地殻・上部マントル圧力での含水メルトの密度・圧縮率モデル
The density and the compressibility model of hydrous silicate melts at crustal and upper mantle conditions

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研究は、0.5GPaの圧力、コマチアイ、フォノライトやライオライトまでの幅広いメルト組成に適用可能な含水メルトの密度モデルの構築を行った。状態方程式としては、バーチマーナガス方程式を用いた。無水のメルトのモル体積とパルクモジュラスは、高圧実験と比較性を確認した上で、Lange and Carmichael (1990) の実験値を使って計算した。ドライメルトのK’（パルクモジュラスの圧力微分）は、メルトのSiO2含有量に依存と仮定してパラメータ化を行った。これらの方程式パラメータの組み合わせは、これまで報告されている無水メルトの実験結果を適切に再現することを目指した。メルト中の水成分の圧縮率、熱膨張率および、密度の温度依存性とK’に関して、先行研究で報告された常圧および地殻上部マントル実験値を参照して、コンパイルおよびキャリブレーションを行った。

構築したパラメータセットを用いて様々なメルト組成や水含有量を含むすべての密度などを計算を行った結果、過去の論文が提示していたパラメータを使用するよりも高精度で、幅広いパルクレフミ水含有でのメルトの密度を再現することに成功した。本研究で作成した密度モデルは、沈み込み帯メルトの圧力、化学組成、水含有量の幅をカバーしており、噴火・分離モデル計算の際の温度とメルトの密度差の計算のほか、地震波速度からのインパルサンスによるマントルや地殻のメルト分率やメルト組成の推定、そして、含水メルトを含む地の熱力学モデル作成に向けて有用である。含水メルトの体積変化率は、ドライメルトと水成分の相関を満たすで表現できた。この結果は、メルト中の水成分の体積変化率に、含水メルト組成への依存性が存在していないことを表している。このことは、含水系の溶融の熱力学モデル作成に向けて大きな制約となる。

キーワード: マグマ, 密度, 含水
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 (H2O mol species) and hydroxyl groups, OH. The latter are commonly considered bonded to Si4+, 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 29Si Single-Pulse Magic-Angle Spinning Nuclear Magnetic Resonance (29Si 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 H2O 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:

H2O mol ⇌ H+ + OH−, [1]
H+ + OH− + T-O-T ⇌ 2 TOH , [2]
H+ + OH− + T-O-M ⇌ TOH + MOH , [3]

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 former 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 (H₂Om), and the species interconversion reaction between H₂Om 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 H₂Om 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 $3.5 \times 10^{-17}$ to $5.9 \times 10^{-16}$ m$^2$/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, Niihama 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 tuffisite 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 tephras 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 207Pb/206Pb-208Pb/206Pb isotope ratios in the glass shards. The tephras 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 tephras 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 tephras 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 tephras. 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 tephras, Geochemistry, Crustal melt, Subduction zones
Water content of glass inclusions in the 1813 ejecta at Suwanosejima volcano by micro FT-IR reflectance method

SHIMANO, Taketo

FT-IR reflectance method

1813-year eruption of Suwanosejima volcano

1.0-2.0 wt.%

2.0-2.4 wt.%

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

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1.0-2.0 wt.%

0.6-1.2 wt.%

1.0-2.0 wt.%

1.4-3.0 wt.%

2.0-2.4 wt.%

24 November 2015

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1.0-2.0 wt.%

2.0-2.4 wt.%

3.0 wt.%

2001

2013

2001

2001

Housh and Luhr (1991)

Luhr (1991)
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, \( \text{SO}_2 \) 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 (19x10^6 m^3) is of the same order of magnitude as the observed inflation of the magma chamber during February-November 2011 (10x10^6 m^3), 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 (3x10^6 m^3/d) was estimated, based on sulfur content of melt inclusions in products by eruption on 6 June 2014 and \( \text{SO}_2 \) flux (500 t/d) on 29 January 2014. The amount of degassed magma is similar to lava effusion rate (3x10^6 m^3/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 CO$_2$ and $\delta^{13}$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 ($\delta^{13}$C) composition of CO$_2$ 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 $\delta^{13}$C of CO$_2$ emitted from the volcano.

Data acquired along the route Catania?Etna, while car was moving, showed an excess of $^{13}$C-depleted CO$_2$ 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 $\delta^{13}$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 $\delta^{13}$C=-2.2±0.2, accordingly with collected crater fumaroles.

Data collected in 2014 campaign are under processing, but preliminary results confirm a less negative signature of $\delta^{13}$C of CO$_2$ 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 CO$_2$ content of ~100 ppm of CO$_2$ 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

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 SO\textsubscript{2} 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 km\textsuperscript{3}.

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

キーワード: magma, volatiles, magma storage, decompression, eruption

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 × Mg/[Mg+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 what 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.


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