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Effect of water on the phase relations of primitive K-basalts: implications for high-pressure differentiation in the Phlegraean Volcanic District magmatic system.

Perinelli Cristina^{1,*} cristina.perinelli@uniroma1.it, Gaeta Mario¹, Bonechi Barbara¹, Granati Serena F.¹, Freda Carmela², D'Antonio Massimo^{3,4}, Stagno Vincenzo¹, Sicola Stefania⁵, Romano Claudia⁵

¹Dipartimento di Scienze della Terra, Sapienza Università di Roma, Italy

²Istituto Nazionale di Geofisica e Vulcanologia, Rome, Italy

³Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università degli Studi Federico II di Napoli, Italy

⁴Istituto Nazionale di Geofisica e Vulcanologia - Osservatorio Vesuviano, Naples, Italy

⁵Dipartimento di Scienze, Università Roma Tre, Italy

*Corresponding author.

ABSTRACT

Phase relations, compositions, and modes of two natural primitive alkaline basalts were determined through experiments performed at 0.8 GPa, temperatures between 1000 and 1310 °C, and nominal water (H_2O_i) contents varying from < 1 (natural water rock content) to 6 wt.%. The two natural samples used as starting material are high-Mg, moderate-K, alkaline basalt scoria clasts ($Mg\# = 0.68-0.66$, $\Sigma_{alkalis} = 4.4$ wt.%) dispersed within the hydromagmatic tuff of the Solchiaro eruption (Procida Island, southern Italy). These samples are considered representative of parental magmas feeding the Phlegraean Volcanic District, which includes the Campi Flegrei caldera and the Procida and Ischia islands. The composition of the experimental phases has been compared with that of natural rocks to constrain the early stages of crystallization of poorly differentiated magmas from the Phlegraean Volcanic District. Our study shows that the liquidus temperature at $H_2O_i < 1$ wt% is ~1300 °C whereas with water contents between 1.5 and 3 wt.%, and between 4 and 6 wt.%, the apparent liquidus temperature decreases of about 50-100 °C, respectively. Under natural water conditions (<1 wt%), the liquidus phase is clinopyroxene, followed by olivine and Cr-spinel and, then, by plagioclase. The increase of H_2O content in the system enhances olivine stability along with clinopyroxene at the liquidus temperature. The 4-6 wt.% water bearing experiments show evidence of H_2O saturation at 1100 °C, with olivine being replaced by orthopyroxene later joined by pargasitic amphibole and minor amounts of oxide starting from 1080 °C. The composition of glasses in the experiments with low H_2O_i content is consistent with the trachybasaltic products of Procida; glasses obtained in the runs with 1.5-3 wt.% water resemble the trend formed by the shoshonitic products of Campi Flegrei. The water-saturated experiments produced variably alkali-depleted residual glasses whose composition converges toward the subalkaline field. The compositions of the experimental clinopyroxenes match well those found in the Campi Flegrei products for which we have estimated crystallization

conditions from 1140 to 1200 °C of temperature and from 0.6 to 0.9 GPa of pressure (22-33 km). Phase equilibria constraints and clinopyroxene compositions suggest that the parental magmas of Procida likely contained < 2 wt.% of H₂O and were affected by an early stage of fractionation at a depth corresponding to the local Moho (~ 25 km corresponding to ~ 0.8 GPa assuming an average crustal density of 2.8 g/cm³). Based on our results, an early magmatic storage at this level could have caused a deep degassing process able to remove variable proportions of Na and K from the melt.

KEYWORDS: hydrous primitive magmas; K-alkaline basalts; experimental petrology; phase equilibria; high pressure storage and differentiation; Phlegraean Volcanic District.

1. Introduction

The Phlegraean Volcanic District (PVD-southern Italy; Fig.1), includes the Campi Flegrei and Ischia and Procida islands and it represents one of the most active volcanic areas in the Mediterranean region. This volcanic area is located near the south-western margin of the Campania Plain, within a graben linked to the extension occurred along the south-western margin of the Apennine Mountains during the opening of the Tyrrhenian Sea basin in the Pliocene-Quaternary (Acocella et al., 1999). Its volcanic products, mostly pyroclastic rocks, show a well-documented compositional variation spanning from rare K-basalt and shoshonite through latite to predominant trachyte and slightly peralkaline phonolite, identifying a potassic, mildly alkaline series (e.g. Armienti et al., 1983; Civetta et al., 1997; D'Antonio et al., 1999a, 1999b; de Vita et al., 1999; Melluso et al., 2012; Orsi et al., 1995; Pappalardo et al., 1999). The origin of the PVD magmatism has been identified in a K-rich mantle, whose enrichment, according to the most accredited hypothesis, is due to fluids/melts released by the subducting Ionian oceanic lithosphere, which was part of the wider Tethys Ocean (Avanzinelli et al., 2009; D'Antonio et al., 1999a, 1996; Mazzeo et al., 2014; Peccerillo, 2017; Schiano et al., 2004; Tonarini et al., 2004). The 2 Ma old, calc-alkaline volcanic products found in Parete and Castelvoturno bore-holes (north-west of Campi Flegrei; Beccaluva et al., 1991 and references therein) may represent a distinct cycle of volcanic activity associated to a source different from the one that originated the recent potassic magmas of the Campania Province. The change from calc-alkaline to variable K-alkaline rock series, also observed in other volcanic districts of the circum-Tyrrhenian region (Beccaluva et al., 2013; Conticelli et al., 2009), provides evidence of the increasingly marked metasomatic modification of the upper mantle following the recycling of crustal components via subduction. To date many petrological and geochemical studies (Peccerillo, 2017 and references therein) have been addressed to reconstruct the differentiation processes at the

origin of the PVD igneous rock types (from silica-saturated to slightly silica-undersaturated, potassic compositions). Nevertheless, to unravel the differentiation processes affecting PVD magmas is not a trivial task. Indeed, most of the erupted magmas are characterized by evolved compositions with their trace-element distributions and isotopic characteristics masked by shallow processes like fractional crystallization and mingling/mixing (e.g. Armienti et al., 1983; Civetta et al., 1997; D'Antonio et al., 1999b; de Vita et al., 1999; Melluso et al., 2012; Orsi et al., 1995; Pappalardo et al., 1999; Peccerillo, 2017). Moreover, very few experimental investigations, all carried out on differentiated rock samples (latitic to trachytic compositions), focused on the role of those parameters controlling the differentiation processes of PVD magmas, namely pressure (0.0001 – 0.2 GPa), temperature (750-1300°C), oxygen fugacity (f_{O_2} ; ~ NNO + 1 buffer) and (0-8 wt.%) H₂O (Arzilli and Carroll, 2013; Calzolaio et al., 2010; Fabbrizio and Carroll, 2008; Iezzi et al., 2008). The least-evolved volcanic rocks of the whole PVD, are K-basaltic scoria clasts occurring in the hydromagmatic tuff of the Solchiaro eruption (Procida Island, ~ 22 ka ago; Morabito et al., 2014). The similarity in geochemical and isotopic features among Procida, Ischia and Campi Flegrei and between the PVD and Somma-Vesuvio products highlights a strong relationship within the Campania Province magmas and allows to consider the K-basaltic scoria clasts from Procida as the parental magmas of the recent (< 50 ka) volcanic products of the Campania Province (Civetta et al., 2004; Fedi et al., 2018; Mazzeo et al., 2014; Pappalardo and Mastrolorenzo, 2012). Therefore, to perform experiments aimed at investigating the effect of water on mineral phase equilibria, as starting material we used natural samples from the Solchiaro deposit (APR16 and SCE) and a glass (APR16GL) made from the APR16 sample. Our investigations allowed us to retrieve the early stages of evolution of PVD magmas. All experiments were performed at 0.8 GPa since this pressure can be considered representative of the crustal-mantle boundary in the Phlegraean area (~ 25 km of depth; Di Stefano et al.,

2011). At that depth the presence of a possible crystallization zone was hypothesized on the basis of the results of melt inclusion studies (Moretti et al., 2013; Mormone et al., 2011), seismic data interpretations (Chiarabba et al., 2008; Di Stefano et al., 1999; Piochi et al., 2005) and gravimetric and petrological modelling (Fedi et al., 2018). In particular, the latter authors hypothesize the occurrence of a layer of dunitic and gabbroic cumulates at the Moho depth formed by ~ 26 vol.% of crystallization from a near-primary magma, and of less dense cumulates and magma pockets at shallower depth to account for the wide gravity low evidenced by Bouguer gravity anomalies in the Campania volcanic area (Florio et al., 1999). In this view, the high-pressure crystallization (i.e. at the local crust base) is a process that possibly contributed to the differentiation of primitive magmas of the Campania Province. Therefore experimental investigation on the phase relationships and melt compositions in the K-basalt system is critical to highlight the role of pressure and water contents on magmatic differentiation processes (e.g. Perinelli et al., 2017; Tecchiato et al., 2018).

2. Methods

2.1. Starting materials and capsules preparation

Details on petrography and mineral chemistry of K-basaltic scoria clasts are described by D'Antonio et al. (1999a), De Astis et al. (2004) and Mazzeo et al. (2014); here we briefly describe the main textural and compositional features of the rocks selected as starting material. The APR16 and SCE samples are unaltered, dm-sized, porphyritic scoriae (porphyritic index 12% by volume for both samples) with phenocrysts of olivine (Fo_{80-87}) sometimes including Cr-spinel, and clinopyroxene ($\text{Wo}_{46-48}\text{En}_{46-31}\text{Fs}_{6-23}$). The groundmass consists of olivine, clinopyroxene, plagioclase (An_{79-52}), Ti-magnetite ($\text{Usp}_{4.1-4.4}$) and scarce glass. The two selected samples show Mg# ($\text{MgO}/(\text{MgO}+\text{FeO})$, molar - calculated assuming all iron as $\text{FeO}_{\text{total}}$) of 0.66 and 0.68, SiO_2 content of 49 and 48 wt.%, alkalis amount of 4.4 and

4.3 wt.%, MgO content of 9 and 10 wt.%, respectively, and CaO content around 12 wt.% (Table 1). In both samples, some trace elements, namely Sc, Cr, Sr and Ba, are highly concentrated and light Rare Earth Elements (REE) are slightly enriched with respect to the heavy REE. The isotopic composition of APR16 is characterized by low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.70506) and high $^{143}\text{Nd}/^{144}\text{Nd}$ (0.51273) representing, therefore, the least radiogenic composition of the whole area reported in literature to date (Mazzeo et al., 2014). The near-primary character shown by APR16 and SCE geochemistry indicates that these compositions are the most appropriate to be used as starting materials for the purpose of this study.

The APR16 and SCE clasts were crushed and grinded in an agate mortar under acetone to a grain-size $\leq 10\text{ }\mu\text{m}$. Despite the fine grinding, the occurrence of phenocryst fragments into the starting material, albeit very small in size, can influence the kinetic of reactions during the experiments, possibly forcing the crystallization of metastable phases and then influencing the phase relations. To evaluate this effect, we prepared a glassy starting material (APR16GL) at the Bayerisches Geoinstitut by melting the APR16 powder at $1400\text{ }^{\circ}\text{C}$ for 15 minutes at atmospheric pressure and oxygen fugacity buffered at Nickel-Nickel Oxide level by means of a CO/CO_2 gas mixture fluxed inside the furnace. The composition of the obtained glass is reported in Table 1. As reported in the “Experimental results” section the different starting materials do not produced appreciable differences in the experimental products.

The three powdered starting materials (APR16, SCE, APR16GL) were dried at $110\text{ }^{\circ}\text{C}$ for at least 2 hours to remove the moisture before being loaded in $\text{Au}_{75}\text{Pd}_{25}$ capsules. In some capsules we added water in known amounts by using a $1.0\text{ }\mu\text{L}$ microsyringe (Table 2). Loss of H_2O by vaporization during welding was prevented by freezing the crucible with nitrogen. Water loss was checked by the weight test before and after welding. For the sake of simplicity, we refer to the experiments conducted with $< 1.5\text{ wt.}\%$ of initial water content

(H₂O_i) as *NWA* (No Water Added), to those with 1.5-3 wt.% H₂O_i as *damp* and to those with 4-6 wt.% H₂O_i as *wet*.

2.2. Experimental techniques

The experiments were carried out at the HP-HT Laboratory of the Department of Earth Sciences of Sapienza University of Rome. We used a ½ inch end-loaded piston cylinder apparatus to perform experiments at pressure of 0.8 GPa and 1000-1310 °C. The employed assemblies consisted of outer CaF₂ cell, graphite furnace and MgO crushable spacers. The capsules were surrounded by alumina powder in the case of *NWA* starting materials, while pyrophyllite has been used as buffer in those experiments containing free water (Freda et al., 2001). The temperature was measured using a D-type (W₃Re₉₇-W₂₅Re₇₅) thermocouple with an uncertainty of ± 5 °C.

Run duration was between 3 and 9 hours (Table 2). Previous results from our laboratory (e.g., Conte et al., 2009; Bonechi et al., 2017) demonstrated that these are durations suitable to achieve an acceptable approach to equilibrium also in experiments performed on natural finely-powdered rock at anhydrous conditions.

The oxygen fugacity (fO_2) was not externally buffered. However, we determined the intrinsic fO_2 using the equation of Kress and Carmichael (1991) calculating the Fe²⁺ and thus the liquid Fe³⁺/Fe_{tot} mole ratios, from K_D^{Fe-Mg} between olivine and coexisting liquid computed as function of temperature and pressure by means the thermodynamic equation of Toplis (2005). This procedure yielded fO_2 between -1.0 to +0.8 ΔNNO, in agreement with previous estimates from runs performed with the same kind of CaF₂ cell assemblages (Conte et al., 2009; Weaver et al., 2013).

2.3. Analytical methods

After recovering, each capsule was mounted in epoxy resin and polished for microanalyses. Textures and phase assemblages were analysed using a FEI Quanta-400 scanning electron microscope equipped with an EDAX Genesis microanalysis device available at the Department of Earth Sciences of Sapienza University of Rome. Phase compositions were analysed at the CNR-Istituto di Geologia Ambientale e Geoingegneria (Rome), with a Cameca SX50 electron microprobe equipped with five wavelengths dispersive spectrometer (WDS). Quantitative analyses were performed using 15 kV accelerating voltage and 15 nA beam current. As standards we employed pure 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. Counting times were 20s for elements and 10s for backgrounds. Light elements were counted first to prevent loss by volatilization. The PAP correction routine was used. Core/rim compositions of minerals were obtained by using a beam diameter of 1 μm whereas for glasses a defocused electron beam of 10 to 15 μm was used. Glasses that were suspected to have undergone alkali loss during the analysis (e.g. those with ≥ 6 wt.% H_2O) on the basis of mass balance calculations were re-analysed setting the beam current at 2nA (Morgan and London, 1996).

The precision of the analytical totals of the glasses was estimated as described by Gaeta et al. (2009). The water contents of residual glasses ($\text{H}_2\text{O}_\text{f}$) were estimated using the *by-difference* method (Devine et al., 1995). Because this approach is not recommended for H_2O -poor glasses ($\text{H}_2\text{O} \leq 1$ wt.%) due to its associated uncertainty (~ 0.5 wt.%), the water content of some NWA and *wet* experimental products has been determined by using micro-Raman spectroscopy (Le Losq et al., 2012; Di Genova et al., 2017; Table 2). The criteria for experimental samples selection include the occurrence in the charge of glass portions free of minerals or bubbles large enough for analyses. Raman spectra were acquired with a Horiba Lab Ram HR 800 spectrometer at the Department of Science, Roma Tre University. Data

were collected using a 600 grooves/mm spectrometer grating and CCD detector. Error in water determination is estimated ± 0.15 wt.% (see Appendix 1 in supplementary materials for analytical details). H₂O-glass contents by micro-Raman analyses are in all cases higher than those determined *by-difference* method, however the two approaches show a good linear correlation (correlation coefficient $R^2 = 0.97$; Fig. A.1 supplementary materials). Therefore, the H₂O_f values from EMP analyses have been corrected according to the regression function reported in Figure A1 and the data are reported in Table 2. Finally, phase proportions were calculated using bulk and experimental phase compositions, and the least squares regression routine implemented in the EXCEL® program. Attainment of equilibrium in the experiments was assessed by textural and geochemical criteria namely, sub- to euhedral shape of the newly formed minerals, chemical homogeneity of phase compositions, mass balance calculations with sum of the squares of residuals (Σr^2) less than 1.0 and major element partitioning; in particular for the latter, we have verified that the Fe-Mg exchange coefficients for clinopyroxene-liquid pair is consistent with literature experimental data .

3. Experimental results

The experimental conditions, phase assemblages and proportions are reported in Table 2; the compositions of residual glasses and mineral phases are given in Table A.1 and Table A.2 (Supplementary Materials), respectively.

Mass balance calculations show that the loss of Fe (% ΔFe) for most of runs is between 1 and 25%. However, no systematic change in mineral assemblage and composition appears in charges with different Fe losses, as demonstrated by the comparison between the products of APR16 ($\Delta\text{Fe} = -25\text{-}26\%$) and APR16GL ($\Delta\text{Fe} = -1\%$) wet experiments (see later and Table 2). The low Fe values calculated for the latter experiments are probably due to the redox conditions at which APR16GL starting material was prepared that are close to the

experimental ones ($fO_2 \sim NNO$ buffer). The experimental products for which the Fe-loss resulted so relevant to affect the composition of crystallized minerals ($\Delta Fe > -26\%$) have been reported in the Tables, but not considered in the discussion.

All the experimental products consist either of glass or glass coexisting with crystal phases. When present, crystals are homogeneously distributed over the capsule, demonstrating the absence of thermal gradients. The crystallized minerals are olivine (Ol), clinopyroxene (Cpx), plagioclase (Plg), amphibole (Amph), oxides (Ox) and orthopyroxene (Opx), all ranging from $< 5 \mu m$ to $600 \mu m$ in size (Fig. 1 and Fig. A.2). Overall, no significant textural differences have been found between products of both type of starting materials (i.e., natural rock and glassy powders; Fig. 1). Indeed, in both APR16 and APR16GL experiments the habit of crystalline phases is sub- to euhedral and the only significant difference is that, occasionally, the largest clinopyroxenes ($\geq 90 \mu m$) of APR16 experiments show small relict cores in sharp contact with compositionally homogeneous and volumetrically more abundant rims (Fig. 2a, c); the composition of these cores (< 1 vol.%) was excluded from mass balance calculations. Amphiboles are sometimes characterized by a zonation marked by a thin layer ($< 5 \mu m$) at the edge of crystals (Fig. 1d, e). Notably, the presence of abundant bubbles in the *wet* experiments suggests the presence of a fluid phase (Fig. 1e, f).

3.1. Phase relations and melt fraction

The phase relations of the three starting compositions, APR16, SCE and APR16GL, are shown in the T- H_2O_f content projections (Fig. 2). The liquidus temperature is at about $1300^\circ C$ in the NWA runs and below $1150^\circ C$ for H_2O_f contents higher than 8 wt.%. Note that, independently from the water content in the system, about 50 wt.% of crystallization takes place within a $\Delta T \sim 100^\circ C$ below the liquidus temperature (Fig. 3).

In the *NWA* runs, clinopyroxene is the liquidus phase (1270 – 1295 °C) followed by olivine and oxide (Cr-spinel) at 1250 °C (for Mg# = 0.68 starting materials) and by plagioclase at 1190-1235 °C (Table 2) and at this temperature about 30 wt.% of the system is crystallised (Fig. 3).

In the *damp* runs, i.e. 1.5-3 wt.% H₂O_i, olivine begins to crystallize reaching a degree of crystallization (≤ 15 wt.%) lower than that at *NWA* conditions (≥ 20 wt.%). Our experiments suggest the onset of olivine crystallization at H₂O ≥ 1.8 wt.% in the melt. These conditions are close to those predicted by thermodynamically-based rhyolite-MELTS modelling of Gualda et al. (2012) indicating olivine crystallization at a minimum water content of 2.5 wt.% in the studied K-basalt (Bonechi et al., 2017).

In the *wet* runs, i.e. 4-6 wt.% H₂O_i, olivine joins clinopyroxene at 1150 °C and it is replaced by orthopyroxene coexisting with oxide at 1100 °C. The occurrence of orthopyroxene in the mineral assemblage is as well predicted by the rhyolite-MELTS modelling for both, low and high H₂O_i contents in the system (Bonechi et al., 2017), although primitive Procida magmas are nepheline normative (2.1-9.4 wt.%; D'Antonio et al., 1999a). By lowering the temperature ($T = 1080$ °C), amphibole becomes stable and the resulting mineral assemblage for temperatures down to 1000 °C is composed by Cpx + Amph + Ox + Opx (Table 2). Notably, the phlogopite does not crystallize neither in APR16 nor in SCE composition, notwithstanding their relatively high K₂O contents and suitable experimental conditions (Conte et al., 2009). The absence of phlogopite suggests that this phase, although potentially present along with amphibole in the subduction-modified peridotitic mantle source (see Mazzeo et al., 2014), does not play a significant role in the origin PVD parental magmas; this strongly differs from what evidenced in the Roman Province (e.g. Gaeta et al., 2011, 2016).

3.2. Composition of experimental products

Glasses compositional variation obtained from each of the starting materials APR16, SCE and APR16GL experiments shows the typical trends of progressive crystallization depending on temperature and H_2O_i in the system (Fig. 4). Overall, glass composition in *NWA* and *damp* experiments varies from K-basalt to K-trachybasalt (APR16) up to shoshonite (SCE and APR16GL) compositions with decreasing temperature. In particular, in the *NWA* runs, before reaching the temperature at which plagioclase significantly crystallizes, the glass composition is controlled by clinopyroxene thus leading to a very limited SiO_2 increase in the residual glasses (from ~49 to ~50 wt.%, Fig. 4). In *damp* experiments, the earlier crystallization of olivine±spinel causes a slightly more marked increase of SiO_2 abundance in the residual glasses (from ~49 to ~51 wt.%; Table A.1). Differently, in *wet* experiments the differentiation path of the liquids is characterized by a remarkable increase of SiO_2 content (e.g. up to ~61 wt.%) coupled to a decrease of alkali content, leading the glass composition to the basaltic-andesite and andesite fields. Moreover, by using MgO as differentiation index, it appears that in *NWA* and *damp* experiments, the dominant crystallization of clinopyroxene drives to a decrease of CaO contents and to an increase of Al_2O_3 contents until plagioclase crystallizes. In the *wet* experiments the crystallization of amphibole (SiO_2 = ~43 wt.%, and TiO_2 = 1.9 wt.%), causes the strong increase of SiO_2 content in the residual melts coupled to a significant decrease of TiO_2 ; this behaviour is not observed in the *NWA* and *damp* glasses (Fig. 5a, b, c).

Clinopyroxene crystallized in *NWA* experiments from APR16 is augitic in composition ($Wo_{43-44}En_{46-52}Fs_{4-10}$) whereas in both *damp* and *wet* runs it is diopsidic ($Wo_{46-48}En_{41-46}Fs_{8-11}$; Table A.2); clinopyroxene from SCE is diopsidic in composition ($Wo_{44-50}En_{41-50}Fs_{5-9}$) in all experiments; APR16GL clinopyroxenes in *NWA* and *damp* experiments are augitic in composition ($Wo_{43-45}En_{43-48}Fs_{7-12}$) while those crystallized in the *wet* runs are diopsides ($Wo_{48-50}En_{40-41}Fs_{10-11}$). Overall, Mg# values (calculated as the molar $MgO/(MgO+FeO_{tot})$ ratio) vary between 0.77 and 0.88 and decrease over all investigated H_2O_i contents and with

the degree of crystallization (Fig. 6). Moreover, the DiHd (diopside-hedbergite- $\text{CaFmSi}_2\text{O}_6$) and CaTiTs (titanium-calcium Tschermak - $\text{CaTiAl}_2\text{O}_6$) components of clinopyroxenes calculated according to the Putirka approach (2008), show a positive correlation with H_2O content while a broad negative correlation is apparent with respect to the Jd (jadeitic molecule- $\text{NaAlSi}_2\text{O}_6$; Fig. 6). The Fe-Mg distribution coefficients between clinopyroxene and melt (K_D Fe-Mg), calculated assuming all Fe as Fe^{2+} in both phases, are 0.29 ± 0.05 (1σ), 0.29 ± 0.04 (1σ) and 0.30 ± 0.04 (1σ) for APR16, SCE and APR16GL, respectively; this is in agreement with experimental data in basaltic compositions (e.g. 0.26-0.31, Sisson and Grove, 1993; 0.28 ± 0.08 , Putirka, 2008; 0.27 ± 0.06 , Pichavant et al., 2014; 0.31-0.36, Iacovino et al., 2016). Due to the preference of Al to occupy tetrahedral and octahedral sites at high T and P, respectively (Herzberg, 1978; Thompson, 1974), the Al^{IV} vs Al^{VI} diagram provides good indications on pressure conditions at which clinopyroxene crystallizes. Figure 7a compares Al coordination of experimental clinopyroxenes from this study with those produced in experiments at different pressures selected from LEPR database (Library of Experimental Phase Relations; <http://lepr.ofmresearch.org>) on the basis that: 1) all experiments are “crystallization-type”; 2) the crystallization degree is $\leq 60\%$ (close to the maximum value calculated for our experiments); 3) the starting material has a high-K calcalkaline to shoshonite or K-basaltic composition, similar to APR16 sample (i.e. Conte et al., 2006); 4) the initial H_2O content ranges between 0 and 5 wt.% and 5) the Mg# of clinopyroxenes is ≥ 80 . Figure 7a shows that most of the APR16, SCE and APR16GL clinopyroxenes fall in the compositional field defined by clinopyroxenes crystallized in the range from 0.7 to 1 GPa of pressure. The small amount of clinopyroxenes approaching the low-pressure field are those in equilibrium with residual glasses characterised by the highest water content (APR16 and APR16GL *wet* runs; Fig. 7a). A similar behaviour is observed in Figure 7b, where the diagram Al^{VI} is plotted versus Na, suggested to be a pressure-sensitive

element (Putirka, 2008). This behaviour is likely due to the preference of Al^{IV} to be incorporated into clinopyroxene crystal lattice when increasing the H_2O in the melt (Perinelli et al., 2018 and references therein); this leads to higher content of the titanium-calcium Tschermak molecule ($\text{CaTiAl}_2\text{O}_6$) and lower content of the jadeitic molecule ($\text{NaAlSi}_2\text{O}_6$) (Fig. 6c, d). Moreover, the coexistence of Al-Na-bearing amphibole in these experiments further decreases the aluminium and sodium activity in the melt (e.g. see Grove et al., 2003). *Olivine*, unzoned in almost all experiments, shows Fo content varying in a very narrow range (Fo_{86-89} ; Table A.2).

Oxides occur as traces characterized by a grain size of $\leq 5 \mu\text{m}$ making the acquisition of accurate EMP analyses difficult in most of the experimental charges. Measurable oxides resulted to be solid solutions of spinel *stricto sensu*, hercynite and chromite. In particular, oxides crystallized in the *NWA* and *damp* experiments show comparable MgO contents ($\sim 14-16 \text{ wt.}\%$) and Cr#, calculated as $\text{Cr}^{3+}/(\text{Cr}^{3+} + \text{Al}^{3+})$ atom ratio, varying between 0.44 and 0.58 (Table A.2). Differently, the oxides in the *wet* amphibole-bearing runs are significantly richer in FeO ($> 50.63 \text{ wt.}\%$) and poorer in Cr_2O_3 contents ($< 12 \text{ wt.}\%$; Table A.2).

Orthopyroxene crystallized in the *wet* experiments from both APR16 and APR16GL compositions are classified as enstatites ($\text{Wo}_5\text{En}_{73-80}\text{Fs}_{17-15}$). The main compositional differences concern the relative MgO and FeO contents (e.g., Mg# from 0.85 to 0.76; Table A.2) which reasonably reflects differences in the starting material and a different degree of achieved crystallization.

Amphibole crystallized only in the *wet* experiments of APR16 and APR16GL starting materials. It is pargasitic in composition, according to the Hawthorne and Oberti (2007) classification, showing no significant variations as function of temperature decrease or water content in the residual melts: Mg# value is ~ 0.75 .

Plagioclases are both bytownitic and labradoritic in composition (An_{59-76}). As expected, the anorthite content in plagioclase varies as function of temperature and H_2O content in the melt (e.g. Panjasawatwong et al., 1995): it decreases with decreasing temperature and increases, at the same T, with increasing H_2O content in the system (e.g. at 1200 °C the anorthite content in plagioclase of NWA runs is 61 mol % while it is 74 mol % in plagioclase of *damp* experiments; Table A.2).

4. Discussion

The experimental results on the APR16, SCE, and APR16GL compositions allow us to constrain the stability fields of the crystalline phases and the composition of the residual liquids in a K-basaltic system at upper mantle-lower crustal level as a function of temperature and water content (Fig. 2). In the following sections we then discuss emplacement conditions, constraints on the H_2O amount at high $P = P_{H_2O}$, and the liquid line of descent of the PVD parental magmas at high pressure.

4.1. Emplacement conditions of the PVD parental magmas

To constrain the storage conditions of the PVD magmas, we compare, primitive, natural clinopyroxenes (i.e. $Mg\# \geq 80$) from Campi Flegrei and Procida and Ischia islands with experimental clinopyroxenes from literature and from this study. The Al^{IV} vs Al^{VI} and Al^{VI} vs Na diagrams (Fig. 8a, b), show that only few PVD natural clinopyroxenes fall in the relatively high-pressure field (0.7-1.0 GPa) whereas most of them appear to have crystallized at pressure ≤ 0.5 GPa. It should be noted that some natural clinopyroxenes fall into the three pressure-fields overlapping area thus suggesting a possible influence of the water content on their composition. Indeed, the preference of Al to occupy octahedral sites at high pressure

(Aoki and Kushiro, 1968; Herzberg, 1978; Thompson, 1974) is limited by the increase of H₂O content in the melt as show the experiments with H₂O > 4wt.% (this study; Perinelli et al., 2018 and references therein). These experimental evidences enlarge the range of natural clinopyroxene compositions suitable to constrain the high-pressure crystallization by means geothermobarometry. Thus, to provide an estimate of T-P crystallization conditions of primitive PVD clinopyroxenes, we used the geothermobarometer of Putirka (2008) based on the clinopyroxene-liquid equilibrium, selecting the natural minerals that fall in the experimentally defined fields of intermediate and high pressures ($P \geq 0.3$ GPa; Fig. 8a, b) and that, according to the Putirka's criteria, are in equilibrium with the composition of APR16 rock. Calculations indicate crystallization temperatures and pressures between 1140 and 1220 °C and between 0.6 and 0.9 GPa, respectively, corresponding to a depth of 22-33 km (assuming an average crustal density of 2.8 g/cm³). For the Procida K-basalts, this implies the occurrence of a ponding level at the boundary upper mantle-lower crust. Moreover, by using the compositions of the above selected PVD clinopyroxenes, we estimated the water contents in the related magmas by applying the clinopyroxene-based hygrometer of Perinelli et al. (2016); the calculated H₂O-melt concentrations vary between 2 and 4 wt.%, this range is in good agreement with data from melt inclusions analysis (e.g. Moretti et al., 2013).

On this basis, the experimental pressure conditions (0.8 GPa) used in this study can be considered as representative of conditions at which natural clinopyroxenes crystallized from poorly evolved PVD magmas (0.6-0.9 GPa). Moreover, our experiments indicate that in the temperature range 1140 - 1220 °C, batches of K-basalt magma characterised by up to 4 wt.% of water and a degree of crystallization > 45 vol.% (Figs. 3 and. 4; Tables 2 and Table A.3 in Supplementary material), ponding at the Moho level, would generate pyrossenitic/gabbrous cumulates associated with shoshonitic residual melts (Fig. 4). The crystallization degree value resulting from our experiments is higher than the ~26 vol.% estimated by Fedi et al.

(2018) on the basis of gravimetric and petrological modelling, to produce shoshonitic magmas from the K-basalts of Procida coupled to gabbrous cumulates. Nevertheless, the experimental value is in agreement with the crystallinity windows 50-70 vol.% proposed by Dufek and Bachmann (2010) for an efficient crystal-liquid separation.

4.2. Constraints on the H_2O amount at high $P = P_{H_2O}$

The occurrence of vapour bubbles in the experimental products obtained in *wet* runs suggests water-saturated conditions (Fig. 1 d, e and f). Only few literature data on the solubility of H_2O in basaltic melts are available for the pressure conditions investigated in this study. These data indicate that at 0.8 GPa pressure the solubility of pure H_2O may be up to > 10 wt.% (Duan, 2014; Mitchell et al., 2017 and references therein). In the *wet* experiments, the H_2O contents nominally added to the K-basalts is between 4 and 6 wt.%, reaching contents between 7-10 wt.% in the bubble-bearing differentiated liquids. By using the thermodynamically-based model of Ghiorso and Gualda (2015), whose advantage consists of its applicability at high pressure (> 500 MPa; see Mitchell et al., 2017 for a review), we estimated the solubility of pure H_2O in melt compositions of *wet* experiments. The calculations produced values of H_2O solubility between 11 and 12 wt.% of H_2O . These values are significantly higher than those determined in the bubbles-bearing residual melts of *wet* experiments (7-10 wt.%), thus suggesting undersaturated conditions for these experiments. A possible explanation for this discrepancy can be the type of experimental apparatus we used in this study. Indeed, as demonstrated by several authors (e.g. Mitchell et al., 2017 and references therein; Ulmer et al., 2018), experiments performed with piston cylinder apparatus typically contain some amount of CO_2 which is known to considerably decrease H_2O solubility (e.g. Dixon et al., 1995). Potential CO_2 contamination sources of the starting materials may result by the diffusion of carbon from graphite furnace and/or from carbon electrode during the capsule

welding or even by absorbance of CO₂ by the very-fine grained and very reactive starting material (Ulmer et al., 2018 and references therein). To evaluate the effect of CO₂ on H₂O solubility in the investigated system, we reapplied the thermodynamically-based model to estimate the minimum concentration of CO₂ to produce saturation conditions in the wet experiments. Modelling results indicate that CO₂ contents in the range 1600-4800 ppm saturate the *wet* liquids with a mixed H₂O-CO₂ fluid limiting the H₂O concentration at 10.5 - 7.4 wt.%. Notably, these calculations give insights into suitable solubility of water in the natural PVD system. Indeed, the inferred CO₂ maximum concentration is comparable to the maximum CO₂ abundance determined for PVD magmas (CO₂ ~ 4601 ppm; Moretti et al., 2013).

4.3. Liquid line of descent of the PVD parental magmas at high pressure

The high-pressure (0.8 GPa) experiments conducted in this study on the APR16 and SCE K-basalts confirm the key role played by the amount of water in determining the liquidus phases and, consequently, the liquid line of descent. In particular, the effect of liquidus phases, either clinopyroxene or Cpx+Ol±Plg, on K-basalt liquid line of descent can be observed on the CaO-MgO variation diagram (Fig. 5). At evolving melt, i.e. decreasing MgO in the liquid phase, CaO decreases more rapidly in *NWA* than in *damp* and *wet* experiments. This is due to the effect of the phase relations (Cpx vs Ol+Cpx±Plg) and to the Ol/Cpx ratio (e.g. in the APR16 runs, the Ol/Cpx ratio is 0.3 and 0.04 in *damp* and *NWA* runs, respectively). Nevertheless, diversity in liquidus phases does not fully explain the three differentiation trends depicted in the TAS diagram at the diverse water contents. In particular, the vertical trend driven by the early crystallization of clinopyroxene in the *NWA* runs produces residual melts with a maximum H₂O_f content of ~2 wt.% (Fig. 4). The *NWA* experimental trend matches the Procida least differentiated natural products which, according to melt inclusions

data, contain a water amount below 2 wt.% (Moretti et al., 2013). The earlier crystallization of olivine in the *damp* runs, as well as the onset of plagioclase in the *NWA* runs, lead to more flattened trend towards a shoshonitic composition. Interestingly, this trend approaches the most primitive magmas of Ischia and Campi Flegrei (Fig. 4). Differently from the two trends above described, the subalkaline experimental glasses (Fig. 4) cannot be explained with a closed melt + crystal system. For example, focusing on APR16 starting material ($\Sigma_{\text{alkalis}} = 4.32$ wt.%, Table 1), the low alkali content in the glasses of *wet* experiments ($\Sigma_{\text{alkalis}} = 1.48$ and 3.26 wt.% at 1050 °C and 1000 °C, respectively) cannot be attributed to analytical procedure (see session on “Analytical methods”) and it is as well inconsistent with the stable minerals and their abundances (Cpx + Ox + Opx at 1100 °C and Cpx + Amph + Ox + Opx at $T \leq 1080$ °C) that would instead produce an increase of alkali in coexisting glasses. To account for this discrepancy, it should be noted that all *wet* experimental products contain bubbles. This feature clearly indicates that melt and crystals were in equilibrium with a free, aqueous fluid phase; consequently, at the thermodynamic equilibrium, the alkalis were distributed among these three coexisting phases (i.e. fluid + melt $\pm$ crystal).

The capacity of aqueous solutions of acting as a solvent for oxide components at pressures corresponding to those of deep continental crust and upper mantle ($0.6 \leq P \leq 4$ GPa) has been demonstrated by several experimental studies (Adam et al., 2014; Ayers and Eggler, 1995 and reference therein; Mysen and Armstrong, 2002). For instance, in a basanitic melt coexisting with aqueous fluid, alkalis preferably partitioning into the fluid phase with increasing pressure (Adam et al., 2014). Moreover, the occurrence of halogens in the system has a strong influence on the partitioning of metals and many other elements (e.g. lithophile trace elements) due to their role as complexing agents. Chlorine, in particular, can extract significant amounts of alkali from the melt (e.g., Ayers and Eggler, 1995; Baker and Alletti, 2012 and references therein) and, notably, Cl⁻ content in the APR16 and SCE is at least

~0.20 wt.% as determined in the glassy NWA experiments (Table A.4) and it is up to ~1 wt.% in the differentiated products of Campi Flegrei (Giaccio et al., 2017). In an aqueous fluid-melt system, Cl^- is strongly fractionated in the H_2O -fluid phase being its partition coefficient ($D^{\text{fluid/melt}} \gg 1$; Baker and Alletti, 2012) and this causes a significant raise of $D^{\text{fluid/melt}}$ values for Na ($D^{\text{fluid/melt}} \sim 1$ or more) and to a lesser extent for K with respect to the values estimated for pure H_2O (Ayers and Eggler, 1995).

The $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio of Campania Province magmas varies significantly, from 0.11 to 2.24. In particular, the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ vs MgO diagram shows an almost random distribution of magma compositions especially for those characterised by $2 \leq \text{MgO} \leq 8$ wt.% (Fig. 9). The $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio variability could indicate, according to the *wet* experimental results, magmatic crystallization in an alkali-non buffered system (alkali open system) caused by the occurrence of a free fluid phase. Consequently, the Campi Flegrei plumbing system could be characterised by a relatively early and deep degassing process able to remove different proportion of Na and K from the melt.

5. Conclusions

The present study documents the effects of H_2O on the phase relations of a K-basaltic melt at pressure corresponding to the crust-mantle boundary beneath the Campania volcanic area (0.8 GPa).

At water content below 2 wt.%, extensive crystallization of clinopyroxene as liquidus phase results in a liquid line of descent reflecting the least differentiated natural products of Procida.

At water content above 2 wt.%, with the system still water-undersaturated, the co-saturation of clinopyroxene and olivine on the liquidus drives the differentiated melts towards shoshonitic compositions similar to the most primitive Campi Flegrei products. Therefore, under water-undersaturated conditions and high pressure, the differentiation process is mainly

controlled by clinopyroxene because olivine does not appreciably increase in modal quantity. Consequently, in the Campi Flegrei plumbing system we should expect cumulitic zones at a crust-mantle boundary formed by clinopyroxenites and gabbros. Abundant crystallization of olivine could be predicted only at relatively low pressure.

Under water-saturated conditions, the partitioning between hydrous melt and coexisting hydrous fluid of those elements showing affinity with H₂O and halogens, produces variably alkali-depleted silicate melts whose composition converges toward the subalkaline field. These residual melts are in equilibrium with Opx, a mineral phase absent in the younger products of Campi Flegrei but occurring in the oldest, high-K calc-alkaline affinity, volcanic deposits of the Campania Province. Thus, the experimental subalkaline liquids, formed at water-saturated conditions, could suggest the early stationing of old parental K-basalts at high pressure (0.7-0.9 GPa) and water-saturated conditions (H₂O >6 wt.%), according to an immature state of the Campi Flegrei plumbing system (i.e. absence of mafic mush column). Overall, our experiments conducted on a poorly evolved K-basalt composition from the PVD, have evidenced the effect that variable water contents might have had on the petrogenesis and degassing history of these magmas. This has important implications for the rheology and volcanic style of the PVD plumbing system that deserves to be further investigated.

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FIGURE CAPTIONS

Figure 1 - Backscattered (BSE) images of selected run products obtained during crystallization experiments at 0.8 GPa, in the temperature range of 1295-1000 °C and water contents <1-6 wt.%. Details of the experimental conditions are reported at the bottom of each image. a) Cpx characterised by a small relictic core surrounded by a volumetrically larger rim; b) unzoned crystals of Cpx and Ol (dark grey) in homogeneous glass; c) large euhedral clinopyroxenes (>100 µm in size) crystallized along with small olivine (<20 µm in size); d) small, scarce orthopyroxene crystallizing in association with clinopyroxene+amphibole+oxides mineral assemblage; e and f) the comparison between APR16 and APR16GL *wet* experiments show no significant textural differences between experimental products obtained from natural rock and glassy powders starting materials. Moreover, note the occurrence of bubbles in the charge (~ 5 to > 15 µm) suggesting vapor saturation of the *wet* experiments. Abbreviation: Cpx: clinopyroxene; Ol: olivine; Ox: oxide; Amph: amphibole; Gl: glass.

Figure 2 - T vs. H₂O_f in melt phase diagram showing experimental saturation curves (dashed when estimated), phase assemblages and stability fields for APR16, APR16GL and SCE compositions. The diagram combines the results from *NWA*, *damp* and *wet* experiments (Table 2). *NWA* solidus temperature of APR16 composition is from Bonechi et al. (2017). The plotted H₂O_f data are water content in the melts recalculated on the basis of micro-Raman spectroscopy measurements (see Table 2). Phase abbreviation Cpx, Ol, Ox and Amph as in Figure 1. Liq: liquid; Plg: plagioclase; Opx: orthopyroxene. Error bars are smaller than symbol size.

Figure 3 - Experimental solid fraction (by weight) as a function of temperature for APR16, SCE and APR16GL compositions. Outlined point represents the damp run SCE-W8 at 1200 °C for which mass balance calculation indicate significant Fe loss ($\Delta\text{Fe} = 59\%$) and chemical disequilibrium ($\Sigma r^2 > 1$) among minerals and melt. Symbols are as in Figure 3.

Figure 4 - Portion of the total alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) vs silica (SiO_2) diagram (TAS, Le Maitre et al., 2002), illustrating the compositional evolution of experimental liquids, recalculated on an anhydrous basis. Residual liquids of *NWA* and *damp* runs cover the range of basalt, trachybasalt and shoshonite, whereas those of *wet* runs fall in the basaltic-andesite and andesite fields. Literature data of Procida Island (ochre coloured field), of Campi Flegrei Volcanic District (blue coloured field) and of melt inclusions (blue dashed-line field) in the phenocrysts of the Solchiaro eruption products are from GEOROC database (<http://georoc.mpch-mainz.gwdg.de/georoc/Start.asp>). The green coloured field represents the high-K calc-alkaline rocks from the Parete and Castelvoturno bore-holes (north-west of Campi Flegrei). *NWA*, *damp* and *wet* identify the experiments with < 1.5 wt.% of initial water content (H_2O_i), those with 1.5-3 wt.% H_2O_i and those with 4-6 wt.% H_2O_i , respectively. Alkaline/subalkaline limit (grey line) is after Irvine and Baragar (1971). Symbols are as in Figure 3. Crosses indicate the composition of starting materials. PR: Procida; CF: Campi Flegrei; MI: melt inclusions.

Figure 5 - a) Mg# variation of residual liquids versus H_2O content in the melt. CaO b), Al_2O_3 c) and TiO_2 d) oxides of the liquid (glass) phase (normalized anhydrous to 100 wt.%) plotted versus MgO contents reflect the stability and proportions of the crystallized minerals as a function of initial H_2O content. Symbols are as in Figure 3. Crosses indicate the composition of starting materials.

Figure 6 – Clinopyroxene compositional variation as function of crystallization degree and melt-H₂O content. a) Mg# values progressively decrease almost linearly due to the combined effect of temperature and H₂O. The DiHe b) and CaTiTs c) molecules versus H₂O diagram shows an increase of these molecules by increasing the H₂O content in the melt; the Jd versus H₂O diagram d) shows a broad negative correlation with the melt-H₂O content. The components of clinopyroxene have been calculated according to Putirka (2008). DiHe: diopside-hedernbergite; CaTiTs: titanium-calcium Tshermak; Jd: jadeite. Symbols are as in Figure 3.

Figure 7 - Clinopyroxenes from this study compared with other experimental clinopyroxenes crystallized from starting materials similar to the investigated ones in Al^{IV}-Al^{VI} (a) and Na-Al^{VI} (b) diagrams. Literature experimental data are from the LEPR database (http://lepr.ofm-research.org/YUI/access_user/login.php). The high pressure Cpx, despite some overlaps, can be distinguished from those crystallized at low pressures ($P \leq 0.2$ GPa); Cpx crystallized at intermediate pressure (0.3-0.5 GPa) are distributed around the line (black dotted line) that bounds the fields of high-low pressure Cpx. The line is an arbitrary limit drawn on the basis of results of experiments on APR16 composition at 0.2, 0.4 (low-P field) and 0.8 GPa (high-P field) and NWA- 3 wt.% initial water contents (Granati, 2016). Low-pressure clinopyroxenes from Granati (2016) are also reported in the diagrams. Symbols are as in Figure 3. Error bars are smaller than symbol size.

Figure 8 - Al^{IV} a) and Na b) versus Al^{VI} (atoms per formula unit) of natural PVD clinopyroxenes compared to clinopyroxenes experimentally crystallized from silicate melts (coloured fields) at different pressures (see Fig. 7)

Figure 9 - Variation $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio as function of MgO content of the PVD volcanic products. Experimental points of residual glasses are reported for comparison. Natural data are from GEOROC database (<http://georoc.mpch-mainz.gwdg.de/georoc/Start.asp>). Symbols are as in Figure 3. Crosses indicate the composition of starting materials.

Figure A.1 - Volatile contents in residual glasses measured by micro-Raman Spectroscopy (RS) compared with H_2O_f determined *by-difference* from electron microprobe analyses (EMP).

Figure A.2 - Backscattered (BSE) images of experimental products showing the wide range of sizes of the minerals crystallized in the experiments at different $\text{T-H}_2\text{O}_i$ conditions.

TABLE CAPTIONS

Run #	T (°C)	H ₂ O _i (wt.%)	Time (hour)	Phases	EMP [†] H ₂ O _f (wt.%)	RS [‡] H ₂ O _f (wt.%)	H ₂ O _f [‡] (wt.%)	Σr ²	% ΔFe [§]
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Table 1 - Composition (wt.%) of APR16, SCE and APRGL starting materials.

Sample	APR16	SCE	APR16GL
Phenocrysts	Ol, Cpx	Ol,Cpx,Plg	
SiO ₂	48.89	47.62	49.30 (0.46)
TiO ₂	1.23	1.23	1.33 (0.03)
Al ₂ O ₃	15.65	15.33	15.31 (0.14)
FeO _{tot}	8.08	8.18	7.79 (0.13)
MnO	0.14	0.14	0.14 (0.05)
MgO	8.89	9.78	9.31 (0.07)
CaO	11.64	11.89	12.02 (0.09)
Na ₂ O	2.88	2.69	2.86 (0.05)
K ₂ O	1.52	1.58	1.60 (0.02)
P ₂ O ₅	0.31	0.29	0.55 (0.02)
Total	99.23	98.74	99.31 (0.29) [§]
L.O.I.	0.61	0.26	
Mg# [*]	0.66	0.68	0.68

Phenocrysts: Ol olivine; Cpx clinopyroxene; Plg plagioclase.

^{*}[MgO/(MgO+FeO_{tot})] molar, assuming all Fe²⁺ and Fe³⁺ as FeO_{tot}. Chemical composition of APR16 is from

D'Antonio et al. (1999); XRF analysis of SCE whole rock powder after ignition at 1050 °C and the average of five

EMP analyses of APR16GL glass are from this study. [§]For APR16GL the analysis is normalized to 100 but the

original total it is reported. Standard deviation is reported in parenthesis.

Table 2 - Experimental run conditions, calculated water contents, phases assemblage and proportions in run products.

APR16-14	1310	NWA	1	Gl(100)	0.48		1.04		
APR16-11	1290	NWA	3	Gl(100)	0.34		0.87		-6
APR16-26	1270	NWA	3	Gl(100) + Cpx(trace) [†]	0.43	1.21			-9
APR16-12	1250	NWA	3.3	Gl(89) + Cpx(11)	0.54		1.11	0.90	-1
APR16-35	1225	NWA	6	Gl(86) + Cpx(14)	0.59		1.18	0.22	-10
APR16-24	1190	NWA	9	Gl(70) + Cpx(26) + Ol(1) + Ox(trace) [†] + Plg(3)	1.51		2.31	0.38	-4
APR16-W6	1235	1.5	3	Gl(87) + Cpx(10) + Ol(3)	1.56		2.37	0.11	-10
APR16-W33	1250	3.1	3	Gl(100)	2.7		3.78		
APR16-W16	1190	3	9	Gl(86) + Cpx(12) + Ol(2)	3.48		4.75	0.44	-6
APR16-W22	1150	2.9	9	Gl(68) + Cpx(26) + Ol(6)	5.18		6.85	0.53	-8
APR16-W17	1225	6	3	Gl(100)	5.41	6.73			
APR16-W8	1150	7	3	Gl(100)	6.30	7.38		2.91	-23 [◊]
APR16-W7	1100	4.7	3	Gl(78) + Cpx(22) + Opx(7) + Ox(trace) [†]	7.18		9.32	9.32	-25 [◊]
APR16-W13	1000	4.8	3	Gl(53) + Cpx(14) + Amph(30) + Ox(2) + Opx (trace)	8.13		10.49	2.38	-26 [◊]
APR16-GLAd	1250	NWA	3	Gl(79) + Cpx(20) + Ol(1) + Ox(trace)	1.30		2.05	0.16	-12
APR16-GLAb	1220	NWA	6	Gl(58) + Cpx(30) + Ol(3) + Ox(1) + Plg (8)	1.56		2.37	0.20	-7
APR16-GLBd1	1200	NWA	9	Gl(50) + Cpx(36) + Ol(2) + Ox(2) + Plg (10)	2.27		3.25	0.19	-8
APR16-GLBd2	1170	NWA	9	Gl(46) + Cpx(37) + Ol(3) + Ox(2) + Plg(12)	2.55		3.60	0.32	-6

APR16-GLAc	1250	1.9	6	Gl(84) + Cpx(14) + Ol(2)	2.31		3.30	0.81	-16
APR16-GLBb	1200	1.8	6	Gl(63) + Cpx(30) + Ol(4) + Ox(trace) [†] + Plg(3)	2.52		3.56	0.28	-14
APR16-GLBc	1170	2	6	Gl(56) + Cpx(33) + Ol(4) + Ox(trace) [†] + Plg(7)	3.47		4.86	0.18	-14
APR16-GLAd2	1080	4.2	3.5	Gl(46) + Cpx(13) + Amph(40) + Ox(1) + Opx(trace) [†]	7.50	9.92		1.99	-1 [◇]
APR16-GLBd3	1030	3.7	3.5	Gl(37) + Cpx(10) + Amph(52) + Ox(1) + Opx(trace)	5.68	7.61		1.86	-1 [◇]
SCE-9	1295	NWA	3	Gl(100) + Cpx(trace) [†]	0.37		0.90		
SCE-11	1270	NWA	3	Gl(72) + Cpx(23) + Ol(5)	1.13		1.84	0.54	-15
SCE-12	1235	NWA	6	Gl(59) + Cpx(30) + Ol(6) + Ox(3) + Plg(2)	1.53		2.34	0.25	-17
SCE-W8	1200	2	3	Gl(81) + Cpx(17) + Ol(2)	2.28		3.26	1.35	-59
SCE-W5	1180	2	3	Gl(74) + Cpx(20) + Ol(3) + Ox(3)	2.33		3.33	0.15	-16
SCE-W4	1125	4	3	Gl(75) + Cpx(20) + Ol(5)	5.63		7.40	0.99	-24 [◇]
SCE-W3	1150	6	3	Gl(82) + Cpx(14) + Ol(4)	6.88		8.94	7	-36 [◇]

NWA = No Water Added; Gl = glass; Cpx = clinopyroxene; Ol = Olivine; Plg = plagioclase; Ox = oxide minerals. H_2O_i is nominal content (wt.%) of water added to the charge. $H_2O_f^{EMP}$ = water content in the melt determined by the by-difference calculation method (respect to the total of EMP analyses); $H_2O_f^{RS}$ = water content in the melt determined by Raman spectroscopy analyses; $H_2O_f^{\dagger}$ = water content in the melt recalculated on the basis of RS measurements. Σr^2 values from mass balance calculation. ⁵Percent of relative Fe loss from starting material based on difference between the starting material and calculated bulk composition of experiment obtained from mass-balance calculations. [†]Crystals too small for analysis and not considered for mass balance calculations. [◇]Experiments that record Na and $\pm$ K loss on the basis of mass balance calculations (see text).

Highlights

- Phase relations of K-basalt at high-pressure and at anhydrous-hydrous conditions
- Piston cylinder experiments on the primitive Phlegraean magmas
- Differentiation of Phlegraean Volcanic District parental magmas at the Moho depth
- Deep degassing process removes variable proportions of Na and K from the melt

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

▲ APR16 (0.2-0.4 GPa; Granati, 2016)

Figure 7

△ Cpx Procida △ Cpx Campi Flegrei ▲ Cpx Ischia

Figure 8

Figure 9

Figure 10

Figure 11