

## **Thermodynamic models of mantle melting to very high pressures: Objectives, motivations and sources of data**

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A quantitative understanding of the chemistry and physics of major-element differentiation of silicate planetary bodies requires thermodynamic data and solution models that facilitate calculation of liquid-solid phase equilibria to pressures on the order of 135 GPa. At present, the development and calibration of such databases and models is hampered by both a lack of direct experimental phase-equilibrium constraints and by uncertainty regarding the structures of the constituent phases – especially liquids – at elevated pressures. Few experimental data are available to infer structural characteristics of silicate melts at pressures higher than 35 GPa, yet spectroscopic studies of glasses quenched from melts made at high pressure, and density-pressure systematics of melts inferred from analysis of mineral fusion curves, mineral buoyancy experiments and shock-compression studies, suggest that variation in melt structure with pressure is systematic and has a first order effect on bulk thermodynamic properties. One of the primary goals that must be achieved in order to construct melting models of the Earth's deep interior is a quantitative understanding of the relation of melt structure – or alternately, the configurational entropy of a melt – and density; from such a relation all thermodynamic properties of the liquid can be derived. A technique that generates data that are ideally suited for unambiguous correlation of density with melt structure is molecular dynamics (MD) computer simulation. Recent advances in computer hardware/software and the routine use of parallel computing platforms has made feasible the systematic application of MD simulation for the generation of data sets relevant to the calibration of thermodynamic models of silicate liquids at elevated pressures. The successful exploitation of these simulations depends on a suitable and robust set of transferable interatomic potentials, which are utilized to calculate forces between atoms. Such potentials are available for liquids and solids in the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>; this system is an excellent analogue for investigating the chemistry of melting in the lower mantle. Several examples of the use of MD data to calibrate thermodynamic models of liquids will be presented.

## **Petrographic clues to overturn and eruption of open-system magma chambers: Santorini, Greece**

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Over the last 3000 years, post-caldera eruptions of Santorini, Greece, resulted in the formation of the Kameni Islands, which comprise a series of compositionally similar dacitic lava flows. Each lava flow has a distinct population of partially-crystalline mafic enclaves, which were derived from the break-up of a layer of replenishing magma responsible for triggering the eruption. Five of the flows (erupted in 1570, 1939, 1940, 1941 and 1950) include enclaves with essentially identical andesitic bulk compositions. The absence of phenocrysts in the enclaves shows that they formed from the crystallisation of originally aphyric melt which intruded the uppermost chamber prior to eruption.

The crystal framework of the enclaves comprises euhedral plagioclase, with prominent hopper-like extensions due to quench growth. Angles subtended at the junctions between pairs of plagioclase grains are modified from the original angle formed by random impingement of euhedral grains. Prominent re-entrants result in curved pore corners and reduced angles, and are best developed where the initial impingement angle was low, occurring entirely in an outer, quench-related zone. We interpret these re-entrants as a consequence of diffusion-limited growth during a period of rapid crystallisation. Thus the extent of angle reduction reflects the amount of growth during quenching.

Measurement of angle populations using the Universal Stage shows that the enclave population in each flow is distinct. We suggest that this reflects differences in the timing of cooling, crystallisation and attainment of neutral buoyancy of the replenishing layer. For magma which reached the density of the host dacite while relatively hot, overturn would result in significant quenching and angle reduction compared to a layer which had to cool and crystallise more in order to trigger overturn. Since the CSD and bulk composition of the andesite in the 5 flows are indistinguishable, we suggest that small differences in pre-eruptive H<sub>2</sub>O content of the andesite and/or the host dacite control the details of chamber overturn and eruption triggering.

## Calorimetric glass transition temperatures and magmatic processes

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Glassy rocks have long held a special fascination for petrologists and geochemists because they record the composition of the melt phase attending magmatic processes. Naturally-occurring silicate glasses form under a variety of geological conditions and they commonly form the main constituent in silicic volcanic rocks and in rapidly cooled mafic rocks. Glass also occurs in rocks with cooling histories that are substantially slower, such as the interiors of lava flows or mantle xenoliths. The glass transition temperature ( $T_g$ ) marks the transition from the liquid to the glassy state. From a petrological perspective, the calorimetrically-defined glass transition temperature is an important limiting value for the temperature conditions at which many magmatic processes take place. Glass formation is a boundary between changing environmental states. Above  $T_g$ , rates of nucleation, crystallization and vesiculation are sufficiently fast to drive magmatic processes. Conversely, where the liquid line of descent (e.g., T-X path) intersects the  $T_g$  of the melt, glass forms and many magmatic processes effectively cease.

The purpose of this paper is to provide a means of exploring the T-X conditions for glass formation in natural magmatic systems. Specifically, we present an empirical model of predicting the thermodynamic glass transition temperature ( $T_g$ ) as a function of melt composition. Operationally, the model produces temperature-dependent expressions for the heat contents of a silicate melt and glass of known composition. The point of intersection of the heat content curves for glass and melt defines the calorimetric value of  $T_g$ . Our model is constructed from experimental calorimetric heat content and differential scanning calorimetric (DSC) heat capacity measurements on silicate melts and glasses produced over the past 20 years. Calorimetric data in the model include over 500 experiments on 60 melt compositions and 250 observations on 30 glass compositions. Additional constraints on the model derive from independent estimates of the thermodynamic  $T_g$ . The model reproduces most of the measured calorimetric-values of  $T_g$  to within 30°C. The model also provides volcanologists with a tool for tracking ( $T_{\text{magma}}$  vs.  $T_g$ ) through magmatic processes such as fractional crystallization, vesiculation, partial melting. It can be used to forecast the termination of liquid lines of descent by glass formation and provides geothermometric constraints on magmatic systems by converting glass compositions into minimum pre-eruption temperatures.

## Thermodynamic models of mantle melting to very high pressure: Molecular dynamics and the macroscopic scale

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In order to characterize melting in the earth's mantle throughout geological time, a thermodynamic model of silicate liquids in the system  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaO-FeO-H}_2\text{O}$  at elevated temperature and pressure in the range 0-135GPa is needed. This is a tall but important task; it represents completion of the agenda NL Bowen set down more than 75 years ago. Because it is unlikely that laboratory-based experimental methods will be able to comprehensively study the relevant portions of P-T-X space, we are using the Molecular Dynamics (MD) method to estimate the structure, thermodynamic and transport properties of multicomponent melts in the mantle system. Although a first-principles MD approach is the most accurate, the computational resources needed to realistically study mantle melting are excessive. We use the simpler approach of empirical two and three body potentials that have been shown to faithfully capture the structure and properties of molten silicates. A key link between the MD (microscopic) and thermodynamic (macroscopic) realms is recognition that profound changes in the short-range order (structure) of molten silicates occur upon increasing pressure. The MD method enables one to capture structural changes systematically and easily in P-T-X space. This information enables development of robust macroscopic entropic 'speciation' models (e.g., mol fraction of  $\text{SiO}_4$ ,  $\text{SiO}_5$ ,  $\text{SiO}_6$ , etc) and hence development of liquid EOS's. The MD algorithm is explicitly parallel and uses the Particle-Ewald Mesh (PEM) formalism for computation of long-range forces. In addition to the structure, many properties including the internal energy, Helmholtz free energy, isochoric heat capacity, tracer diffusivity of all atoms and the melt shear viscosity can be computed self-consistently. Computed results can be compared to sparse shock wave, phase equilibria and spectroscopic information. Typical results for the compositions  $\text{MgSiO}_3$  and  $\text{Mg}_2\text{SiO}_4$  using available potentials in the equilibrium and metastable liquid field demonstrate the ability of MD methods to provide constraints for macroscopic thermodynamics EOS's. The issue of polyamorphism in the system  $\text{MgO-SiO}_2$  is considered as well.

## Effect of water on magma and crustal density: Highly fractionated lavas in the Lau Basin and other wet spreading centers

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Mid-ocean ridges worldwide typically erupt basalts with approximately 8% MgO. This can be understood if eruption is primarily controlled by the density of magmas relative to the crust: high-MgO primary MORB is denser than the porous layer 2 of oceanic crust, leading to ponding and fractionation. Stolper & Walker (1980) and Sparks *et al.* (1980) pointed out the density minimum along the tholeiitic liquid line of descent at plagioclase saturation, close to typical MORB composition. Certain regions, however, erupt anomalously fractionated lavas. Hotspot-affected and back-arc ridges tend towards values near 6% MgO and a few are dominated by andesites with <4% MgO. An outstanding example is the southern end of the Eastern Lau Spreading Center, particularly the Valu Fa Ridge, sampled by the Lau II Cruise (Leg 0417 of R/V Kilo Moana) in Fall 2004. Data show a systematic trend towards highly fractionated samples with proximity to the Tonga trench, including axial andesites and dacites. As pointed out for calc-alkaline lavas by Grove and Baker (1983), water lowers the density of magma and the effect increases with extent of fractionation because water is incompatible and because it suppresses plagioclase fractionation. MELTS calculations show that these effects together eliminate the density minimum for primary MORB lavas with >0.4% H<sub>2</sub>O. Together with increasing porosity of the upper crust (confirmed by seismic data), this effect of water provides a neat explanation for the decrease in mean MgO with moderately elevated H<sub>2</sub>O and the rather sudden transition to highly fractionated samples at higher H<sub>2</sub>O concentrations. This is a regional effect and results from feedback between the density of roof-rocks derived from earlier dikes and eruptions with the material in the present magma chamber.

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## Physical and chemical controls on the viscosity of crystallizing and degassing magma

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The viscosity of magma exerts a fundamental control over the rates and styles of many geological processes: magma ascent and emplacement, mixing and mingling, and eruption style. Silicate *liquid* viscosity depends primarily on temperature, liquid composition, and dissolved volatile content, while the viscosity of natural *magmas* depends also on crystal content. Here I quantify viscosity changes accompanying crystallization due to (i) the physical effect of rigid inclusions, and (ii) chemical effects of changing composition and volatile content of the residual liquid.

Recent advances in experimental techniques have enabled the development of empirical predictive equations for non-Arrhenian liquid viscosity as a function of temperature and water content for a range of compositions from rhyolites, andesites and phonolites, to basalts and foidites. Combining published data with the Einstein-Roscoe equation for the effect of crystals leads to several important conclusions:

1. When calculating magma viscosity for modeling petrologic processes it is essential to consider the residual liquid composition, and to apply the mechanical effect of crystals separately, e.g. dacites typically have rhyolitic matrix glasses; viscosities of andesitic-dacitic liquids are lower than those of crystal-bearing rhyolitic magmas (although the difference is small at high water contents).

2. During rapid ascent and degassing, if crystallization is negligible, *liquid* viscosity remains nearly constant until volatile saturation is reached, then dramatically increases at shallow levels (typically  $\geq 4$  orders of magnitude increase as  $P$  decreases from  $\sim 400$  to 1 bar). Disequilibrium degassing enhances the abruptness of this viscosity increase.

3. During crystallization, *magma* viscosity may initially decrease (as the effect of increasing volatile content outweighs that of increasing crystal fraction), followed again by a sharp increase as either water is lost (during ascent) or crystal fractions become large. Thus an initially andesitic liquid may produce a *less viscous* rhyolitic magma during closed system crystallization.

4. Various feedback relations link magma physics and chemistry via viscosity and diffusivity, which control growth and settling / ascent rates of crystals and bubbles.

## Feedback relationships between magma properties and volcanic eruption dynamics

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Complex, non-linear feedback relationships between magma properties and volcanic eruption dynamics are revealed by numerical simulations of coupled magma chamber, volcanic conduit, and atmospheric dispersal dynamics. The numerical simulations solve the 2D transient compressible-to-incompressible, multiphase, homogeneous magma chamber and volcanic conduit dynamics, 1D steady, multiphase separated conduit flow dynamics, and 2D transient, multiphase, separated gas/pyroclast atmospheric dispersal dynamics. The thermodynamic and rheological properties accounted for by numerical simulations describe multicomponent gas-liquid equilibria and Newtonian to shear-dependent viscosities of the multiphase magmatic mixture, as a function of magma composition and phase distribution, and of local flow conditions. The occurrence of magma fragmentation, and the transition from liquid to gas continuum, is described in terms of the visco-elastic properties of sheared magma. Complete feedback between properties and processes is allowed in the numerical simulations, which solve the transport and constitutive equations closed by selected initial and boundary conditions. The numerical results highlight the often non-intuitive roles in the global eruption dynamics of changes in the composition and properties of the erupted magma. Lower magma viscosities are associated with a more rapid pressure drop in the volcanic conduit and magma chamber during the initial transient phase of an eruption, and with the onset of velocity and pressure oscillations in deep conduit regions close to the conduit inlet. Initially volatile-oversaturated magma chambers may result in lower gas phase volumes at a given time after eruption onset, depending on magma viscosity and total volatile distribution. A feedback relationship involving pressure drop, volatile exsolution, magma acceleration, magma viscosity, and friction forces is found to largely control the steady phases of volcanic conduit flow. Large changes of underground flow variable distributions are sometimes associated with only minor modifications of the sub-aerial eruptive style, while in other cases minor compositional changes can produce significant variations and result in convective/collapsing transitions of the eruptive column.

## Laboratory investigations into the causes of explosive volcanic eruptions

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Scientists have long known that volcanic eruptions are powered by the release of magmatic gas, predominantly H<sub>2</sub>O and CO<sub>2</sub>. What is less widely recognized is that it is not simply the amount of gas that determines the intensity of eruption, but also the depth and rate of its release. High temperature and pressure degassing experiments reveal that these three factors—amount, depth, and rate of gas release—are intimately tied to the thermodynamics and kinetics of gas bubble nucleation [1]. The activation energy involved in creating a bubble is supplied by the volatile supersaturation pressure. The required degree of supersaturation varies as a function of melt-vapor surface tension, and the extent to which crystals act as favorable nucleation sites.

Experiments with polymerized silicate melts show that surface tension varies with bulk composition and dissolved water [2]. The addition of H<sub>2</sub>O and other network modifiers (MgO, FeO, CaO) lowers surface tension. The efficacy of crystal surfaces as nucleation sites also depends on bulk composition, and on crystal type [3]. Crystals that are strongly wetted by the melt (e.g., feldspars) are ineffectual. Generally, when surface tension is high and the facility of crystals to support bubble nucleation is low, nucleation requires large supersaturation.

Experimental results combined with numerical conduit flow models show that the kinetics of bubble nucleation dictate whether volatiles exsolve early and deep under quasi-equilibrium conditions, or late and shallow at extreme supersaturation [4]. Delayed bubble nucleation maximizes eruption intensity by limiting degassing to a rapid-fire burst over a narrow depth interval close to the surface.

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## Consequences of exsolution of H<sub>2</sub>O-, CO<sub>2</sub>-, SO<sub>2</sub>-, Cl-bearing volatile phases on the physical and chemical properties of magma

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Magmatic volatiles exert a strong influence on the melting/crystallization behavior, phase equilibria, viscosities, and densities of silicate melts. Each of the volatiles H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, and Cl exhibits different and varying solubilities in silicate liquids as a function of melt composition (X), pressure (P), and temperature (T). How these volatiles partition between silicate melts and magmatic volatile phases also varies with P, T, and X. The exsolution of a volatile phase or phases in open-system conditions can sequester significant quantities of these volatiles from melt, alter the activities of the most dominant volatiles in the melt, and influence the physical as well as chemical properties of melts. Most experimental constraints on volatile behavior are limited to systems containing silicate melts plus only one or two volatiles, but experiments are beginning to determine volatile behavior in systems containing melt-H<sub>2</sub>O-SO<sub>2</sub>-Cl and melt-H<sub>2</sub>O-CO<sub>2</sub>-Cl. New experimental data for molten rhyodacite (Botcharnikov et al., 2004) and phonolite (Webster et al., 2005) show that the addition of a third volatile can lead to dramatic changes in the solubility behaviors of the other volatiles. These new solubility data are applied to processes of exsolution of Cl-enriched volatile phases, differentiation, and eruption of Mt. St. Augustine volcano, Alaska, and Mt. Somma-Vesuvius, Italy.

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## Lithium transport by a magmatic volatile phase beneath Mount St. Helens volcano

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81 plagioclase-hosted rhyolite melt inclusions in dacites erupted from Mount St. Helens in May-October 1980 have been analysed by ion-probe for trace elements and H<sub>2</sub>O. Inclusion H<sub>2</sub>O varies from 0.4 to 6.4 wt%. Inclusions from May 18th white pumice have higher H<sub>2</sub>O than those from the cryptodome and subsequent eruptions. Negative correlations between H<sub>2</sub>O, SiO<sub>2</sub> and incompatible trace elements, and positive correlations between H<sub>2</sub>O and Sr indicate of plagioclase-dominated decompression crystallisation of H<sub>2</sub>O-saturated dacite magma. Decrease in MgO and FeO with increasing SiO<sub>2</sub> show that post-entrapment crystallisation of inclusions was minimal.

Most melt inclusions contain 25-40 ppm Li, weakly positive-correlated with H<sub>2</sub>O. About 15 inclusions, from the cryptodome and post-May 18th samples, have high Li (≤100 ppm) at near-constant H<sub>2</sub>O (4.0±0.5 wt%, equivalent to  $p_{\text{H}_2\text{O}}=90\text{-}140$  MPa). The same samples are also characterised by Li-rich plagioclase phenocrysts and excesses of (<sup>210</sup>Pb) over (<sup>226</sup>Ra), but otherwise show no anomalous chemical features. Our data suggest sub-volcanic transport of Li (and Pb) via a magmatic volatile phase. We propose that Li-bearing vapour was released from dacite magma with ~6 wt% dissolved H<sub>2</sub>O ( $p_{\text{H}_2\text{O}}=240$  MPa). This is the magma reservoir from which the Plinian pumice was derived. The most H<sub>2</sub>O-rich inclusions contain 0.10 wt% Cl, from which we calculate that the coexisting aqueous fluid contained ≥1.0 wt% Cl, or ≥1.6 wt% NaCl equivalent. At 800-900 °C such a fluid will condense to low-salinity vapour and brine at ~110 MPa. Cl-complexed cations such as Li and Pb will become concentrated in the dense brine phase; the low salinity vapour will tend to escape upwards. Re-equilibration between residual brine and magma will enrich the residual rhyolite melt in Li (+Pb) and buffer Cl at brine saturation (0.12-0.20 wt% Cl) as observed in melt inclusions with ≤4.5 wt% H<sub>2</sub>O. We propose that vapour-brine unmixing at ~110 MPa (~4 km depth) is an important process of mass transfer beneath Mount St. Helens and other calc-alkaline volcanoes.

## Feedback between physical and chemical characteristics of an evolving open-system magma body

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Energy-Constrained Eruption, Recharge, Assimilation and Fractional Crystallization (EC-ERAFC) is a computational model that tracks the evolution of an open-system magma reservoir undergoing simultaneous eruption, recharge, wallrock assimilation, and fractional crystallization. EC-ERAFC is formulated as a set of coupled, nonlinear differential equations, the solutions of which provide detailed thermal, mass and chemical (trace element/isotope) information about the evolution of melt and solids as all parts of a composite system (host magma, recharge magma, wallrock, eruptive reservoir) approach a common equilibration temperature ( $T_{eq}$ ). Fundamental to the structure of EC-ERAFC is the premise that changes in physical conditions, such as initial, liquidus and equilibration temperatures, will cause changes in chemical signatures. Mass addition by recharge and removal by eruption also impact geochemistry. Two forward models highlight possible feedback effects. For cases in which other parameters are held constant, increasing the wallrock initial, liquidus  $T_s$  from 300°C, 1100°C to 600°C, 1150°C, respectively, yields magmas that have more crustal  $^{87}\text{Sr}/^{86}\text{Sr}$  because, at  $T_{eq}$ , wallrock with the higher liquidus  $T$  has undergone a smaller degree of partial melting. Because melting is approximated as a fractional process, and Sr is modeled as behaving incompatibly, smaller degrees of partial melting add relatively large masses of crustal Sr to the host magma, thus yielding a more crustal fingerprint. A second example examines the coupling between  $T_{eq}$  and chemistry. For a case in which hydrothermal circulation is vigorous and magmatic heat is efficiently transported away from the magma-wallrock boundary,  $T_{eq}$  is likely to be low. Such conditions yield more crust-like magmas because the degree of wallrock partial melting is smaller. In contrast, for higher  $T_{eq}$ , larger degrees of partial melting add proportionally less crustal Sr to the host magma, yielding magmas that bear a smaller crustal imprint. Numerous other examples provide additional analysis of feedback effects and demonstrate the critical importance of applying integrated computational models to an understanding of how magma plumbing systems evolve.

## Reverse zoned feldspars in Suswa Volcano, Kenya Rift: Evidence for magma mixing and eruptions triggered by recharge

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Suswa Volcano is a Holocene volcano in the axis of the Kenya Rift. It is composed of trachytes that culminated in the formation of the caldera, followed by phonolites. We have studied two of the post-caldera phonolites.

The first flow is characterized by phenocrysts of olivine ( $\text{Fa}_{67}$ ), diopside ( $\text{En}_{31}\text{Fs}_{23}\text{Wo}_{46}$ ), ulvöspinel ( $\text{Fe}_{2.5}\text{Ti}_{0.5}\text{O}_4$ ) and zoned feldspars. Some feldspars show oscillatory zoning with K-rich cores ( $\text{An}_{<10}\text{Ab}_{62-66}\text{Or}_{28-34}$ ), followed by euhedral overgrowths with either Ca or K-rich compositions; the An-rich zones are  $\text{An}_{7-13}\text{Ab}_{66-68}\text{Or}_{14-20}$  and the Or-rich zones are  $\text{An}_{7-13}\text{Ab}_{67}\text{Or}_{19-25}$ . A second type of feldspar lacks oscillatory zoning and has trapped melt inclusions with the same glass composition as the matrix. Thin rims on the oscillatory zoned crystals ( $\text{An}_{56}\text{Ab}_{44}\text{Or}_0$ ) show the same composition as these Ca-rich overgrowths.

A second flow has a number of feldspars with Ca-rich cores and another type with K-rich interior and subtle zoning ( $\text{An}_{<10}\text{Ab}_{62}\text{Or}_{28-34}$ ). A third type of feldspar has euhedral overgrowths with internal zones of  $\text{An}_{12}\text{Ab}_{66}\text{Or}_{22}$  and rims of  $\text{An}_8\text{Ab}_{65}\text{Or}_{28}$ . Finally, a fourth type has a Ca-rich part ( $\text{An}_{50}\text{Ab}_{50}\text{Or}_0$ ), also with melt inclusions with compositions similar to the glass in the matrix. This feldspar is very similar to the second type of feldspar in the first flow, both with melt inclusions trapped in the Ca-rich portion.

The zoning in feldspars implies magma mixing of felsic and basaltic compositions. We also interpret the thin rims with  $\text{An}_{50}\text{Ab}_{50}\text{Or}_0$  found in most of the feldspars to represent recharge of the chamber by a magma that triggered the eruption. Because melt inclusions are in the portions of the feldspars that have the same composition as the magma, these feldspars most have grown before the eruption.

## Nonequilibrium H<sub>2</sub>O-CO<sub>2</sub> exsolution and obsidian formation

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The ratio of CO<sub>2</sub> to H<sub>2</sub>O in volcanic glasses is one of the few available measurements directly related to syneruptive magma dynamics. Ascent-driven magma decompression results in the exsolution of dissolved volatiles from the melt. This in turn leads to bubble growth and possibly to gas loss from the permeable magma. Pyroclastic obsidian samples from the ca. 1340 A.D. Mono Craters, California eruption (Newman et al., 1988) have relatively high CO<sub>2</sub>/H<sub>2</sub>O values. These can be explained in terms of equilibrium closed-system (Newman et al., 1988), as well as open-system (Rust et al., 2004), magma degassing. However, both scenarios require the presence of CO<sub>2</sub>-rich vapor to buffer CO<sub>2</sub> exsolution from the melt.

We present results from numerical modeling of nonequilibrium joined CO<sub>2</sub>-H<sub>2</sub>O exsolution under open- and closed-system conditions. We find that the Mono Craters CO<sub>2</sub>/H<sub>2</sub>O trend is well explained by nonequilibrium open-system degassing. Our results are a consequence of the low diffusivity of CO<sub>2</sub> (Watson, 1994). If, during decompression, open-system gas loss occurs at a rate comparable to the rate of volatile exsolution, bubbles remain small. Consequently, the surrounding melt shell remains relatively thick and CO<sub>2</sub> diffusion through the melt is slower than the rate at which CO<sub>2</sub> solubility decreases at the bubble wall. Thus, CO<sub>2</sub> concentrations throughout much of the melt remain above equilibrium.

Consistent with Rust et al. (2004), we conclude that throughout the Mono Craters eruption, even at ascent rates sufficiently fast to sustain explosive activity, open-system degassing of some magma fraction took place. This resulted in the formation of obsidian. Because open-system gas loss at slow ascent rates will result in equilibrium degassing trends, we conclude that, contrary to conventional views, slow ascent rates or degassing at or near the surface are not a requirement for obsidian formation.

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## Origin of UG2 and other chromitite layer of the Bushveld Complex

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Chromitite layers are common in large layered intrusions. One widely held view is that the chromitites formed as a consequence of the mixing of more primitive with less primitive magma (Irvine, 1977). This model predicts that the rocks immediately above and below the chromitite layers should be different. In the Bushveld Complex many chromitites are underlain and overlain by lithologically similar orthopyroxenite, suggesting that Irvine's model does not apply. To understand how the Bushveld chromitites may have formed, we have conducted a detailed study of the pyroxenites above and below the platinum group element-rich UG2 chromitite of the upper and another chromitite of the lower Critical Zone (CZ).

In the eastern Bushveld, the UG2 is a massive, 70 cm-thick layer. Electron probe data indicate that the Mg# of opx ranges from 79.3–80.6 (En<sub>77.4–78.3</sub>) in footwall and 80.5–80.9 (En<sub>77.7–79.1</sub>) in hanging wall pyroxenite, while cpx compositions are En<sub>45.3–46.3</sub> in the former and En<sub>45.3–48.9</sub> the latter. Minor element compositions are variable, probably due to post-accumulation reequilibration, but fall within the same range in each pyroxenite. In contrast, interstitial plagioclase of the lower pyroxenite is more sodic than that of the upper pyroxenite (An<sub>45.4–54.5</sub> vs An<sub>64.9–72.5</sub>). This difference is not reflected by differences in Al/Si or Na/Ca ratios of coexisting opx or cpx. Furthermore, major and minor element compositions of all three minerals are identical in the rocks underlying and overlying the lower CZ chromitite. Field relations demonstrate that the UG2 acted as a permeability barrier to upwardly percolating interstitial melt. Therefore, we interpret the relatively sodic nature of plagioclase of the footwall pyroxenite to be due to the pooling of interstitial melt in this layer. Despite the difference in plagioclase compositions, the formation of the UG2 chromitite by magma mixing cannot be rationalized in terms of phase equilibria. A different model, such as the pressure release one of Lipin (1993), may better explain the Bushveld observations.

### References

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## Effects of sulfur degassing and sulfide separation in some products of Mt. Etna volcano (Sicily, Italy)

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Application of an internally-consistent model (Moretti and Ottonello, 2005) for melt oxidation state and sulfur solubility allows to study how Etna magmas release sulfur and how the redox control is operated in a volatile-rich basaltic environment.

Different Etna magmas, corresponding to the products of the current activity and of the 122BC plinian eruption, follow different paths of S elimination and during their evolution they reach soon or later the lower limit of sulfide saturation. Interestingly, melt inclusion data indicate that along this threshold (i.e., for  $m_{S2}$  of 18 mmol/kg) the magma involved in the high-energy Plinian eruption of 122 BC is much richer in sulfate (and total S) than the magmas erupted by low-energy Strombolian eruptions from the Bocca Nuova and SE crater. The direct relationship between the high sulfate contents at the lower limit of sulfide saturation and the energy of the eruption does not seem to be fortuitous. The availability of a relatively large amount of S, largely present as sulfate, in the magma of the 122 BC Plinian eruption is confirmed by the distinct  $^{34}S/^{32}S$  isotopic ratios and total S concentrations measured in these products with respect to other rocks of the volcano. Again, this large amount of S, to be eliminated through degassing only, could be considered as a proxy for the high energy of this volcanic event, although further investigations are needed to corroborate this inference. Accepting this explanation, the next question is: why do Etna magmas experience different evolution paths leading to these large differences in sulfate contents at the lower limit of sulfide saturation?

### Reference

Moretti R. and Ottonello G. (2005) *Geochim. Cosmochim. Acta*, In press.

## Identification of the hydrous environments in volcanic glasses

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The hydrous species distribution in magmatic systems has considerable influence on the style of a volcanic eruption and on many of the physical and chemical properties of silicate melts. In particular, in the understanding of explosive volcanism a source of uncertainty is the process of fragmentation such as the rising magma disintegrates into a spray, resulting from the expansion of hydration bubbles through the progressive drainage of water from the surrounding melt by diffusion, or as a consequence of the interaction with external water. The water speciation and the nature of the solute in high-silica volcanic glasses from the explosive activity in the Phlegrean Volcanic District (Italy) has been determined by  $^1H$  MAS-NMR spectroscopy and Sr isotopic data by TIMS.

The  $^1H$  MAS NMR spectra are characterized by a large spinning sideband pattern with peaks spaced at integer multiples of the spinning speed, resembling a Pake doublet, with an overlapping central contribution. The spectra are best simulated by the contribution of three different types of proton nuclei with  $^1H$ - $^1H$  dipolar couplings of 45 kHz, 18 kHz and 1 kHz. These are attributed to isolated, rigid water molecule; to water molecules or clusters rather mobile and to micropore liquid water or clusters, respectively. Since the strontium of the solute in groundwater or surface water is likely to be isotopically distinct from that of the melt, the  $^{87}Sr/^{86}Sr$  ratio allowed to distinguish hydrous component of probably magmatic origin in isotopic equilibrium with the melt and hydrous components due to the interaction of magma with external fluids during phreatomagmatic fragmentation.

Glasses in deposits from magmatic fragmentation show evidence of water diffusion in response to decreasing gas solubility during magma decompression and the gas partitioning into a separate phase. Glasses from phreatomagmatic fragmentation are characterized by the increasing of water more strongly bonded and less mobile into the structure. This requires an intimate, fine-scale mixing of water and magma during the water-magma interaction process, which is also promoted by shock wave propagation. This also suggests that water and magma were probably close to attain thermal equilibration during the interaction.

## How gabbro zircons contain more U than zircons from the co-mingled granodiorite: Lessons from U-Pb and Hf-zircon isotope investigations

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Mantle derived magmas in convergent tectonic zones experience a complex evolution from their generation to the crystallisation in the upper crust. They commonly display large compositional variations due to the enrichment with incompatible chemical elements that are introduced into the upper mantle by slab-derived fluids or melts. This effect is strongly overprinted by the mantle-crust interaction. U-Pb and Hf-zircon isotope-geochronological and geochemical investigations are crucial to evaluate the role of both processes as well as the kinematics of the mixing between mantle and crustal derived magmas.

The present study is focused on Upper Cretaceous plutons from Central Srednogie Zone, Bulgaria. Sheet-like gabbro or gabbro-diorite bodies are intruded into magma chambers containing coeval felsic upper parts and lower parts of crystal rich porphyry granodiorites. Granodiorite: concordant zircons, U content range from 70 to 161 ppm. Three of them determine a mean <sup>206</sup>Pb/<sup>238</sup>U age of 84.6 ± 0.3 Ma. Inherited zircons are also present. The calculated initial (<sup>87</sup>Sr/<sup>86</sup>Sr) ratio of 0.70492 and ε-Hf-zircon values of +4.7 to +8.7 argue for mixed crust-mantle origin. The gabbro contains three types of zircon: (i) brown zircons are U-rich (600-4400 ppm), two of them lying concordant at 82.16 ± 0.10 Ma; ε-Hf-zircon values are mantle dominated +7.6 to +10.5; (ii) milky zircons are less rich in U (270-350 ppm) and define a mean <sup>206</sup>Pb/<sup>238</sup>U age of 85.0 ± 0.5 Ma; (iii) colorless zircons of mixed origin and an age of 442.7 ± 8.3 Ma are sparse. The initial strontium ratio of the gabbro is 0.70401. Transparent and milky prismatic zircons prevail in the mixed layers. Five of them yield a concordant age of 84.87 ± 0.13 Ma. All Upper Cretaceous zircons reveal similar REE distributions with positive Ce and weak or absent negative Eu anomalies. Brown gabbroic zircons are slightly richer in the REE compared to the zircons from intermediate rocks.

Mixing of the mantle magma (additional to the mingling) with crustal melt at mid- to upper crustal level is proposed to explain the change of the magma chemistry leading to zircon saturation and fast crystallisation of U- and REE-rich zircons.

## Element partitioning between ferrobasalt-rhyolite immiscible liquids

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Evidence from natural rocks show that liquid immiscibility can be encountered by common basalts at advanced stages of crystallization. However, the partitioning of trace elements between the immiscible liquids are still poorly constrained therefore we have carried out a comprehensive study of liquid-liquid element partitioning. In contrast to similar previous experimental studies, we employed high temperature centrifuge phase separation, in order to get a better spatial separation of immiscible liquids. Three thermocouples and two independent heaters were used to minimize temperature gradients. Two starting compositions were prepared from synthetic silicate glass and reagent-grade FeO. The first being rich in FeO (24 wt. %) and SiO<sub>2</sub> (57 wt. %) in order to ensure liquid immiscibility to take place, the second starting composition had 50 wt. SiO<sub>2</sub> and 22 wt. % FeO close to liquid compositions suggested for the Skaergaard magma where liquid immiscibility has been speculated. These mixtures were doped with 33 trace elements. Runs were carried out at 1050-1150 °C in sealed Fe containers at 1 atm. Quenched products were analyzed by electron microprobe and LA ICP-MS. Two immiscible liquids are present in all the products separated by sharp menisci. One of these is rich in SiO<sub>2</sub> (65 wt. %) whereas the other is having a moderate SiO<sub>2</sub> content (48 wt. %) but is rich in FeO (32 wt. %). Even at the highest rotation speeds, the centrifuge phase separation after 3 hours was incomplete, mostly because of the high viscosity of the silica-rich immiscible liquids. Partition coefficients show that all the elements analyzed, except K, Na, Rb, Al and Si, concentrate in the Fe-rich immiscible liquid. The ferrobasalt/rhyolite Nernst partition coefficients (D) are the highest for Zn (3.3) and Fe (2.6) and the lowest for Rb and K (0.4-0.5). The D values against ionic potential shows in general a convex upward trend that closely resembles the liquid-liquid partitioning of trace elements by Soret diffusion. Complementary Soret diffusion experiments are underway to further explore bulk compositions controls on immiscibility in Skaergaard-like magma compositions.