melt properties. As a result, exsolution of water from magmas may have different eruptive consequences as a function of the initial solution mechanisms of water dissolved in the magmatic liquid.

However, and despite their importance, the bonding mechanisms of water in silicate melts are not clear, particularly in regards of their variation with the chemical composition of the melts. In this experimental study, pieces of such information are reported from determination of how water bonds with the ionic network of alkali (Li, Na and K) silicate quenched melts. From ^{29}Si Single-Pulse Magic-Angle Spinning Nuclear Magnetic Resonance (^{29}Si SP MAS NMR) and Raman spectroscopy, decreasing ionic radius of alkali in silicate melts results in decreasing the fraction of water dissolved as OH groups as well as in changing the OH bonding mechanism. Indeed, in K silicate glasses, water resides mostly as OH groups bonded to Si, whereas in Li silicate glasses, the OH content is low and the OH groups are not bonded exclusively to Si. Therefore, present data support previous inferences about a control exerted by the ionic field strength of alkali and alkaline-earth cations on the H_2O_{mol}/OH ratio as well as on the bonding of OH groups with the ionic network of hydrous silicate melts.

This implies that water has different effects on the polymerization of melts as a function of their chemical composition. Such dependence can be modeled through the following reactions:



where T = Si, Al and M is an alkali or an alkaline-earth cation. Equation [1] is the self-ionization reaction of water. The product ions can react with bridging oxygen in T-O-T bonds (eq. 2) or with non-bridging oxygen in T-O-M bonds (eq. 3). The fraction and ionic field strength of the various T and M elements will influence the equilibrium constants of equations 1, 2 and 3. As a consequence, the water effect on the melt viscosity must change with its chemical composition, because equations 2 and 3 have different implications for the melt polymerization. Such effect is highlighted when comparing the viscosity reduction produced by water solution in rhyolitic and andesitic melts for instance. Indeed, solution of 1 wt% water produces a viscosity reduction ~ 1 order of magnitude greater in a rhyolitic melt than in an andesitic melt.

This conclusion, in turn, may affect the eruptive processes linked to viscous phenomenon, such as, for example, the fragmentation of magmas in explosive eruptions. Indeed, the fragmentation of an ascending magma in a conduit can occur when the elongation strain rate of the magmatic flow becomes greater than the magma viscous relaxation time, because at this point the magma behaves as a fragile solid. Magmas with different compositions will present differences in the equilibrium constants of equations 1, 2 and 3 as well as in water solubility, because the formers define the latter. This will define different evolution paths as a function of depth for their viscous relaxation time and their vesicularity that will eventually affect their fragmentation threshold.

Keywords: water speciation, water bonding, silicate melt, silicate glass, viscosity of magma, fragmentation

Interpreting water contents of submarine pumice: insights from water speciation

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Studies of submarine eruptions are hindered by the logistical difficulties and costs of directly observing and sampling submarine volcanic edifices, and by the difficulties of identifying the eruption source of pumice rafts that may drift for great distances. Many questions remain about the impacts of the overlying water column on eruption processes and, in particular, at what depth explosive pumice-producing eruptions can occur. H₂O solubility in magma increases with increasing pressure so if the magma is saturated with respect to H₂O, the dissolved H₂O content of volcanic glasses provides a way to estimate the pressure at the time of quenching; hence the eruption depth. Silicic pumice however is particularly susceptible to post-eruption hydration by seawater at ambient temperature, which causes high glass H₂O contents with anomalous H₂O speciation. Obtaining meaningful data thus requires distinguishing between the original dissolved magmatic H₂O content and the H₂O subsequently added via post-eruption hydration. H₂O speciation data may enable us to do so. Since H₂O added during hydration is added in the form of molecular H₂O (H₂O_m), and the species interconversion reaction between H₂O_m and hydroxyl (OH) species is negligible at ambient temperature, the measured OH content of hydrated pumice should remain unaltered. Using H₂O speciation models, the corresponding original H₂O_m content can be estimated from the measured OH content, thereby allowing reconstruction of the original H₂O content of the glass. By measuring H₂O speciation in silicic submarine pumice by FTIR, we will examine whether this methodology provides a means to get at the magmatic H₂O content, which can then be used to estimate eruption depths and help locate potential sources of rafted pumice deposits.

Diffusion experiments of chlorine in rhyolitic melts using a pure chlorine source

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<Introduction>

The chlorine degassing in magma is crucial in the control of vapour-induced magma differentiation, ore formation, hydrothermal alteration, and volcano-atmosphere interactions, because the chlorine-rich fluids have high chemical reactivity. Since the degassing is a process involving diffusive transport of the volatiles, it is necessary to quantify the diffusivity of chlorine in silicate melts for the detailed understanding of these phenomena. Bai and Koster van Groos (1994) carried out systematic experiments of chlorine diffusion in rhyolitic melts by using molten NaCl or NaCl aqueous solutions for the chlorine source. In these cases, however, it is possible that sodium infiltrates into the melt to modify the original composition, resulting in the increase of the diffusivity because sodium efficiently cuts the silicate network. In this study, I carried out diffusion experiments of chlorine in rhyolitic melts using pure chlorine to measure the diffusivity without any significant change of the alkali content.

<Experimental>

Chlorine was generated by means of electrolysis of a sodium chloride solution, and it was then purified cryogenically in a vacuum line. A rhyolitic glass slab prepared from natural obsidian was sealed in a quartz glass pressure vessel together with the pure chlorine, and annealed in a furnace at 750 to 950 °C for up to 20 days. The pressure in the vessel was calculated to be 12 to 128 bars. In a selected experiment, water was added to chlorine in the vessel to examine the water-content dependence of the chlorine diffusivity. After quenching, the chlorine contents were quantified along the diffusion profile using an EPMA.

<Results and discussion>

The diffusivity of chlorine under the dry condition was determined to be 3.5×10^{-17} to 5.9×10^{-16} m²/s at 750 to 950 °C. These values are about three orders of magnitude smaller than those previously measured for dry rhyolitic melts using the molten NaCl for the chlorine source (Bai and Koster van Groos, 1994). This difference may be attributed to the difference in the melt composition caused by sodium infiltration. The activation energy of the chlorine diffusion was calculated to be 89 kJ/mol, and is similar to that of Bai and Koster van Groos (86 kJ/mol). This indicates that the mechanism of chlorine diffusion is identical irrespective of the chlorine source. In the water-added experiment, the diffusivity was an order of magnitude greater than that in the dry experiments. Here, the water content of the melt was calculated to be 1.2 wt%.

<Implications>

The present study showed that the diffusivity of chlorine was much lower than previously considered. The chlorine diffusivity showed a strong dependence of the water content. These observations may indicate that the chlorine degassing occurs only when the magma has the high water content before eruption. This idea is consistent with the observation that the groundmass glass of obsidian pyroclasts, pumice, and lavas from Mukaiyama volcano, Nijima island, have the constant chlorine content (0.13 ± 0.01 wt%), while the melt inclusions in quartz contained 0.18 ± 0.02 wt% chlorine (Yoshimura, in preparation).

Keywords: chlorine, degassing, magma

Lava Domes: Eruptions in Chemical Disequilibrium

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Active lava domes display a range of eruptive behaviours which are defined by the local rheological properties of the magma. Magma ascent results in changes in P-T-X which forces volatile exsolution and crystallisation; yet, as these conditions are transient, the magma remains in constant disequilibrium with its surroundings. Volatiles, and principally water, have been argued to be the most important control on magma rheology; they influence the viscosity of the melt and the total production of gas bubbles, which define ascent rates via buoyancy and challenge the physical coherence of magma prompted to fragment. Decompression has long been considered the main variable controlling volcanic eruptions; however, here we assess the effects of temperature.

We present field and experimental results which argue for the importance of thermally-driven disequilibrium in water content. First we test effects of cooling using in situ hydration measurements in a unique simultaneous thermal analyser: Cooling is shown to increase the solubility of water in the melt (both in the relaxed and unrelaxed states), which we find resorbs at rapid rates with the implication that sintering can be accelerated several-fold. This may have significant implications for tuffsite formation in volcanic conduits. Second we test the effect of rapid heating using a high-velocity rotary shear apparatus. Rapid heating is found to trigger foaming and melting of surrounding crystals. The textures developed in these experiments match those observed in ash collected from gas-and-ash explosions at Santiaguito volcano. We use these results to elaborate a new model of fragmentation, in which the mechanical work of ascending magma may induce superheating that triggers partial melting, foaming and fragmentation. Comparison of our findings with current water solubility models suggests that heat may be an overlooked control on eruptive behaviour.

Keywords: foaming, volatiles, fragmentation, fault, frictional melting, sintering

Geochemistry of tephra glasses and sources and origins of huge-volume felsic magmas in Japanese subduction zones

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Dacitic to rhyolitic glass shards from eighty widespread tephra erupted in the past 5 Mys from large calderas in Kyushu, and SW, central, and NE Japan were analyzed. Laser ablation inductively coupled plasma mass spectrometry was used to determine 10 major and 33 trace elements and $^{207}\text{Pb}/^{206}\text{Pb}$ - $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios in the glass shards. The tephra were classified into three major geochemical types and their source rocks were identified as intermediate plutonic, sedimentary, and amphibolite rocks in the upper crust. Few tephra from SW Japan were identified as adakite and alkali rhyolite and regarded to have originated from slab melt and mantle melt, respectively. Pb isotope ratios of the tephra are comparable to those of the intermediate lavas in the source areas but are different from the basalts in these areas. The crustal assimilants for the intermediate lavas were largely from crustal melts and are represented by the rhyolitic tephra. A huge heat source is required for forming large volumes of felsic crustal melts; these are usually supplied by the mantle via basalt. Hydrous arc basalt formed by cold slab subduction is voluminous and its high water content lowers the solidus of the crustal rocks leading to effective felsic magma production. The frequency of caldera eruptions is thus thought to be fundamentally controlled by the basalt production rate depending on the subduction setting either cold-wet or hot-dry and by the subduction rate of the oceanic plate slab, which controls the amount of water being transported beneath subduction zones.

Keywords: Large volume tephra, Geochemistry, Crustal melt, Subduction zones

Water content of glass inclusions in the 1813 ejecta at Suwanosejima volcano by micro FT-IR reflectance method

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Volcanic eruption has wide variety from effusive to explosive eruptions. Volatile content, or mostly water content, at magma chamber has been attributed as one of the driving forces of explosive eruptions. Although degree of degassing, or loss of gas, during ascent in conduit is thought to be a major factor that control eruption styles so far, initial volatile content is still one of the strong factors as a driving force for explosive eruptions because this value would give the upper limit for explosive eruptions. In terms of the initial water content, glass inclusions in phenocrysts have been targeted for years, but it is still difficult to prepare many doubly polished thin sections of small glass inclusions for micro-transmission FT-IR method. Recently Yasuda (2013) developed micro-reflectance FT-IR method for the first time that enables us to analyze many small inclusions without any special treatment of small samples.

Suwanosejima volcano is one of the most active volcanoes in Japan with successive Strombolian eruptions recently. On the other hand, the volcano had experienced much voluminous explosive eruptions, such as Plinian eruptions, every some hundred years in its geologic history (Shimano et al., 2013). It is surely important to know how much water contents of magma was just before such eruptions with different intensity. The 1813 eruption of Suwanosejima volcano is the best example for such objectives. Shimano and Koyaguchi (2001) reconstructed eruption sequence of this eruption and showed that various types of eruptions took place in contrast to homogeneous composition of magma throughout the sequence. By using petrological hygrometer of Housh and Luhr (1991), they have reported that the initial water content was constantly about 3.0 wt.% for all variety of eruption styles assuming equilibrium between melt and the rim of plagioclase phenocryst. Then they showed that difference in the degree of degassing during ascent had controlled eruption styles on the basis of bulk rock water content of the products. However, there are no initial water content reported to be analyzed directly for natural samples. There are also rooms for discussion in terms of heterogeneity of magma because phenocrysts show reverse zoning that may indicate magma mixing just before its ascent. To uncover such aspects, we carried out water content measurement of glass inclusions by micro-reflectance FT-IR method for the 1813 products as well as for those of 10 ka eruption for comparison.

The results of the 1813 products were 1.0-2.0 wt.% and 0.6-1.2wt.% for plagioclase and pyroxene phenocryst, respectively. Those of the 10ka products were 1.4-3.0 wt.% and 2.0-2.4 wt.% for plagioclase and pyroxene phenocryst, respectively.

For the 1813 products, the results show that glass inclusions show systematically lower water content than those estimated by Shimano and Koyaguchi (2001). There may be two possible interpretations; 1) the estimated water content by Housh and Luhr (1991) was incorrect, and 2) the values reflect those at different stage of phenocryst growth. The latter is most likely as most glass inclusions are trapped in the central part of the phenocrysts whereas most phenocrysts show reverse zoning. Thus we interpret that melt has been trapped by phenocrysts when magma had up to 2.0 wt.% of water, and then the rim of phenocryst has crystallized when new magma (or water) came and mixed to be one with water content around 3.0 wt.%. The systematically higher water content of the 10 ka glass inclusions are consistent with that this eruption was more voluminous than the 1813 eruption.

This is the preliminary report and the number of glass inclusion analyzed is not yet enough to cover all the variety of inclusions and host phenocrysts, and we will continue analysis to better constrain water content and its heterogeneity at the onset of eruptions.

Keywords: glass inclusion, water content, micro-reflectance FT-IR, Suwanosejima

Chronology of degassing and magma mixing at Surtsey (Iceland, 1963-67)

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In 1963-67, Surtsey (Iceland) provided the type example of shallow-emergent explosive volcanism; however, magma ascent and degassing in this benchmark eruption remain unconstrained. We use major/trace elements and volatiles in olivine-hosted melt inclusions and glasses to show that multiple distinct melts were stored at 9.5-12 km and subsequently mixed at 6-8 km below Surtsey. The chronological contribution of each melt body to surface processes can be tracked by correlating volatile (H/C, S/C), trace element (HSFE/LILE), and rare earth element (LREE/HREE) ratios of inclusions to the time series of gas and lava compositions that were measured syn-eruptively. This captures progressive shallowing and mixing of melts through time, and allows time-stamped modeling of degassing and melt+gas redox evolution over a 3-year period. Novel correlation between inclusions from surface tephra and historical measurements permits temporal and spatial controls on activity at Surtsey to be determined >50 years after the eruption.

Keywords: volatiles, degassing, geochemistry, pyroclastic, subaqueous, Iceland

Degassed-magma volume estimated from melt inclusion analysis: Kirishima 2011 eruptions and Nishinoshima 2014 eruptions

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Magma ascent and degassing process is essential in order to know how eruption occurs and what controls eruption styles. Melt-inclusion analysis is a powerful method for estimating volatile content of melt in magma before eruption. Combining the melt-inclusion analysis with observation of volcanic gas, we can estimate degassed-magma volume. In this study, degassed-magma volume of recent two eruptions in Japan, Kirishima 2011 eruptions and Nishinoshima 2014 eruptions, was estimated from melt inclusion analysis. Comparing the degassed-magma volume with geological and geophysical observations, magma ascent and degassing processes is discussed.

(1) Kirishima 2011 eruptions. Eruption activity of Shinmoedake began with phreatomagmatic and subplinian eruptions in January 2011, followed by lava effusion within the summit crater, vulcanian explosions, and ash emissions from February-September 2011. The amount of degassed magma was estimated, based on sulfur and chlorine contents of melt inclusions of the mafic and felsic magmas, SO₂ flux and volcanic gas composition during the period of January 2011 to September 2012. The amount of degassed magma was larger than that of eruptive products in 2011, indicating the degassing of magma in the chamber due to convection in a conduit. Considering the mixing ratio of mafic and felsic magmas (0.4), the estimate of degassed mafic magma (19×10^6 m³) is of the same order of magnitude as the observed inflation of the magma chamber during February-November 2011 (10×10^6 m³), suggesting injection of mafic magma into the chamber from deeper down is likely to have caused the inflation and eruption activity of Shinmoedake in 2011.

(2) Nishinoshima 2014 eruptions. The Nishinoshima eruptions started on 20 November 2013 and lava effusion has continued up to present (February 2015). The amount of degassed magma (3×10^6 m³/d) was estimated, based on sulfur content of melt inclusions in products by eruption on 6 June 2014 and SO₂ flux (500 t/d) on 29 January 2014. The amount of degassed magma is similar to lava effusion rate (3×10^6 m³/d, Earthquake Research Institute, The University of Tokyo), suggesting that gas-melt separation did not occur during its ascent from a magma chamber before the eruption.

Keywords: magma, degassing, volatile, melt inclusion, kirishima volcano, nishinoshima volcano

Real-time atmospheric measurements of CO₂ and $\delta^{13}\text{C}$ in volcanic gases emitted from Mt. Etna (Italy)

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We present new data of real-time measurements of concentration and isotope ($\delta^{13}\text{C}$) composition of CO₂ in fumarolic-plume gases emitted from Mt. Etna volcano, performed by using a Delta Ray Isotope Ratio Infrared Spectrometer. The first two campaigns of measurements were carried out on 11 July and on 5-6 September 2013, while a third campaign was performed in mid-July 2014. With the assumption of a two components mixing, a simple linear regression was applied to the data in order to obtain the volcanogenic $\delta^{13}\text{C}$ of CO₂ emitted from the volcano.

Data acquired along the route Catania-Etna, while car was moving, showed an excess of ¹³C-depleted CO₂ when passing through inhabited centers due to atmospheric pollution produced by the cars exhaust. A similar signature was obtained when measuring car exhaust of our car. Fumaroles of Torre del Filosofo (2,900 m a.s.l.) displayed a $\delta^{13}\text{C}$ between -3.2 ± 0.03 ‰ and -3.7 ± 0.05 ‰, comparable to IRMS measurements of discrete samples collected in the same date and in previous investigations. Diluted plume gases were collected at more than 1 km from the craters and showed $\delta^{13}\text{C} = -2.2 \pm 0.2$ ‰, accordingly with collected crater fumaroles.

Data collected in 2014 campaign are under processing, but preliminary results confirm a less negative signature of $\delta^{13}\text{C}$ of CO₂ emitted from Central Craters if compared to Torre del Filosofo fumaroles, with some interesting variations over time that must be compared with other parameters simultaneously acquired.

Considering the huge amount of data that may be acquired in a very short time by Delta Ray, we demonstrate that the addition to the atmospheric CO₂ content of ~100 ppm of CO₂ from an unknown source is enough to allow a mathematical calculation of the end-member with an uncertainty generally <0.15 ‰. This is feasible with the assumption of a binary mixing. We thus infer that these measurements performed at Mt. Etna, if performed continuously, may contribute to a better comprehension of the magmatic processes.

Keywords: Isotope Ratio Infrared Spectrometer, volcano gas monitoring

The role of volatiles during magma storage, decompression and eruption at Stromboli Volcano

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Open system volcanoes are natural laboratories to investigate how volatiles migrate and concentrate under dynamic conditions. Among them Stromboli plays a key role due to its persistent activity. Fluid phases are involved in magma decompression and pressurization, modulate Strombolian activity and rule magma rise and fragmentation processes.

Thermobarometric estimates indicate that the deeper detected part of the plumbing system is located in the upper mantle, at approximately 34-24 km. During their ascent basaltic magmas will interact with lower crust materials represented by cumulates of earlier Stromboli-type basalts at 13-10 km depth. This zone is also the sector of the plumbing system where the feeder dike is entering the chamber. Current primitive Stromboli basalts equilibrate at about 0.3-0.13 GPa for temperatures approaching 1150-1200 °C, and progressively crystallise, cool and degas before being erupted. Crystal Size Distributions on lavas and juvenile tephra recently erupted give variable residence times. Although further refinements are needed to identify the time-related variations in fluid diffusion coefficients, the estimated times for the exsolution of the gaseous phases, based on average bubble distances, range from 44-126 minutes for the lavas and scorias, down to about 12 minutes for the pumices ejected during paroxysmal explosions.

Pure extensional regimes and geophysical data indicate the existence of a prolate ellipsoidal magma chamber below Stromboli. To assess its volume we calculated the magma volumes associated with SO₂ degassing (during the 2007 major eruption) by applying a refined petrological model to estimate the magma flux entering the degassing zone. The trend of this magma flux follows an exponential decay, typical of pressurised magmatic systems. This trend has been interpreted as due to the release of elastic strain accumulated either by pressurisation of the rocks surrounding the magma reservoir, or by pressurisation of the magma itself, or both. The reservoir elastic response during magma decompression suggests that Stromboli magma chamber volume may be constrained to 1-2 km³.

Keywords: magma, volatiles, magma storage, decompression, eruption

Magmatic processes and eruption triggers at openly-degassing volcanoes

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Open vent volcanoes typically have a prominent volcanic plume that passively releases abundant gas for months, or years between eruptive events. Some examples of such types of volcanoes are Etna, Mayon, Llaima, and surely some others in Japan (e.g. Asama, Satsuma-Iwojima). The fact that there is a permanent or semi-permanent volcanic plume during quiescence shows that there are some pathways or connections between the magma (perhaps the reservoir itself) and the surface. This allows the coupling of theoretical numerical models, monitoring gas data, and petrological/geochemical data from the erupted rocks, in a holistic model that can be used for improved eruption forecasts. In this study we focus on the quiescent degassing at Mayon volcano (Philippines) using a combination of numerical modeling and petrologic observations.

Our new lumped parameter model correlates the pressure of shallow magma reservoirs with the mean degassing rates measured with monitoring systems. The model accounts for the conduit and reservoir sizes, the viscoelastic properties of the crust, the exsolution and expansion of bubbles at depth, the magma density changes, and the connectivity between the shallow reservoir and deeper magma sources. Our theoretical analysis demonstrates that there are many realistic scenarios under which depressurizations between 1-10 MPa occur in only a few months or years, that is, within the inter-eruptive timescale of persistent degassing volcanoes (Girona et al., 2014). Our results suggest that degassing-induced depressurization could induce new magma replenishment, sudden bubble expansion at depth, collapse of the crater floor, and fractures in the reservoir wall-rock.

On the other hand we also studied the petrology and geochemistry from several historical eruptions of Mayon that span over 35 years of activity (1947, 1968, 1978, 1984) to see if we can identify any magmatic processes that could be related to triggering of the eruption. We concentrated on orthopyroxene crystals, which show a variety of compositions and zoning patterns (reverse, normal or complex) with Mg# ($= 100 \cdot \text{Mg}/[\text{Mg}+\text{Fe}]$) varying from 67 to 81. The variety of core compositions and patterns can be interpreted simply as mixing and mingling between an evolved resident magma and a more mafic one. There is a general increase in the maximum Mg# of the Opx from 1947 to 1984, indicating a higher proportion or/and more mafic intruding magma. Mg-Fe diffusion modelling of orthopyroxene from all four eruptions indicates that time interval between magma injection and eruption is between 2 to 4 months. Thus these times appear to be characteristic of Mayon, and are consistent with the results from our numerical simulations.

We propose that many eruptions at Mayon could be driven by a complex series of events that involve underpressure followed by overpressure. The sequence starts with the underpressure created by the gas loss at the top, which triggers new magma replenishment from depth when depressurization reaches a critical value in turn. This is what ultimately drives the eruption by creating an overpressure. The complexity lies in being able to identify, with monitoring datasets (e.g. gas, deformation, seismicity), the cycles of decompression and compression of the system. This is especially important as open vent volcanoes are notoriously seismically silent and do not appear to deform significantly during or before eruptions, possibly because the magma is close to the surface most of the time.

Girona, T., Costa, F., Newhall, C., Taisne, B. (2014) On depressurization of volcanic magma reservoirs by passive degassing. *Journal of Geophysical Research*, Doi: 10.1002/2014JB011368.

Keywords: eruption, forecasting, petrology, geochemistry, Mayon, degassing

Bimodal Distribution of Geyser Preplay Eruptions: Lone Star Geyser, Yellowstone National Park, USA

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Geyser eruption intervals are determined by rates of water and heat discharge into shallow subsurface reservoirs and the conduit. In some geysers, small amounts of water discharge prior to a main eruption ('Preplay') can affect eruption intervals. Water discharge during preplay reduces the hydrostatic pressure, which in turn, induces boiling of water that is at, or near the critical temperature. Ascending steam slugs from depth can also lead to shorter eruption intervals (Namiki et al., 2014). In April 2014, we carried a five day experiment at Lone Star Geyser, Yellowstone National Park. Eruptions and their preplays were recorded with an infrared sensor that measured temperature variations immediately above the geyser cone (3.4m high), temperature loggers that measured water temperature at the base of the cone and in the outflow channels, water discharge, and visual observations. At Lone Star Geyser, during the preplay phase of the eruption, mainly liquid water is erupted, whereas the main phase of the eruption begins with the liquid-water dominated eruption and turns into the steam discharge. The temperature rise in an outflow channel indicates the occurrence of preplays and initiation of the main eruption. The acquired data suggests that the preplay patterns of Lone Star Geyser are vigorous and complex, consistent with previous observations (Karlstrom et al., 2013). Our new observations reveal two typical styles: 1) vigorous preplays with few events (<5) and long intervals (>20~minutes), and 2) less vigorous preplays that include several events (>5) with short intervals (few minutes), and continue approximately for one hour. Probability distributions of preplay durations show two peaks indicating the bimodal activity. The bimodality of Lone Star preplays may be a result of subtle change of temperature distribution in a convecting reservoir which has been observed in laboratory experiments (Toramaru and Maeda, 2013).

Keywords: geyser, preplay, bimodal

The analogue experiment to investigate the condition of bubble detachment from magma chamber wall by seismic wave

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Volatile components, such as SO₂, CO₂ and H₂O, are saturated in magmas. These components are nucleated as bubbles when magmas are further oversaturated. Seismic waves will reduce the nucleation barrier to facilitate the heterogeneous bubble nucleation under a low supersaturation. Bubbles which heterogeneously nucleate on the wall or bottom of magma chamber get buoyancy then detach the wall or bottom and ascent with keeping internal pressure. According to the principle of advective-overpressure, the magma chamber is overpressurized. This overpressure may trigger eruptions and other geophysical phenomena such as low frequency earthquakes at geothermal fields. Thus the detachment condition of bubbles from wall or bottom surfaces is a key factor to control the onset of seismic triggering. In order to evaluate the effect of seismic wave and surface tension on the detachment condition, we conduct the analogue experiment.

Using a carbonated water as magma and experimental vessel as magma chamber, we design the experimental setup to find out that what kind of waves cause the bubble departure. We oscillate the experimental vessel containing a supersaturated carbonated water at various frequency and amplitude. In addition, we conduct the experiment to evaluate the effect of the bubble shape on the detachment condition because buoyancy to drive the detachment is controlled by bubble shape, such as contact angle and bubble radius. The contact angle is decided by surface tension which varies with ethanol concentration in carbonated water. Further, we investigate the effect of oscillation on the bubble morphology such as bubble radius or contact angle.

From a series of experiments, we obtained following results. 1) If the amplitude is small, the bigger CO₂ bubbles are detached and when the frequency is higher, the amplitude is small at the moment of detaching of bubble. 2) The increase in the ethanol concentration decreases the contact angle and detachment bubble radius. 3) When the experimental vessel is oscillated at the same frequency and amplitude, the increase in the ethanol concentration decreases the detachment bubble radius but contact angle is various and has no systematic features.

We consider that the reason why the contact angle has no systematic features is that during vertical oscillation, the contact angle has different value because the contact angle becomes small, when the experimental vessel goes down, whereas when the experimental vessel goes up, the contact angle becomes large.

Integrating experimental results, we summarize the detachment condition as follow: The thresholds of oscillation amplitude and bubble radius at the detachment condition decrease as the frequency of oscillation increases and as the contact angle decreases. In natural systems, it has been reported that the contact angle is small approximately 20 degrees for silicate minerals such as quartz or feldspar in magmas rather than oxide minerals (larger than 90 degrees) such as magnetite. So we can speculate that the seismic triggering for overpressure may occur in the ordinary magma chamber with silicate minerals-rich walls. Furthermore, the addition of other volatile components reduces the surface tension, leading to less threshold of oscillation amplitude and bubble radius.

Significance of vapor bubbles to the volatile budget of melt inclusions from West Zealandia seamount, Mariana arc

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Vapor bubbles are common in glassy silicate melt inclusions. They can develop during post-entrapment cooling and crystallization because the melt phase contracts more than the host crystal and crystallizing minerals resulting in the formation of a void within the melt. If the melt contains volatiles, such as H₂O or CO₂, that become less soluble with decreasing pressure, the decrease in pressure associated with melt contraction causes some of the volatiles to exsolve into the void (bubble) (1, 2). A significant proportion of the volatiles originally dissolved in the melt at the time of entrapment can reside in the bubble once the inclusion and its host have been erupted and quenched. If the volatiles in melt inclusion-hosted vapor bubbles are not considered, this could result in a significant underestimation of the original volatile budget of the trapped melt. Volatiles in the vapor bubble can be analyzed directly by Raman spectroscopy and then added to the volatiles still dissolved in the melt to reconstruct the volatile content of the melt at the time of entrapment (e.g., 1, 3). Alternatively, prior to analysis of the quenched, glassy melt inclusion, the inclusion can be heated until the bubble dissolves and the melt inclusion rehomogenized (e.g., 3). However, for an inclusion that has already been analyzed, if a vapor bubble was present, sample preparation is likely to have opened the bubble resulting in its volatiles being lost. In this case, calculations based on the volume of the inclusion, the volume of the vapor bubble and the ideal gas law can indirectly estimate the contribution from the vapor bubble to the overall volatile budget of the melt inclusion (e.g., 4).

The melt phase of olivine-hosted glassy basaltic melt inclusions from West Zealandia seamount (16° 53' N) in the southern Mariana arc have already been analyzed for H₂O and CO₂ (by FTIR spectroscopy), major elements, S and Cl (by EPMA), and trace elements (by LA-ICP-MS). Dissolved volatiles range from 1.9-4.5 wt % H₂O, below detection (20 ppm)-856 ppm CO₂, 952-2260 ppm S and 454-2590 ppm Cl. Vapor bubbles were present in most of the inclusions, but as the inclusions were prepared for micro-analysis, the bubbles have been opened and the vapor phase lost. As a result, after correction for post-entrapment crystallization and Fe-loss, the measured volatile concentrations underestimate the original volatile content of the melt, and indirect calculations of the amount of volatiles that these bubbles could contribute to the overall volatile budget of each inclusion need to be performed. Firstly, we estimate the volatiles that were in the bubble based on the volume of the bubble after quenching, using photomicrographs of the inclusions collected during their preparation for analysis. However, because the bubble may grow during the final quench from eruption temperature to the glass transition temperature on a timescale too fast to allow significant diffusion of volatiles from the melt to the vapor phase, this may result in an overestimation of the volatiles residing in the bubble. Thus, secondly we estimate the volatiles that were in the bubble based on the volume as a function of the difference between the trapping and pre-eruption temperatures calculated using the olivine liquidus temperature of the measured melt inclusion composition and the extent of Fe-loss that has occurred in the melt inclusions during cooling between trapping and eruption. We will evaluate the effects that volatiles in the vapor phase estimated in these two ways have on the total volatile budget of each inclusion. In turn, we will examine how this affects inclusion trapping pressures inferred from the volatiles in the melt inclusions, and the significance this has for interpreting the magma plumbing system and crustal structure beneath West Zealandia.

1 Moore et al., In Press, Am Min.

2 Wallace et al., In Press, Am Min.

3 Hartley et al., 2014, EPSL, 393, 120.

4 Shaw et al, 2008, EPSL, 275, 138.

Keywords: arc volcanoes, melt inclusions, volatiles, vapor bubbles