

THE ARCHITECTURE OF THE MAGMATIC FEEDING SYSTEM OF THE CAMPI FLEGREI VOLCANIC DISTRICT: CONSTRAINTS FROM EXPERIMENTAL PETROLOGY

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INTRODUCTION

Experimental petrology is a powerful tool for the understanding of physical conditions controlling chemical variation displayed by magmatic systems through space and/or time. Experimental studies can, indeed, help constraining pre-eruptive parameters of magma bodies such as temperature, pressure, volatile content, and oxygen fugacity.

Generally there are relatively few experimental studies on the Phlegraean Volcanic District (PVD; Iezzi *et al.*, 2008; Fabbriozzi & Carroll, 2008; Calzolaio *et al.*, 2010; Arzilli & Carroll, 2013) none of them performed on poorly differentiated products.

Despite the relative paucity of volcanic rocks representative of primary/primitive magmas in this area, some lithic lava fragments found in products from the hydromagmatic Solchiaro eruption (23 ky ago; Morabito *et al.*, 2014) are considered representative of the most mafic and quasi-primary end members for the PVD magmatic series (D'Antonio *et al.*, 2013 and references therein).

Thus, two natural sample of K-basaltic composition collected from the "Solchiaro Unit I" have been used in this work that would be a first attempt to produce experimental data on the earliest evolutionary steps at the PVD.

STARTING MATERIALS AND EXPERIMENTAL METHODOLOGIES

The two starting materials are named APR16 and SCE. The first, kindly supplied by Massimo D'Antonio in powdered form, was collected at about 1-2 m a.s.l at Punta Solchiaro, Procida Island. The sample is porphyritic (P.I. 12% by volume) with phenocrysts of olivine (including Cr-spinel) and diopsidic clinopyroxene included into a groundmass made up of olivine, clinopyroxene, plagioclase, Ti-magnetite, and rare alkali feldspar and glass (D'Antonio *et al.*, 1999a).

Conversely the SCE sample was collected during my Ph.D work at Ciraccio bay (Procida Island). The hand specimen is porphyritic (12% vol.) in a texture with visible crystals of olivine and clinopyroxene. The paragenesis is represented mainly by phenocrysts of olivines and clinopyroxenes followed by extremely rare plagioclases. Similarly to the APR16 sample chromian spinels are sometimes found as inclusions in olivines. The groundmass was made up of the same phases, albeit with a greater amount of plagioclase, clinopyroxene, and Ti-magnetite and a less amount of glass. Such features fit well with the description of lithic lava clasts in D'Antonio *et al.* (1999a) and for these reasons the sample SCE may be compared to APR16.

About 30 experiments were performed on the two natural samples using variable $X_{\text{H}_2\text{O}}$, T, and P conditions.

In particular for the latter parameter the multilevel structure of the PVD magmatic system was reproduced using the three different pressures of 800, 400, and 200 MPa. These pressures were selected on the base of previous studies and present-day bibliographic knowledge, as well as the real skills of available devices.

This allowed to investigate a depth interval going from below the base of the crust to about 7 km above the surface (*i.e.*, from the deepest magmatic reservoir hypothesized, see Cecchetti *et al.*, 2001, to the widely recognized 7-10 km depth magma chamber).

To perform the experiments two piston-cylinder were used. For the higher pressure an *end loaded* type, whereas for the intermediate and lower pressure a *non end loaded* type. Both devices were used for equilibrium

experiments and according to Masotta *et al.* (2012) thermal gradient experiments, at pressures of 400 and 200 MPa as a support to the more classical equilibrium runs, were also performed.

End loaded piston-cylinder

The majority of phase equilibrium experiments at 800 MPa were performed at the HP-HT laboratory of Sapienza University of Rome using a ½ inch *end loaded* piston-cylinder. The apparatus is calibrated to perform experiments in the range of pressure 0.7 - 3 GPa and can reach a maximum temperature of 1450 °C. Experiments were carried out in the temperature range from 1310 to 1125 °C. These temperatures were selected to investigate the liquid line of descent starting from the liquidus temperature (slightly below the maximum experimental temperature) for the given composition and pressure. Assemblies were pressurized up to 20% of the final value before heating and then the working pressure was reached and maintained at constant value until the final isobaric quench. Temperature was monitored using a factory calibrated D type (W₃Re₉₇-W₂₅Re₇₅) thermocouple with ±5 °C of uncertainty. The powdered natural samples selected to be used as starting material were sealed into a 3×6 mm tube of a Au₇₅Pd₂₅ alloy. The assembly was formed by a fluorite cell, a straight-walled graphite furnace, an MgO crushable support drilled to host the capsule. The space between capsule and support wall were filled with alumina or pyrophyllite powder for anhydrous and hydrous experiments, respectively. Indeed, according to Freda *et al.* (2001), pyrophyllite powder allows to reduce water loss during hydrous experiments. The entire assembly was wrapped in a Pb foil of 0.001 inch (0.0254 mm) having function of lubricant during the compression step of the experiment. All the runs were self-buffered; an attempt to estimate f_{O_2} through the equation of Kress & Carmichael (1991) using the liquid Fe³⁺/Fe_{tot} mole ratios from K_D Fe-Mg ol/liq calculated according to Toplis (2005) yielded f_{O_2} values of -1.0 to +0.8 ΔNNO, in agreement with those estimate for similar furnace assemblages (Conte *et al.*, 2009; Weaver *et al.*, 2013).

Non end loaded piston-cylinder

The experiments conducted with the *non end loaded* piston cylinder were performed at the HP-HT laboratory of Istituto Nazionale di Geofisica e Vulcanologia (INGV) of Rome using a Quick-Press device. The apparatus can perform experiments in the range 150-1000 MPa and reach temperatures up to about 1400 °C. Two different pressure plates are available (1 ¾ inch). The plates are calibrated to perform experiments in the range of 150-300 MPa and 400-1000 MPa respectively.

As previously mentioned both equilibrium and thermal gradient experiments were performed at pressures of 200 and 400 MPa. Experiments were carried in the temperature range 1200-1025 °C at 200 MPa and 1235-1100 °C at 400 MPa. This temperature range was chosen following the same criterion of the *end loaded* experiments. The hot piston out technique was used in all experiments, pre-pressurizing the charge up to 20% of the final value. The temperature was monitored using a factory calibrated C type (W₉₅Re₅-W₇₄Re₂₆) thermocouple with ±5 °C of uncertainty. Only Pt capsules were used. For thermal gradient experiments a capsule length of about 7 mm was used, whereas for the equilibrium experiments the initial length was of 4 mm.

Two assemblies were employed (19-25 mm and 19 mm) as described in Masotta *et al.* (2012). They are composed by a NaCl cell, a pyrex cylinder, the straight-walled graphite furnace, the MgO crushable and a pyrex or pyrophyllite powder. The latter one used to prevent water loss in hydrated experiments (Freda *et al.*, 2001). This kind of assembly produces a f_{O_2} of NNO +2 (Masotta *et al.*, 2012).

ANALITICAL TECHNIQUES

First characterization, morphological study, and back scattered image acquisition were obtained for both the natural samples and all run's products by scanning electron microscope (SEM) using a FEI quanta 400 equipped with microanalysis system EDAX Genesis at the CNR Istituto di Geologia Ambientale e Geoingegneria, Rome.

Electron microprobe analyses (EMPA) were performed with a Cameca SX50 electron microprobe equipped with five-wavelength dispersive spectrometer (WDS). A 15 kV accelerating voltage, 15 nA beam

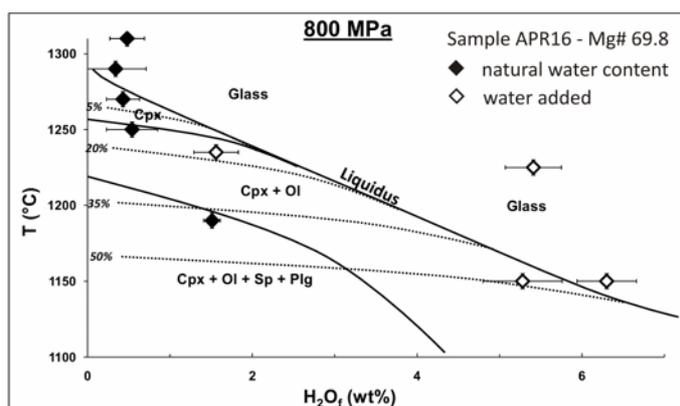


Fig. 1 - Temperature versus final water in residual melt (H_2O_f) phase relations diagram for experiments conducted on the APR16 composition at 800 MPa. Percentage of crystallization reported as thin dotted lines.

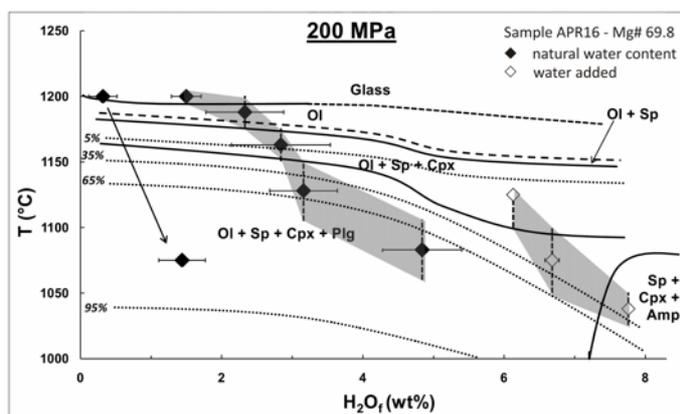


Fig. 2 - Phase relations diagram in the T- H_2O_f space for the 200 MPa experiments conducted on the APR16 composition. The black arrow on the left indicates liquid evolution for equilibrium experiments. Shaded areas for thermal gradient experiments. All other symbols as in Fig. 1.

the two “end member” pressures investigated are displayed in Fig. 1 and 2) and changing of phase’s composition with different experimental conditions (Fig. 3 and 4).

DISCUSSIONS AND CONCLUSIONS

Starting from the analysis of phase relations (Fig. 1 and 2) it is interesting to note that high pressure runs gave a contribution in clarifying the possible mantle source mineralogy underlying the Phlegraean area. As suggested by some authors (Mazzeo *et al.*, 2014 and references therein), the mantle source for PVD magmas may be an amphibole and/or phlogopite bearing veined lherzolite. Notably, in the 800 MPa experiments from this work, neither phlogopite nor amphibole appear (Fig. 1). The absence, in these runs, of amphibole (stable instead at low pressure; Fig. 2) must be related to the used experimental conditions (namely, temperatures not suitable for the amphibole stability field). On the contrary, the same conditions are suitable for phlogopite crystallization (Conte *et al.*, 2009), therefore the absence of this phase can be related to the low K/Na ratio in the

current has been used. Together with the following standards: metals for Mn and Cr; jadeite for Na; wollastonite for Si and Ca; orthoclase for K; corundum for Al; magnetite for Fe; rutile for Ti and periclase for Mg. Glasses were analysed using a defocused electron beam from 10 to 15 μm to avoid alkali loss, whereas for minerals the beam diameter was of 1 μm . The ZAF correction method was used. Also this device was available at the CNR Istituto di Geologia Ambientale e Geoingegneria, Rome.

Equilibrium and thermal gradient experiments have been treated in a specific different way. Indeed the first ones show a homogenous capsule and a single paragenesis whereas the thermal gradient ones, being not homogeneous, commonly display zones at different paragenesis. These last can be identified by the use of a SEM device. For the analysis of thermal gradient experiment the procedure described in Masotta *et al.* (2012) was used.

RESULTS

The sub-liquidus experiments show variable mineralogical assemblages: stable phases observed by use of the scanning electron microscope are: olivine, clinopyroxene, plagioclase, spinel, and amphibole.

The main results derived from the experimental runs are phase relations at the three pressures investigated (examples from

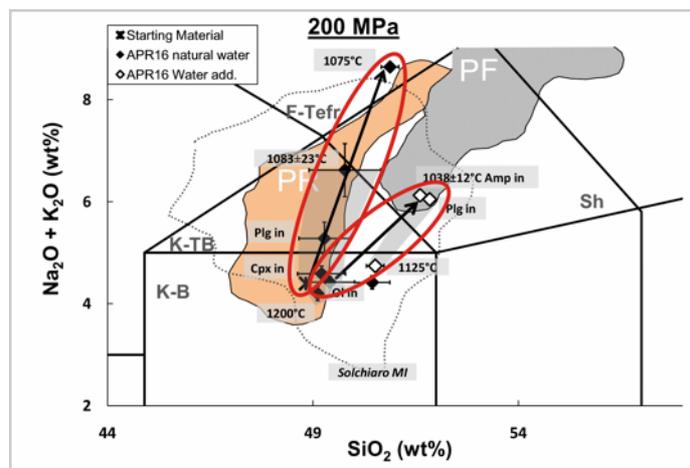


Fig. 3 - Example of the two trend (for more detail see section discussions and conclusions) recognizable in the experimental glasses when reported on of total alkali *versus* silica diagram (TAS). Here are reported results from the 200 MPa experiments. The starting material is indicated as a double cross, other symbols are as in Fig. 1. When not shown, error bars are smaller than symbol size. The grey field represents natural bulk compositions erupted at Phlegraean Fields, whereas the salmon pink field depicts Procida mafic products (D'Antonio & Di Girolamo, 1994; D'Antonio *et al.*, 1999a; 1999b; De Astis *et al.*, 2004), dotted bordered field represents melt inclusion compositions (MIs) from Solchiaro (Esposito *et al.*, 2011; Mormone *et al.*, 2011). Labels indicate run's temperature.

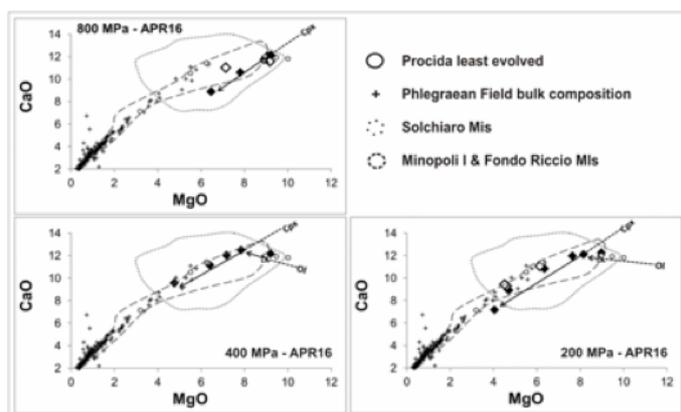


Fig. 4 - Example of CaO *versus* MgO diagrams for experimental glasses at the three pressures carried on composition APR16. For comparison, are also reported natural samples (data from D'Antonio *et al.*, 1999a; Di Girolamo *et al.*, 1984; Civetta *et al.*, 1991, 1997; Orsi *et al.*, 1995; De Vita *et al.*, 1999; Pappalardo *et al.*, 2002; De Astis *et al.*, 2004; Esposito *et al.*, 2011; Mormone *et al.*, 2011; Cannatelli *et al.*, 2007).

starting composition. This suggests that phlogopite, if present, may occur with a negligible abundance or even that amphibole may have played a major role during magmas formation.

Phase relations obtained from the low pressure experiments (200, but also 400 MPa) show olivine as liquidus phase for all initial water content investigated. Fowler *et al.*, (2007), starting from a shoshonitic composition, considered as the Campanian Ignimbrite parental magma, calculated, by MELTS software, that about a 5 wt.% of olivine should segregate in the first 100 °C of cooling. This, along with the 200 and 400 MPa results, points out the olivine as an ubiquitous and relevant phase during the differentiation steps of PVD primitive magmas. Moreover, it should be noted that olivine does not occur in the most evolved natural PVD products, such as the trachytes from Campanian Ignimbrite.

The overall results drives towards the hypothesis of a deep (crust/mantle boundary) liquidus crystallization of clinopyroxene (alone or in co-saturation with olivine, see 800 MPa results in Fig. 1). This is supported by major element compositional trends defined by least evolved melt inclusions of the PVD compared with our results from high (800 MPa) and low (200 and 400 MPa) pressures experiments (Fig. 4) as well as by the comparison between the composition of natural and experimental clinopyroxenes (Fig. 5). Focusing on the initial steps of differentiation (Fig. 4) depicted by the melt inclusions (MIs) found in Minopoli I and Fondo Riccio volcanic products (representing the least evolved Phlegraean Fields compositions) on the CaO vs. MgO diagram, and comparing them with the experimental results, the natural trend can be reproduced if clinopyroxene is the liquidus phase indicating, then, the start of PVD magma differentiation at high pressure (greater than 400 MPa). This conclusion is enforced comparing the composition of

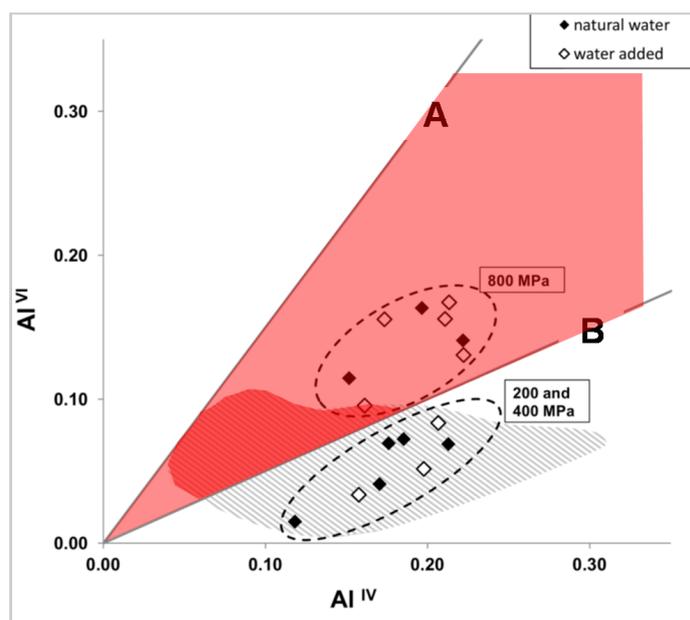


Fig. 5 -Diagram of Al^{VI} vs. Al^{IV} (from Aoki & Kushiro, 1968) for natural clinopyroxenes from the less differentiated products of the PVD together with the experimental points (means). Symbols as in Fig. 1.

that the difference between CF and Procida, at least in the first differentiation, can be attributed to a different water content in the respective primitive magmas. This hypothesis closely agrees with that of Moretti *et al.* (2013) in which, on the basis of the study of melt inclusions in phenocrysts of Ischia lavas, the initial water amount at CF is constrained to be almost double compared to that of Procida (~ 4 wt.% and ~ 2 wt.%, respectively).

Interestingly, the experiments from this work show that there is no need to consider limestone assimilation in order to explain the compositional features of the PVD magmas as invoked by several authors. Actually, carbonate would indeed shift the compositions toward a strong silica undersaturation (Mollo *et al.*, 2010 and references therein).

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natural clinopyroxenes with that of experimental ones. Indeed as shown in Fig. 5, part of natural clinopyroxenes well match the composition of the crystals obtained from the 800 MPa experiments.

Focusing on the experimental glasses compositions, two main TAS trends have been reproduced despite the three different pressures investigated (Fig. 3). An approximately vertical one (going from K-basalt toward phono-tephrite) better representing the Procida least evolved naturals and a more flattened one (*i.e.*, from K-basalt toward shoshonites) reaching the least evolved natural products from Campi Flegrei.

The difference between the two experimental trends reflects the conditions of initial X_{H_2O} (*i.e.*, less than 2 wt.% produce the more vertical trend whereas a greater amount of initial water flattens the trend). Consequently, experimental results suggest

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