

PETROLOGICAL AND EXPERIMENTAL CONSTRAINTS ON THE PRE-ERUPTIVE CONDITIONS OF LA SOMMATA BASALT AND BROWN TUFFS TEPHRA (AEOLIAN ISLANDS)

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INTRODUCTION

This work is focused on two key eruptions of Vulcano Island: 1) the most primitive magma of Vulcano erupted by the La Sommata scoria cone, a silica-undersaturated Ca-rich shoshonitic basalt with olivine-hosted primitive melt inclusions having an ultra-calcic character; 2) the most energetic eruptions of the whole Aeolian Archipelago, the Brown Tuffs (BT) eruptions, which produced several pyroclastic deposits, covering an ample age interval, spread out over a large portion of all Aeolian islands up to the northern coast of Sicily (Lucchi *et al.*, 2008).

By complementary studies of melt inclusions and experimental petrology, we pursued the following main objectives: (i) to constrain the pressure-temperature-fluid activity during the ascent paths of La Sommata primitive magma and BT basaltic andesite; (ii) to experimentally investigate the influence of H₂O in these magma and its effects on the phase relations; (iii) to try to depict a petrological model and to constrain the pre-eruptive conditions of these very different eruptions. In order to obtain the BT pre-eruptive H₂O and CO₂ contents, preliminarily to the experimental petrology, we performed several analyses on melt inclusions hosted in loose clinopyroxenes sampled from the BT deposits at Vulcano. This step greatly adjuvated the restriction of T, P, H₂O_{melt} conditions for the later experimental petrology approach on BT composition.

The experimental petrology study (realized at CNRS-ISTO: Centre National de la Recherche Scientifique - Institut des Sciences de la Terre d'Orléans) was performed by simulating the volcanic conditions (P, T, and aH₂O) experienced by La Sommata basalt and BT basaltic-andesite scoriae from Vulcano. All the experiments were run loading H₂O+CO₂ together with the chosen starting material. Experiments were carried out under two main guidelines:

- a well characterized isobaric section at 150 MPa for La Sommata basalt and BT eruptions;
- an isothermal section at 1150°C in the pressure range 150-50 MPa, in order to simulate the ascent path for La Sommata basalt.

While experiments on La Sommata were sufficient to allow us to discuss the evolution of La Sommata magma, experiments on BT are still at their early steps, and the results must be taken as purely indicative.

The P-T-*f*O₂, H₂O_{melt} constraints derived from our experiments could hopefully give an useful tool for (i) future research on mafic magmatism on the Aeolian Archipelago and also (ii) contribute to the petrological aspects of Ca-rich magmas (such as those of La Sommata) at very low pressure, since all experimental studies concerning Ca-rich magmas are at P well above 250 MPa (*e.g.* Médard *et al.*, 2004).

ANALYTICAL TECHNIQUES

Scanning Electron Microscope (SEM-EDS) and Electron Microprobe (EMP) were used for phase identification and composition determination (analytical data are not reported). The EDS analyses of natural samples (using an Oxford LEO 440 SEM-EDS housed at Dipartimento di Chimica e Fisica della Terra of Palermo) were also acquired. SEM conditions consisted of an acceleration voltage of 20 keV and 600pA of beam current, both for analyses and imaging.

The quantitative major element analyses of experimental samples (analytical data are not reported) were performed by a Cameca SX50 EPM, housed at BRGM-CNRS (Bureau des Recherches Géologiques et Minières

- Centre National de la Recherche Scientifique) of Orléans. The EPM analytical conditions were: acceleration voltage 15 kV, sample current of 6 nA and counting time of 10 seconds on peak for all the elements. Analyses of sensors (Ni-Pd alloys) were obtained employing an acceleration voltage of 15 kV, a beam current of 20 nA.

In order to infer the dissolved H₂O and CO₂ contents in melt inclusions, absorption FTIR spectra (performed by a Hyperion 2000 Bruker FTIR - available at the C.F.T.A. Department, Palermo - and adopting a Domnik Hunter purge system) were acquired; measurements were performed employing a Globar source, a KBr beam splitter with a narrow range MCT detector; for each spectrum 256 scans were accumulated with a resolution of 2 cm⁻¹.

STARTING MATERIAL

La Sommata natural sample

The deposits of La Sommata eruption (about 50 ka BP; De Astis *et al.*, 2006a, b) are represented by basaltic scoriaceous products outcropping within the Caldera del Piano at Vulcano Island. La Sommata basalt is the most primitive Vulcano magma and contains one of the most primitive Aeolian Arc melt inclusions with MgO ~ 10-11% and CaO/Al₂O₃ ratio > 1.1 (Métrich & Clocchiatti, 1996; Gioncada *et al.*, 1998); these features make La Sommata shoshonitic basalt as a silica-undersaturated ultra-calcic primitive melt with a nepheline-normative character and an ankaramitic affinity (Schiano *et al.*, 2000).

The total rock analysis of La Sommata scoriae (SOM-1 starting material) was performed on anhydrous glass (deriving from melting natural rock) by electron microprobe (CNRS-ISTO). SOM-1 is a nepheline-normative ultra-calcic absarokite. No weathering (Chemical Index of Alteration, C.I.A.: Nesbitt & Young, 1982) and/or hydrothermal (Large *et al.*, 2001) alterations did affect this scoria. Scoriae are low-porphyrific (10-20 wt.%) with rare phenocrysts with respect to the microphenocrysts. Olivine pheno- and microphenocrysts showed a more forsteritic component (up to Fo₉₂) than microlites, which were characterized by a forsteritic contents of about 86-87 mol%. Few olivines host clinopyroxene and chromite as microphenocrysts. The most abundant phase of La Sommata scoria is represented by Al-diopsidic pyroxene. MgO contents were higher in phenocrysts (En₅₂Fs₄) than in microlites (En₃₆Fs₁₆). In the same way, X_{Mg} decreases from 0.92 (in phenocrysts) to about 0.80 (in microlites) and the Al₂O₃ increase from 2 to 5 wt.%. Plagioclase phenocrysts are rare and the groundmass is crowded with plagioclase microlites. Compositions range between An₆₇₋₅₅ (labradorite) and An₇₉ (bytownite). Groundmass is thickly dotted by microlitic aluminian spinels (Usp 25-37 mol%).

Brown Tuffs natural sample

The whole BT succession was broadly divided into 3 groups (Lower, Intermediate and Upper BT) covering a depositional time span between 78 and 8 ka BP (De Astis *et al.*, 1997; Lucchi *et al.*, 2008). The emplacements of the deposits are characterized by hydromagmatic explosions with the coarse material deriving from partial eruptive cloud collapse (Lucchi *et al.*, 2008).

Vulcano BT deposits (De Astis *et al.*, 2006a, b) are represented by Grotta dei Pisani, Molineddo 3 (which both represent the Lower and the Intermediate Brown Tuffs) and Grotte dei Rossi Tuffs (the Upper BT); they occur with a variety of textures: massive, parallel/sub-parallel, or sandwave beddings.

BT lateral variation and stratigraphic unconformities were also considered. BT deposits lie on some pyroclastic deposits (De Astis *et al.*, 2006b) as Molineddo 1, Upper Grey Sandtuffs formation described by Keller (1980), and Molineddo 2 (known as the “Tufi varicolori”; Keller, 1980), all reported in the same time-span of LBT-IBT deposits (78-24 ka) and having a common source area (La Fossa cone, approximately). Since Molineddo 2 is characterized by a very altered ash, in our study only comparison between Molineddo 1 and LBT-IBT deposits was possible. After extensive screening, we chose, as starting material for experimental petrology, the Grotta dei Pisani scoriaceous lapilli, whereas we used loose pyroxenes dispersed in the matrix for MI study.

The Grotta dei Pisani whole rock composition (GP-1 starting material) is a qz-norm HKCA basaltic andesite. Although we performed a rigorous selection of the samples, the Chemical Index of Alteration for GP-1 starting material is rather high (C.I.A. > 45), highlighting the influence of weathering processes; no hydrothermal alteration seems to have affected the sample.

GP-1 glassy groundmass is K-rich with respect to the bulk composition and shows a more mafic character with respect to the Molineddo 3 lithofacies. Molineddo 1 displays a glass composition more evolved than the BT glassy groundmass. Olivine crystals (not in equilibrium) are rare, occur with small dimensions, with respect to the pyroxenes, and have a homogeneous composition (Fo₆₀₋₆₄). The GP-1 clinopyroxenes are augitic/diopsidic in composition. The pyroxenes phenocrysts are characterized by optical and chemical zoning; the rims are Al-rich (Al₂O₃ up to 3.7%) whereas the cores are more enstatitic (En₄₇Fs₇ on average), with Mg-number up to 0.80. The cpx composition of Molineddo 1 and 3, correspond to En₃₈₋₄₀ with a slightly constant Mg-number (0.7). GP-1 scoria presents plagioclases with variable composition (bytownite-labradorite) and the phenocrysts show the highest anortitic content (An₈₀). The spinel composition is slight constant (Usp 36-37 mol%).

Melt inclusions approach

The melt inclusion (hereafter named MI) are hosted in loose pyroxenes (meanly salitic) sampled from the BT levels (Grotta dei Pisani, Molineddo 3, and Grotte dei Rossi Tuffs); in order to highlight volcanological differences between the BT and the basal deposits (on which BT lie) we also selected the loose pyroxenes from the Molineddo 1 formation (pre-BT deposits). The MI compositions were corrected for post-entrapment crystallization by adding the pyroxene component to obtain clinopyroxene-liquid equilibrium with a K_d = 0.31.

Although the small number of MI (due to a very low successfulness rate), some considerations can be discussed.

The MI glasses are potassium enriched (K-suite) with two different silica contents (shoshonites and banakites; Fig. 1) that well differentiate the LBT-IBT from UBT MIs; moreover, these latter (Grotte dei Rossi Tuffs: UBT), show compositional features more evolved than the previous BT formations (Grotte dei Pisani and Molineddo 3) but similar to Molineddo 1 MIs (pre-BT deposits) highlighting that at least two magma types were involved during BT eruptions.

The magma trapped as MI in BT clinopyroxenes is characterized by variable H₂O and CO₂ contents: water concentrations range from 0.2 to 1.69 wt.% and carbon dioxide is up to 1280 ppm with a bimodal distribution (Fig. 2) of H₂O-CO₂ contents (justified by two discrete steps of magma degassing or alternatively by an artifact due to poor statistics for MI). Molineddo 1 is characterized by highest water-carbon dioxide pair concentrations (about 1.2 wt.% and up to 1244 ppm, respectively). The two presumed degassing steps correspond to the following minimum saturation pressures (using the solubility model of Papale *et al.*, 2006): i) the CO₂-rich cluster gives a P = 80 MPa (depth ≈ 2.5 km) and ii) the CO₂-poor cluster translates in a P ≈ 20 MPa (depth ≈ 0.75 km).

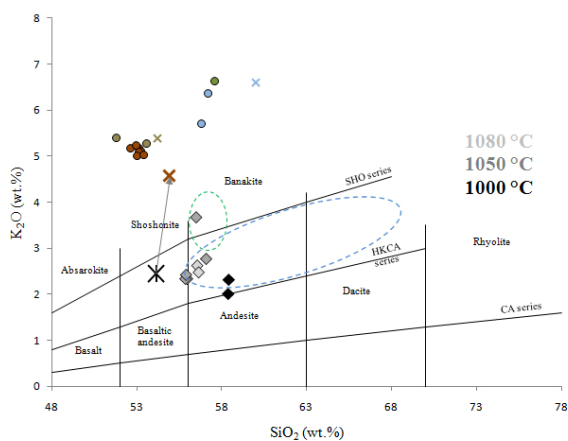


Fig. 1 - K₂O vs. SiO₂ diagram. Star: GP-1 starting composition. Circles: Grotta dei Pisani (brown), Molineddo 3 (light brown), Grotte dei Rossi Tuffs (dark green) and Molineddo 1 (blue) pyroxene-hosted melt inclusion compositions. Crosses: Grotta dei Pisani (brown), Molineddo 3 (light brown) and Molineddo 1 (blue) glassy groundmass compositions. Diagram shows the variation of GP-1 differentiated liquids (diamonds) at 1080°C (grey), 1050°C (dark grey) and 1000°C (black). Liquid line evolution (grey arrow) represents the potassium enrichment of GP-1 melts. Blue ellipse: compositional variations of UBT from Vulcano; green ellipse: compositional variation of Punta di Mastro Minico and Quadrara formations (see De Astis *et al.*, 2006b).

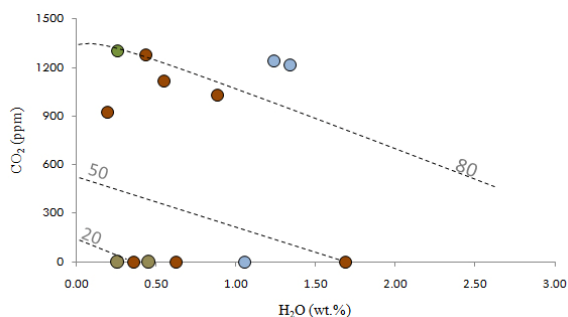


Fig. 2 - Dissolved H₂O and CO₂ contents in clinopyroxene-hosted melt inclusions from: Grotta dei Pisani (brown circle), Molineddo 3 (light brown circle) and Grotte dei Rossi (dark green circle) BT lithofacies. Blue circle: Molineddo 1 formation. Dashed lines represent the saturation pressures (expressed in MPa) calculated using Papale *et al.* (2006) model.

SOM-1 pre-eruptive pressure was instead set considering as a minimum value the highest P derived from Gioncada *et al.* (1998) studies (1.1 and 0.7 kbar). Crystal-liquid thermometry (Putirka, 2008) on olivines-whole rock pairs of SOM-1 scoria, suggested an upper temperature bound at 1200°C (according to Gioncada *et al.*, 1998). The f_{O_2} chosen for SOM-1 experiment was fixed on the basis of: i) the compositional similarity between our rock-sample and the Stromboli Golden Pumice (Di Carlo *et al.*, 2006) and ii) estimation of oxygen fugacity by Métrich & Clocchiatti (1996) with a $\Delta NNO = +0.74$, deduced from S^{6+}/S_{tot} ratios of La Sommata olivine-hosted melt inclusions. The water contents of the glasses were determined using the “by-difference” method (Devine *et al.*, 1995).

Preparation of experiments

Single batches of 20 g of both SOM-1 and GP-1 scoriae powders were molten in air in a platinum crucible by a furnace at 1400°C for 3-4 hours and fused twice with regrinding between. Thirty mg of the resulting powders were loaded in the experimental capsules of Au, Au₉₀Pd₁₀, and Au₈₀Pd₂₀ alloys. All the crystallization experiments were performed in fluid-saturated conditions (H₂O + CO₂, with XH₂O from 1 to 0).

The experiments were carried out in an Internally Heated Pressure Vessel (IHPV), working vertically and pressurized with Ar-H₂ mixture. The vessel was equipped with an inner furnace, consisting of a double parallel winding of a Mo wire. Pressure was recorded by a transducer calibrated against a Heise-Bourdon tube gauge. Two S-type thermocouples allowed a continuous control of the temperature. Each experiment consisted of a set of 6-7 capsules (f_{O_2} -sensor included) for a run duration range of 20-26 hours. A fast quench device was used in order to prevent quench crystallization. In order to support the equilibrium conditions, textural and chemical features (*e.g.* crystal distributions, composition homogeneity, crystal-liquid exchange coefficients, Fe-loss) were tested.

Control and monitoring of oxygen fugacity

The use Ar-H₂ gas mixture, with known partial pressure of hydrogen, allows to impose variable reducing atmosphere and hence to obtain the required final f_{O_2} for each experiment. The f_{O_2} was calculated from the reaction $H_2O \leftrightarrow H_2 + \frac{1}{2}O_2$, where K_w and f_{H_2O} of pure water, at the temperature and pressure of the experiments, were obtained by Robie *et al.* (1979) and Burnham *et al.* (1969), respectively. For the determination of f_{H_2} we used the solid sensor technique by Taylor *et al.* (1992), based on two hand-pressed Ni-Pd-NiO pellets, and the calibration expression by Pownceby & O'Neill (1994).

Molineddo 1 ($P > 80$ MPa) gives us the opportunity to link the BT eruption with the magmatic system of the pre-BT magma system: between Molineddo 1 deposition and BT eruptions, magma chamber was shallower and characterized by mafic injections, as suggested by the MI compositions.

EXPERIMENTAL PETROLOGY

Experimental crystallization and ascent simulation for La Sommata and Grotta dei Pisani BT products were performed at different temperatures (from 1000 to 1150°C) and pressures (from 50 to 150 MPa) and with a f_{O_2} kept always $> NNO$. The choice of these experimental brackets was based on some preliminary results. As regards the GP-1 natural rocks, the upper limit for the pre-eruptive pressure was derived by MI volatile concentrations that enabled us to set the pressure of entrapment at $P > 80$ MPa.

RESULTS AND DISCUSSIONS

La Sommata experimental phase and liquid compositions

Spinel occurs as the liquidus phase readily substituted by clinopyroxene (Figs. 3 and 4) for decreasing pressure (or increasing water contents). Experimental clinopyroxene ranges from augite to diopside in

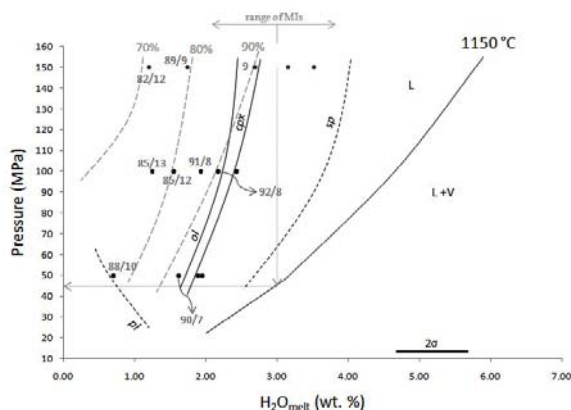


Fig. 3 - Experimentally determined P-H₂O in melt phase diagram for SOM-1 at 1150°C. The water saturation curve is calculated from Papale *et al.* (2006). Isocrystallinity (as liquid percentage) curves (dashed grey lines) and forsterite/ferrosilite (*e.g.* 92/7) contents are represented (single number refers to ferrosilite content only). Liquid (L), vapor (V), Cr-rich spinel (sp), clinopyroxene (cpx), olivine (ol), plagioclase (pl) and magnetite (mt) fields are reported. Dashed lines are used for supposed mineral saturation curves. The grey double arrow-bar represents the range of water contents determined in olivine-hosted melt inclusions by Gioncada *et al.* (1998); the mean value of H₂O concentration (3 wt.%) in melt inclusion (CO₂-free) corresponds to a saturation pressure of 45 MPa. Maximum water determination error is 2σ.

composition (En₄₀₋₄₈Fs₇₋₁₆) but augite, characteristic of the lower experimental pressure (50 MPa) and temperature (1050°C), points to (En₄₀₋₄₃ Fs₁₁₋₁₆). X_{Mg}^{cpx} is characterized by the higher values at the higher temperatures related to the lowest crystallinity runs. The CaO content of pyroxene tends to decrease with dissolved water in the melt, either in the clinopyroxene-only or in the clinopyroxene + olivine ± plagioclase runs: we noted that Ca in clinopyroxene provides a sensitive geo-hygrometric tool. Olivine is the next phase to crystallize and ranges from Fo₉₂ (for liquid + clinopyroxene + olivine assemblage) to Fo₇₈ (for liquid + clinopyroxene + olivine + plagioclase assemblage).

Fo₉₂ saturation occurs between H₂O_{melt} = 2 - 2.5 wt.%; in correspondence with the late appearance of plagioclase the olivine forsteritic component tends to decrease up to Fo₇₈. Plagioclase (An₆₇Ab₃₁) occurs only at low temperatures (≤ 1120°C) and low H₂O_{melt} (≤ 2.20 wt.%). Spinel occurs with compositions variable between a (Mg-Al-Cr)-rich spinel and a Ti-magnetite: with the decreasing temperature, Cr₂O₃ becomes less abundant (from 6.88 wt.% at 1150°C to 0 wt.% at 1050°C) and MgO decreases from 12.37 to 8.05 wt.%.

The most evolved experimental glasses represent multiply saturated crystal-liquid equilibria that drive the liquid composition towards a remarkable K₂O enrichment (covering the shoshonitic and the potassic suites) at a rather moderate SiO₂ variations (from absarokite to shoshonite; Fig. 5). The strongest K₂O enrichment (up to 5.13 wt.%) is achieved for temperatures < 1080°C and H₂O_{melt} < 2.2 wt.%, when plagioclase saturation is reached. Glass compositions increase in potassium contents with decreasing of CaO/Al₂O₃ values.

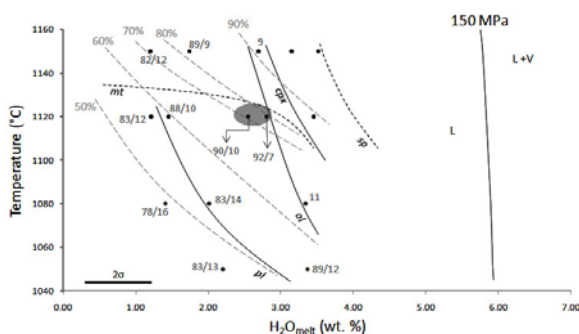


Fig. 4 - Experimentally determined T-H₂O in melt phase diagram for SOM-1 at 150 MPa. Abbreviations as in Fig. 3. Dashed lines are used for supposed mineral saturation curves. Isocrystallinity curves and forsterite/ferrosilite contents are represented. The gray ellipse highlights the likely pre-eruptive conditions. The water saturation curve from Papale *et al.* (2006) model.

An important point of our experiments is that strong K₂O enrichments can be achieved by simple equilibrium crystallization, cumulating essentially clinopyroxene + olivine + plagioclase. If squeezed out from its crystal-mush, this K-rich melt might represent one of the end-member compositions potentially involved in the magma mixing process, or is akin to.

Our data suggest that a SOM-1 type magma can produce liquids akin to latite/shoshonitic magmas at Vulcano (e.g. Saraceno, Molineddo and Vulcanello: De Astis *et al.*, 2006b) if more than 45% of solid is extracted.

Pre-eruptive conditions for La Sommata magma and constraints on ascent pathways

Previous works on olivine-hosted melt inclusions of the La Sommata basalt (Gioncada *et al.*, 1998) suggest a water content between 2.1 and 3.8 wt.% (mean value 3 wt.%), CO₂ concentrations below the detection

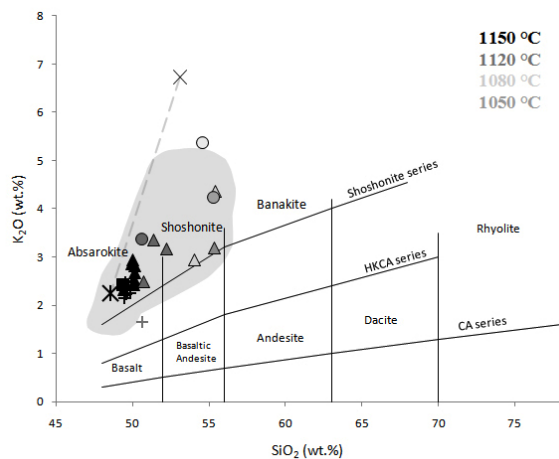


Fig. 5 - SiO₂ vs. K₂O diagram of experimental glasses as a function of temperature and phase assemblage. Symbols: liquid (cross), liquid + clinopyroxene (square), liquid + clinopyroxene + olivine (triangle), liquid + clinopyroxene + olivine + plagioclase (circled), SOM-1 starting glass (star), La Sommata natural glass (X symbol); symbols in grey scale are used for glass compositions at different temperature (see legend). Liquid line evolution (dashed grey arrow) represents the potassium enrichment of SOM-1 experimental melts. Grey half-tone represents the compositional field of the most primitive products of the Vulcano Island (from literature: e.g. De Astis *et al.*, 2000).

limit, and a homogenization temperature (Th) of 1200°C. These inferred temperatures (Th) for the given water content results overestimated since, according to our data, at this conditions (and P = 150 MPa) the SOM-1 composition is in the near-liquidus region (phase diagram in Fig. 3). Moreover, the melt inclusions study of Gioncada *et al.* (1998) was based on olivine-hosted MI, but our phase relationships clearly show that olivine is not in the liquidus phase.

The Comparison between the natural and experimental crystal contents and the phase assemblage allow a first estimation of the La Sommata magma pre-eruptive conditions. The natural phase assemblage (clinopyroxene, olivine, plagioclase and oxide) is coherent with charges characterized by a water content ranging from 2.55 to 2.90 wt.%, temperatures of 1120°C and pressures between 100 and 150 MPa (Fig. 4). The crystallinity of these conditions (between 35 and 15 wt.% of crystals) matches the natural rock crystallinity (10-20 wt.%). Our experimental data clearly show that plagioclase saturation requires a strong reduction of initial water by depressurization-exsolution. The La Sommata magma ascent may be summarized by two discrete crystallization levels. The first stage (100-150 MPa; depth ≈ 3.8-5.6 km) occurred in the deepest reservoir (at 1120°C and H₂O_{melt} = 2.6-2.9 wt.%) and consisting in the crystallization of a Fs₄₋₉

clinopyroxene first and a Fo₉₀₋₉₂ olivine later. The second stage of crystallization at low pressure (50 MPa; depth ≈ 2 km), which involves a significant amount of water exsolution (Fig. 3), allowing thus plagioclase precipitation.

Brown Tuffs experimental phase and liquid compositions

The BT experimental data were affected by noteworthy biases that led us to handle the results with caution; here we detail the results obtained from 3 experiments (12 charge) performed at P = 150 MPa and T = 1000-1080°C, with H₂O_{melt} contents ranging from 1 to 4.9 wt.% (evaluated with the “by difference” method). The isobaric phase equilibria diagram is portrayed in Fig. 6. The Mg-rich Ti-magnetite (MgO < 6 wt.%; Usp 3-13 mol %) occurs at the highest temperature (1080°C) for water contents > 2 wt.%. Interestingly, plagioclase crystallizes very close to the liquidus, just after the Fe-Ti oxide, at 1050°C for H₂O_{melt} < 3.5 wt.%. In the sequence of crystallization, with lowering temperature and H₂O_{melt} content, follow orthopyroxene, subcalcic-pyroxene (pigeonite) and amphibole. Clinopyroxene (augite) and phlogopite occur at

near-solidus conditions, 1000°C, $H_2O_{\text{melt}} > 2.9$ wt.%. The onset of opx on the liquidus is for SiO_2 in the melt > 60 wt.%.

Plagioclase composition ranges from An_{62} to An_{79} . The $K_d^{Ca-Na}_{\text{plg-liq}}$ ranges from 1.2 to 2.3, respectively.

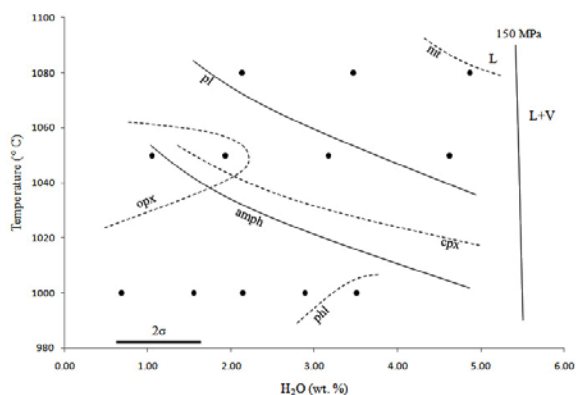


Fig. 6 - Experimentally determined T- H_2O_{melt} phase diagram for GP-1 at 150 MPa. L, liquid; V, vapor; mt, magnetite; pl, plagioclase; amphib, amphibole; cpx, clinopyroxene; opx, orthopyroxene; phl, phlogopite. The water saturation curve from Papale *et al.* (2006).

Thus, we correlate the increase in An content to the increase in H_2O_{melt} , given the well known increase of K_d (*i.e.* resulting in a more Ca-rich plagioclase) with H_2O_{melt} (Sisson & Grove, 1993). Amphibole exhibits compositional variations as a function of temperature and water content in the melt. At 1050°C this phase is characterized by the lowest X_{Mg} ($Mg/(Mg+Fe_{\text{tot}}) = 0.56$), and the highest silica content (*i.e.* low-Ca amphibole). At 1000°C the X_{Mg} decreases from 0.8 ($H_2O_{\text{melt}} = 3.5$ wt.%, high-Ca amphibole) to 0.7 ($H_2O_{\text{melt}} = 2$ wt.%, high-Ca amphibole). Ca-rich pyroxene (augite) stability has a negative slope in the T- H_2O_{melt} space; at higher T and lower H_2O_{melt} orthopyroxene precedes sub-calcic pyroxene (pigeonite) in the crystallization sequence. Our data do not allow us to discuss in depth the chemical variation in pyroxenes. Phlogopite ($X_{Mg} = 0.88$) occurs in platy crystals at 1000°C, at very near-solidus conditions.

The compositions of the GP-1 experimental liquids cover a K_2O range from meanly HKCA to SHO series (Fig. 1) with small silica variations. The progressive potassium enrichment leads to a maximum ($K_2O = 3.7$ wt.%) in the melt produced at 1050°C. The K_2O/Na_2O ratios steadily increase with crystallization and with silica contents; moreover, potassium increase progressively with the water decrease. Comparing the K_2O contents of amphiboles with the coexisting liquids, a regular K_2O enrichment in melt occurs.

Comparison with natural rock: pre-eruptive conditions for Lower and Intermediate Brown Tuffs magma

The limited number of experiments available for this starting composition does not allow the accurate comparison of experimental data with the natural ones. In any case, a purely qualitative use of the experimental phase relationships, give us the opportunity to put some bounds on the probable pre-eruptive conditions of BT magma. If we take the maximum H_2O and CO_2 measured in melt inclusions from BT (*i.e.* $H_2O = 0.44$ wt.%; $CO_2 = 1281$ ppm as a minimum value for the dissolved volatiles in the melt), a minimum pressure of 80 MPa (calculated from Papale *et al.*, 2006) can be inferred. At the same time, if we take the H_2O value ≥ 1.7 wt.% (paired to a CO_2 below the detection limit of the FTIR) as the most likely pre-eruptive H_2O contents for BT magma, phase equilibria and melt inclusion data suggest the following considerations: 1) the absence of phlogopite in the natural rock sets a lower T-bound of $T = 1000^\circ\text{C}$, 2) the absence of amphibole phenocrysts (though reported by Lucchi *et al.*, 2008) sets a lower T limit at around 1050°C and 3) the absence of orthopyroxene phenocrysts in the natural sample (although reported at Lipari BT by Crisci *et al.*, 1983) suggests a melt water contents $H_2O_{\text{melt}} \geq 2$ wt.% .

Finally, the above considerations suggest, in a very preliminary way, that the pre-eruptive conditions of the BT magma might be close to the following conditions: $P > 80$ MPa; $T = 1020\text{-}1030^\circ\text{C}$, $H_2O_{\text{melt}} \geq 2.0$ wt.%. The experimental compositions overlap with the compositional ranges of Vulcano UBT (Piano Grotte dei Rossi Formation; De Astis *et al.*, 2006b), Punta di Mastro Minico, and Quadrara Formations natural rocks (Fig. 1).

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