INTRODUCTION

At the vast majority of volcanic arcs, the dominant erupted magma type is usually too evolved to have equilibrated directly with a mantle peridotite source at depth, suggesting that primary melts undergo significant differentiation at the roots of continental crust (Grove et al., 2003; Melekhova et al., 2015 and references therein). In this environment, high pressure and hydrous conditions favour significant amphibole crystallization, with remarkable effects on arc magmas evolution (Cawthorn et al., 1976; Hilyard et al., 2000; Müntener and Ulmer, 2006; Davidson et al., 2007; Nandedkar et al., 2014). Experimental studies have shown that amphibole crystallizes under hydrous conditions from a wide variety of liquids at crustal pressures - i.e. dacitic and andesitic magmas (Allen and Boettcher, 1983; Rutherford and Devine, 1973; Anderson, 1980) and primitive magmas of arc systems (Moore and Carmichael, 1998; Blatter and Carmichael, 1998; Pichavant and MacDonald, 2007).

ABSTRACT

Equilibrium crystallization experiments were carried out on two primitive basaltic rocks (APR16: Na$_2$O+K$_2$O=4.40 wt%; CM42: Na$_2$O+K$_2$O=2.59 wt%) with the aim to investigate the amphibole stability in the differentiation processes at deep crustal level, of primitive alkaline (APR16) and calc-alkaline (CM42) magmas. The experiments were performed with different initial H$_2$O contents (0-5 wt%), at pressure of 800 MPa, in the temperature range of 975-1225 °C. For the explored conditions, amphibole crystallization occurs in both compositions at H$_2$O in the melt $>$7wt% while the temperature of their occurrence is lower in the alkaline composition (<1050 °C in APR16 and ≥1050 °C in CM42). Moreover, amphibole crystallization seems to be influenced by the Na$_2$O/K$_2$O ratio rather than the absolute Na$_2$O content in the melt. This is evident when experimental results on the APR16 and CM42 are compared with experimental data obtained from a primitive ultrapotassic composition (leucite-basanite: Na$_2$O+K$_2$O=4.58 wt%) and with thermodynamic modelling by the Rhyolite-MELTS algorithm. The comparison shows that amphibole never saturates the leucite-basanite at any of the investigated/modelled conditions, even when an extended crystallization increases the Na$_2$O of melts up to contents like those of calc-alkaline experimental glasses. We conclude that, at pressure of 800 MPa and hydrous conditions, only primitive liquids with Na$_2$O/K$_2$O ratio ≥0.9 are more prone to crystallize amphibole.

Keywords: Experimental petrology; Rhyolite-MELTS modelling; Calcic amphibole; Calc-alkaline melts; Alkaline melts; Na$_2$O/K$_2$O ratio.
Factors that primarily control amphibole crystallization are (i) magma water content (Holloway and Burnham, 1972; Anderson, 1980; Medard and Grove, 2008; Krawczynski et al., 2012), (ii) oxygen fugacity (i.e., ΔNNO between -0.51 and +3; Helz, 1973, 1976; Barclay and Carmichael, 2004; Krawczynski et al., 2012; Melekhova et al., 2015) and (iii) alkali content (Cawthorn and Ohara, 1976; Nandedkar et al., 2014). Cawthorn and Ohara (1976) and Nandedkar et al. (2014) denote that calc-alkaline liquids achieve amphibole saturation for Na2O>3 wt%. Amphibole has been synthesised experimentally from a wide range of starting materials over a pressure range of 1-23 kbar and 400-1150 °C and therefore, it can be a considerable indicator of crystallization conditions, both as a geothermometer and geobarometer. Holland and Richardson (1979) examined equilibria among the end-member species glaucochane, edenite, tremolite, and hornblende in assemblages with chlorite, epidote, albite, quartz and H2O in order to explain zoning profiles in amphibole as P-T-time indicators; Graham and Powell (1984) have formulated a garnet-amphibole thermometer for application to amphibolite grade metamorphic rocks; Hammarstrom and Zen (1986) and Hollister et al. (1987) have proposed an empirical amphibole geobarometer for use with granitoid rocks. Nabelek and Lindsley (1985) proposed a preliminary empirical calibration of a hornblende-plagioclase thermometer while Ridolfi et al. (2010) and Ridolfi and Renzulli (2012), relying on a large number of experimental and natural data, proposed a model requiring only the amphibole compositions to estimate the physico-chemical parameters (P, T, /O2 and the amount of H2O dissolved in the melt) of calcic amphibole crystallization from calc-alkaline and alkaline melts. In order to explore the influence of alkali in primitive melts on amphibole stability at deep-crustal level, we report the results of new phase equilibria experiments performed at P=800 MPa, T=975-1225 °C, on two primitive (Mg#=0.64-0.69; with total Fe as Fe2+) basaltic compositions APR16 and CM42 characterized by different amounts of alkali (Na2O+K2O=4.40 and 2.59 wt%, respectively) and alkali ratio (Na2O/K2O=1.89 and 2.08 wt%, respectively). We also compare the experimental phase relations with those calculated by means of the Rhyolite-MELTS software (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998; Gualda et al., 2012) and those obtained experimentally on primitive ultrapotassic basalt by Conte et al. (2009) to discuss the stability of amphibole in primitive alkaline and subalkaline magmas.

EXPERIMENTAL AND THERMODYNAMIC APPROACH

Starting material

We selected two samples of primitive basalts with different alkali contents (Table S1) as starting material for equilibrium experiments. APR16 is a lithic lava clast (D’Antonio et al., 1999) occurring in the deposit of the Solchiaro hydromagmatic centre located in the Procida island belonging to the Phlegreaean Volcanic District (South Italy; Figure 1a). It consists in a primitive alkaline basalt (Mg#=0.64, Na2O+K2O=4.40 wt%, L.O.I.=0.61 wt%; Figure 2) with 12 vol% of forsteritic olivine and diopсидic clinoptyroxene phenocrysts in a groundmass of olivine, clinoptyroxene, plagioclase, Ti-magnetite, alkali feldspar and glass (D’Antonio et al., 1999). Inclusions of Cr-spinel can be found within olivine phenocrysts. CM42 is a mafic enclaves occurring in the calc-alkaline hypabyssal rocks of the Cape Marargiu Volcanic District (Tecchiato et al., 2015; Figure 1 b-c). The sample is a primitive calc-alkaline basalt (Mg#=0.69, Na2O+K2O=2.59 wt%, L.O.I.=0.55 wt%) with ~50 vol% of clinoptyroxene, amphibole, plagioclase, olivine and magnetite phenocrysts in a groundmass of plagioclase, clinoptyroxene, low-Ca pyroxene and magnetite (Tecchiato et al., 2015). Centimetre-sized fragments of the APR16 and CM42 samples without weathering evidences were crushed in an agate shutterbox and subsequently by hand, under acetone, in an agate mortar. We obtain a final grain-size <60 µm (as estimated through the SEM images).

Experimental procedures

We carried out experiments with different initial H2O contents (from 0 to 5 wt%), at pressure of 800 MPa and temperatures from 975 to 1225 °C, using an end-loaded piston cylinder apparatus installed at the HP-HT Laboratory of the Earth Science Department, “Sapienza” University of Rome (Figure 3a). This device is a solid medium press equipped with a ½ inch pressure vessel (Figure 3b) capable of attaining pressure of 3.5 GPa and temperature of 1500 °C. We load Au25-Pd25 alloy capsules (7 mm of length and 2.8 mm of diameter) with the starting material and appropriate amounts of water (using a microsyringe) before sealing the capsule tip by arc welding.

We use an assembly as described in Figure 3d, whose components are: a) a fluorite cylinder (CaF2), which converts from uniaxial to hydrostatic pressure; b) a graphite cylinder that acts as a heating furnace; c) two cylindrical supports of workable magnesia (MgO) bored to allow the insert of the thermocouple; d) a ceramic sleeve placed between the magnesia supports to prevent capsule and thermocouple to be at direct contact. The assembly is prepared placing the capsule into the MgO supports and filling the spaces with pyrophyllite powder. Pyrophyllite prevents undesired capsule movements during pressurization as well as hydrogen loss produced by water dissociation and hydrogen permeation through the capsule alloy during experimental runs. Before placing the assembly into the pressure vessel it is wrapped
in a lead foil; the lead foil has the function of lubricant between the assembly and the pressure vessel walls. We therefore position in-to the pressure vessel (i.e., above the assembly) a stainless-steel plug surrounded by a pyrophyllite ring; the plug acts as an electric conductor ensuring energy supply to the graphite furnace. We finally set the pressure vessel in the piston cylinder apparatus. We used an insulating mylar foil and a plexiglas support to hold the thermocouple plate above the pressure vessel. We insert a type D thermocouple (W$_{97}$-Re$_{3}$-W$_{75}$-Re$_{25}$) on the upper side of the plate, within a groove accurately designed for this purpose. This thermocouple
allows to monitor temperature in the isothermal zone of
the assembly with accuracy of ±5 °C. At the beginning
of each experiment, we achieve the working conditions
of pressure and temperature using the “hot piston out”
technique. This consists in (i) applying an overpressure
>10% of the run pressure, (ii) gradually increasing the
temperature, and (iii) correcting for pressure drops due
to stress relaxation within the assembly during heating.
We terminate the experimental runs after 3-6 hours; the
isobaric quench was made by turning off the power.

Finally, all the runs were self-buffered; we attempt to
estimate $f_O^2$ through the equation of Kress and Carmichael
(1991) using the liquid Fe$^{3+}$/Fe$_{tot}$ mole ratios from $K_{D_{Fe-Mg}}$
Oliq calculated according to Toplis (2005). This
procedure yielded $f_O^2$ values of ΔNNO +0.2 to +1.1,
in agreement with those estimate for similar furnace
assemblages (Conte et al., 2009; Weaver et al., 2013).
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Analytical methods

After each experiment, we recover and mount the product in epoxy resin for polishing and carbon coating. We characterize textures and phase assemblages by Scanning Electron Microscopy (SEM) using a FEI quanta 400 equipped for microanalysis with an EDAX Genesis system at the Dipartimento di Scienze della terra, SAPIENZA Università di Roma. We estimate the modal proportion of each phase in the experimental products by detailed image analysis using ImageJ freeware (http://imagej.nih.gov/ij/) following the procedure described by Philpotts and Ague (2009). The ease to threshold the experimental phases from SEM images yielded a good estimate of their modal abundance. We analyse phase compositions by Electron Probe Micro-Analysis (EPMA) using a Cameca SX50 equipped with five-wavelength dispersive spectrometer (WDS). The EPMA facility belongs to CNR-Istituto di Geologia Ambientale e Geoingegneria (Rome). A 15 kV accelerating voltage, 15 nA beam current and the following standards are used: 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. Raw data are corrected using the ZAF method. We analyse minerals using a beam diameter of 1 µm, and glasses with a defocused beam from 10 to 15 µm of diameter to minimize the alkali loss. Water contents of experimental glasses are estimated according to the by-difference method (Devine et al., 1995).

Thermodynamic approach

We constrain phase equilibria at high pressure for APR16 and CM42 on a thermodynamic base using Rhyolite-MELTS (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998; Gualda et al., 2012). Similarly, we model the crystallization of a leucite-basanite (MF: Mg#≈0.75, Na2O+K2O=4.58, L.O.I.=0.65 wt%; Table 1) from Montefiascone centre (Vulsi Volcanic District, Central Italy). This latter has been object of a previous experimental study by Conte et al. (2009). For APR16 and CM42, Rhyolite-MELTS calculations are performed at isobaric conditions (800 MPa), consistently with our phase equilibria experiments. Conversely, MF crystallization is modelled at 1000 MPa to match the experimental pressure conditions of Conte et al. (2009). Isobaric cooling simulations start at superliquidus temperatures and, according to the occurrence of euhedral minerals, are characterized by the equilibrium between the melt and crystalline phases (Figure 4).

As regards APR16, clinopyroxene is the mineral crystallized from the NWA (no water added) run at the highest temperature (1225 °C). Olivine (Ol), oxide (Ox) and plagioclase (Plg) are obtained at 1000 °C, and K-feldspar (KFld) crystallizes at 975 °C (i.e., NWA run solidus). In the hydrous experiments (~5 wt% H2O), APR16 crystallizes (i) Cpx+Ox+orthopyroxene (Opx)+Ox at 1050 °C, and (ii) Cpx+Opx+amphibole (Amph)+Ox at 1000 °C (Table 1). Remarkably, Plg never crystallizes under hydrous conditions, whereas Ol is absent at low temperature.

As regards CM42, the mineral assemblage resulting from the damp run (~2 wt% H2O) at 1110 °C is Cpx+Ol+Ox+Plg. In turn, that from the wet run (~5 wt% H2O) at 1050 °C is Cpx+Ol+Amph+Ox (Table 1). Notably, high water contents suppress Opx and Plg crystallization.

Phase compositions

The compositions of minerals and glasses are reported in Table S2-S7. However, both the small size of K-feldspar and of most oxides, as well as the paucity of residual glass in some runs (i.e., APR16-2C), prevent the accurate acquisition of electron microprobe analyses on these phases.

Olivines

Forsterite (Fo) content of APR16 experimental olivines in the NWA runs does not change with the decrease of temperature (Fo_{87}) while the Ol composition at hydrous conditions is Fo_{85} (Table S2). Olivines from CM42 have compositions Fo_{81} and Fo_{79} for the 2 wt% and 5 wt% H2O runs, respectively (Table S2).

Pyroxenes

Clinopyroxenes in APR16 experimental sample are diopsides (Wo_{45-48}, En_{39-48}, Fs_{7-13}; Figure 5) according to the classification scheme of Morimoto et al. (1988). In the NWA runs, the Mg# decreases from 0.87 to 0.76 with temperature, whereas TiO2 increases from 0.67 wt% at 1225 °C to 1.89 wt% at 975 °C (Table S3). In comparison, Cpx from the hydrous runs (5 wt% H2O) at 1050-1000 °C shows higher Mg-number (MgH2-Ox) and lower TiO2 contents (1.35-1.31 wt%; Table S3). Opx is classified as clinopyroxene (Wo_{01}, En_{61}, Fs_{14}; Figure 5).

Experimental clinopyroxenes from CM42 runs are diopsides (Wo_{43-47}, En_{40-47}, Fs_{7-14}; Table S3). Cpx compositions from the wet run (~5 wt% H2O) show lower Al2O3 and higher FeO contents than Cpx crystallized from the damp run (~2 wt% H2O). Interestingly, the initial H2O content of starting material does not influence Cpx Mg-
Table 1. Experimental run conditions, phase assemblages and proportions.

<table>
<thead>
<tr>
<th>Run#</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>Time (h)</th>
<th>H₂Oᵢ</th>
<th>H₂Oᵢ</th>
<th>Phase assemblage</th>
</tr>
</thead>
<tbody>
<tr>
<td>APR16-35</td>
<td>1225</td>
<td>800</td>
<td>6</td>
<td>NWA</td>
<td>1.70</td>
<td>Gl (96) + Cpx (4)</td>
</tr>
<tr>
<td>APR16-2C</td>
<td>1000</td>
<td>800</td>
<td>3</td>
<td>NWA</td>
<td>-</td>
<td>Gl (3) + Cpx (50) + Ol (10) + Plg (28) + Ox (9)</td>
</tr>
<tr>
<td>APR16-3C</td>
<td>975</td>
<td>800</td>
<td>3</td>
<td>NWA</td>
<td>-</td>
<td>Cpx (51) + Ol (10) + Plg (32) + Ox (7) ± KFld (trace)</td>
</tr>
<tr>
<td>APR16-W7</td>
<td>1050</td>
<td>800</td>
<td>3</td>
<td>4.7</td>
<td>6.2</td>
<td>Gl (78) + Cpx (15) + Ol (5) + Opx (2) + Ox (trace)</td>
</tr>
<tr>
<td>APR16-W13</td>
<td>1000</td>
<td>800</td>
<td>3</td>
<td>4.8</td>
<td>7.4</td>
<td>Gl (58) + Cpx (21) + Opx (1) + Amph (18) + Ox (2)</td>
</tr>
<tr>
<td>CM42-2</td>
<td>1110</td>
<td>800</td>
<td>3</td>
<td>2</td>
<td>4.9</td>
<td>Gl (42) + Cpx (23) + Ol (11) + Opx (0.2) + Plg (22.8) + Ox (1)</td>
</tr>
<tr>
<td>CM42-1</td>
<td>1050</td>
<td>800</td>
<td>3</td>
<td>5</td>
<td>7.1</td>
<td>Gl (67) + Cpx (8) + Ol (3) + Amph (21) + Ox (1)</td>
</tr>
<tr>
<td>PC185*</td>
<td>1275</td>
<td>1000</td>
<td>18</td>
<td>NWA</td>
<td>1.6</td>
<td>Gl (83.5) + Ox (0.9) + Ol (3.7) + Cpx (11.9)</td>
</tr>
<tr>
<td>PC106*</td>
<td>1200</td>
<td>970</td>
<td>27</td>
<td>3</td>
<td>4.3</td>
<td>Gl (78.6) + Ox (2) + Ol (5.2) + Cpx (14.2)</td>
</tr>
<tr>
<td>PC111*</td>
<td>1150</td>
<td>1000</td>
<td>70</td>
<td>3</td>
<td>5.3</td>
<td>Gl (54.8) + Ox (1.8) + Cpx (30.5) + Phlog (12.9)</td>
</tr>
<tr>
<td>PC108*</td>
<td>1200</td>
<td>1000</td>
<td>35</td>
<td>4</td>
<td>8.6</td>
<td>Gl (86.2) + Ox (1.2) + Ol (3.9) + Cpx (6.4) + Phlog (2.3)</td>
</tr>
<tr>
<td>PC112*</td>
<td>1150</td>
<td>1000</td>
<td>70</td>
<td>4</td>
<td>4.8</td>
<td>Gl (55.9) + Ox (0.6) + Cpx (23.8) + Phlog (19.7)</td>
</tr>
</tbody>
</table>

NWA = no water added; H₂Oᵢ =% of water added to the charge. H₂Oᵢ as determined by the by-difference calculation method (respect to the total of EMP analyses).

Gl = glass; Cpx = clinopyroxene; Ol = Olivine; Plg = plagioclase; Phlog = phlogopite; Amph = amphibole; Ox = oxide; KFld = KFeldspar. † phases too small for analysis; *: data from Conte et al., 2009.

number (Mgₐ₀.₈₁ and Mgₐ₀.₈₂ from the wet and damp run, respectively). Opx are clinoenstatites (Wo₃, En₇₃, Fs₂₄, Figure 5).

Clinopyroxene-liquid Fe-Mg exchange coefficient have been calculated by using the formula (FeO/MgO)Cpx/(FeO/MgO)²₁₁. The average value is 0.31±0.05 for APR16 and 0.29±0.01 for CM42 runs, taking into account FeO as FeOtot. APR16 KD values are in agreement with experimental data for hydrous basaltic compositions (0.27±0.06, Pichavant et al., 2014; 0.26-0.31, Sisson and Grove,

Figure 4. Backscattered SEM images of APR16-35 and CM42-1 runs; Cpx = clinopyroxene, Gl = glass.
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1993; 0.29±0.08, Pichavant and Macdonald, 2007). Even orthopyroxene-liquid Fe-Mg exchange coefficient has been calculated using the formula \( \frac{(\text{FeO/MgO})_{\text{Opx}}}{(\text{FeO/MgO})_{\text{Liq}}} \); the average value is 0.27±0.01 for APR16 and 0.26 for CM42.

**Plagioclases**

Plagioclase compositions are plotted in the albite-orthoclase-anorthite ternary diagram (Figure 6). Plg from APR16 runs shows decreasing anorthite (An) content from 71 (bytownite) to 66 (labradorite) with temperature decreasing from 1000 °C to 975 °C (Table S4). Plg from the CM42 damp run is bytownite (An<sub>84</sub>).

**Amphiboles**

In both APR16 and CM42 experiments, amphibole crystallizes when H<sub>2</sub>O = 5 wt\%. According to the classification scheme of Hawthorne and Oberti (2007) the amphiboles are pargasite (APR16-W13, 1000 °C run) and magnesiohastingsite (CM42-2, 1050 °C run). Pargasite is characterized by Mg<sub>0.75</sub> and 1.11 wt% K<sub>2</sub>O, whereas magnesiohastingsite shows Mg<sub>0.70</sub> and 0.67 wt% K<sub>2</sub>O (Table S5).

**Oxides**

Oxides in APR16 experiments vary in composition from Cr-rich spinel [Cr# = 0.46-0.44 calculated as Cr<sup>3+</sup>/(Cr<sup>3+</sup>+Al<sup>3+</sup>)] to Ti-magnetite with 24-28 mol% of ulvöspinel content (Usp; Table S6). Similarly, oxides from CM42 products correspond to Usp<sub>28-32</sub> Ti-magnetites showing a negative correlation between Usp and H<sub>2</sub>O: Usp increasing from 28 to 32 with H<sub>2</sub>O decreasing from 5 to 2 wt%.

**Glass**

In the Total Alkali-Silica (TAS) diagram (Figure 7) the composition of residual glass (Table S7) in APR16 experiments evolves from basalt to trachybasalt with Mg# = 0.62 and Na<sub>2</sub>O/K<sub>2</sub>O = 1.85 in the NWA run at 1225 °C, to shoshonite with Mg# = 0.56 and Na<sub>2</sub>O/K<sub>2</sub>O = 1.63 in the hydrous run at 1050 °C. In turn, the chemical composition of residual glass in CM42 experiments varies from basaltic with Mg# = 0.52, Na<sub>2</sub>O/K<sub>2</sub>O = 1.81 and H<sub>2</sub>O<sub>f</sub> (final water content) ≈7 wt% in the hydrous run, to basaltic andesite with Mg# = 0.45, Na<sub>2</sub>O/K<sub>2</sub>O = 0.88 and H<sub>2</sub>O<sub>f</sub> ≈5 wt% in the damp run.

The important crystallization of plagioclase (~22 vol%) in the damp run is responsible for the relative enrichment...
Figure 6. Feldspar compositions plotted in the Ab: albite; Or: orthoclase; An: anorthite classification diagram. Dashed line represent the solvus at 750 °C, $P_{H_2O} = 100$ MPa (Seck, 1971).

Figure 7. Composition of the APR16 and CM42 experimental glasses reported in the TAS diagram; crosses indicate starting material. Damp (2 wt% $H_2O$) and wet (5 wt% $H_2O$) runs are indicated by the numbers near to the dashed lines.
of K$_2$O over Na$_2$O in the melt, reflected by the striking decrease of Na$_2$O/K$_2$O ratio (from 2.08 of starting material to 0.88 wt%).

**Rhyolite-MELTS results**

The phase equilibria predicted by Rhyolite-MELTS for APR16, CM42 and MF are shown in the T-H$_2$O diagrams of Figure 8.

The anhydrous liquidus of APR16 is calculated at 1320 °C and decreases to 1148 °C with increasing water content to 7 wt% H$_2$O$_i$ (Figure 8a). Clinopyroxene is the liquidus phase at 0-3 wt% H$_2$O$_i$, followed by olivine, orthopyroxene and plagioclase at lower temperatures. This mineral assemblage represents the stable paragenesis at H$_2$O contents in the residual melt lower than ~6 wt%. Olivine is the first mineral to crystallize at >3 wt% H$_2$O$_i$ (Figure 8a), followed by clinopyroxene and oxides. The Ol+Cpx+Ox paragenesis is stable until, at peritectic, olivine starts to react with the melt to form orthopyroxene (Figure 8a). Amphibole crystallization is predicted by Rhyolite-MELTS calculations at temperatures <970 °C and with >5 wt% H$_2$O in the residual melt. Phlogopite is the last mineral to crystallize at temperatures ≤900 °C and H$_2$O$_i$ ≥6 wt%. Under such conditions, the stable paragenesis consists of Gl+Opx+Cpx+Amph+Phlog+Ox (Figure 8a).

As regards CM42 composition, the liquidus temperature at anhydrous conditions is found to be at 1340 °C and rationally decreases at 1180 °C with increasing of water content to 6 wt% H$_2$O$_i$ (Figure 8b). Orthopyroxene represents the liquidus phase at <3 wt% H$_2$O$_i$, followed by clinopyroxene, oxide and plagioclase at lower temperatures. Gl+Cpx+Plg corresponds to the stable paragenesis at H$_2$O contents in the residual melt lower than ~4 wt%. Olivine is the first mineral to crystallize at ≥3 wt% H$_2$O$_i$, followed by clinopyroxene and oxides. The Ol+Cpx+Ox paragenesis is stable until the onset of olivine-melt peritectic reaction to produce orthopyroxene, comparably to results from APR16 simulations previously described. Amphibole crystallization is retrieved by Rhyolite-MELTS at temperatures <960 °C and with H$_2$O contents in the residual melt between 11 and 14 wt%. At such conditions, the stable mineral assemblage consists of Opx+Cpx+Ox+Amph.

The MF anhydrous liquidus is predicted at temperature of 1385 °C and it decreases to 1250 °C with increasing water content to 7 wt% H$_2$O$_i$ (Figure 8c). Clinopyroxene is the liquidus phase at 0-1 wt% H$_2$O$_i$, followed by olivine, spinel and leucite during cooling and crystallization (H$_2$O$_i$ = 0-3.5 wt%). The modelled crystallization sequence at >1 wt% H$_2$O$_i$ is Ol → Ol+Cpx → Ol+Cpx+Ox → Ol+Cpx+Ox+phlogopite (Phlog). The onset of phlogopite occurs at temperatures < 1150 °C and with >3 wt% H$_2$O in the residual melt. Garnet (Gt) also crystallizes and coexists with Cpx+Ox+Phlog at temperatures ≤1035 °C and ≥3.5 wt% H$_2$O$_i$.

**DISCUSSION**

In the following section, we discuss the phase relations of primitive subalkaline to alkaline APR16, CM42 and MF compositions combining the results of the Rhyolite-MELTS simulations with those of experiments from both this study and literature (i.e., Conte et al., 2009). We therefore address the effect of alkali content, in particular of the Na$_2$O/K$_2$O ratio, on the stability of amphibole and phlogopite.

**Phase relations in the APR16, CM42 and MF composition**

We find that results from Rhyolite-MELTS modelling on the alkaline basalt APR16 are in substantial harmony with experimental phase equilibria. Indeed, we observe a good correspondence between predicted models and observed phase relations from both the NWA experiment at 1225 °C (APR16-20 run) and the hydrous (~5 wt% H$_2$O$_i$) experiment at 1000 °C (APR16-W13 run; Table 1). In detail, the NWA assemblage of Gl (~1 wt% H$_2$O$_i$) +Cpx at 1225 °C is well simulated by Rhyolite-MELTS particularly when the calculations are performed using an initial water content similar to the APR16 L.O.I. value (0.61 wt%; Figure 8). In turn, for hydrous experiments the paragenesis of Gl (~7 wt% H$_2$O$_i$)+Cpx+Amph+Opx+Ox at T=1000 °C is modelled by Rhyolite-MELTS at slightly lower temperature (~970 °C; Figure 8a). At lower temperatures, olivine is unstable and replaced by Opx (Figure 8). Notably, experiments and Rhyolite-MELTS calculations show that orthopyroxene crystallizes in the APR16 magma at H$_2$O-rich conditions (≥5 wt% in the melt). This unexpected result indicates that at high pressure, hydrous conditions the phases driving the liquid line of descent of the primitive magmas of the Phlegrean Fields could be different from those modelled at lower pressure (e.g. Fowler et al., 2007).

The subalkaline basaltic composition of CM42 shows a higher degree of mismatch between experimental and Rhyolite-MELTS results (Figure 8b). While the paragenesis of the dry run (~2 wt% H$_2$O$_i$) at 1110 °C (CM42-2; Table 1) is Gl (~5 wt% H$_2$O$_i$)+Cpx+Ol+Opx+Plg+Ox, that computed by Rhyolite-MELTS is Gl+Cpx+Ox+Ox. Analogously, the paragenesis of the wet run (~5 wt% H$_2$O$_i$) at the 1050 °C run (CM42-1) is Gl (~7 wt% H$_2$O$_i$)+Cpx+Ol+Amph+Ox, whereas that predicted by Rhyolite-MELTS modelling is Opx+Cpx+Ox+Amph at temperatures <960 °C and with H$_2$O contents in the residual melt between 11 and 14 wt%. The coexistence of Ol and Opx is never predicted for CM42 basalt at any of the T-H$_2$O conditions investigated.
Figure 8. $T$ (°C) vs $H_2O$ (i.e. $H_2O$ in the melt phase) diagrams showing the phase relations at $P = 800$ MPa for APR16 (a) and CM42 (b) compositions and $P = 1000$ MPa for MF (c) composition obtained by means of the Rhyolite-MELTS calculations. The diagrams also display the data obtained from the piston cylinder experiments; dashed lines represent the amphibole/phlogopite saturation curves extrapolated from the experimental data. Numbers near symbols indicate phases crystallized in the experiments but not predicted by Rhyolite-MELTS modelling: 1=Ol, 2=Opx, 3=Amph, 4=Plg, 5=Ox, 6=Cpx, 7=Phlog. 1*=absence of Ol in experimental runs; 2*=absence of Opx in experimental runs. The asterisk (*) indicates data from Conte et al. (2009). Amph: amphibole, Cpx: clinopyroxene; Gl: glass; Lc: leucite; Ol: olivine; Opx: orthopyroxene, Ox: oxide, Phlog: phlogopite, Plg: plagioclase.
Moreover, Rhyolite-MELTS yields Plg crystallization exclusively when the H$_2$O$_i$ in the system is lower than or equal to 3 wt% and T=1110 °C.

As regards the basanite composition of MF, phase relations modelled by Rhyolite-MELTS are fully consistent with experimental results of Conte et al. (2009; Figure 8c). In the anhydrous run at 1275 °C (PC185) and in the hydrous run (3 wt% H$_2$O$_i$) at 1200 °C (PC106) the glasses (1.6 and 4 wt% H$_2$O$_i$, respectively) are at equilibrium with Opx, OI and Cpx. Rhyolite-MELTS is unable to predict the Opx crystallization at experimental conditions of PC106 run (T=1200 °C; 3 wt% H$_2$O$_i$); this may be due to the fO$_2$ imposed for calculations. Further differences concern the temperatures of Phlog saturation, which occurs at equilibrium with Ol+Cpx+Ox+Gl (8 wt% H$_2$O$_f$) in the charge at 1200 °C and at equilibrium with Cpx+Ox+Gl (5 wt% H$_2$O$_f$) in the charge at 1150 °C. The temperatures provided by Rhyolite-MELTS for Phlog crystallization are lower than ~100 °C (Figure 8c).

**Effect of alkali on the amphibole stability**

Experimental results show that amphibole crystallizes from both APR16 and CM42 in the hydrous experiments (~5 wt% H$_2$O$_i$) at 1000 °C (APR16-W13) and 1050 °C (CM42-1), respectively.

In these runs, Amph is in equilibrium with a melt containing ~7 wt% H$_2$O$_i$. Conversely, in runs with lower water content in the melt, amphibole does not crystallize (e.g., APR16-7W; Figure 9a; Table 1). This agrees with many experimental studies on similar compositions showing that at the similar P-T-H$_2$O-fO$_2$ conditions, amphibole crystallizes from liquids with H$_2$O contents higher than ~6 wt% (Krawczynski et al., 2012; Melekhova et al., 2015 and references therein). The most relevant differences between APR16 and CM42 amphiboles are K$_2$O contents (1.11 and 0.67 wt% in APR16 and CM42, respectively) and Mg# compositions (0.75 and 0.70 in APR16 and CM42, respectively). While the compositional diversity of the respective starting material (i.e., 1.52 and 0.84 wt% K$_2$O for APR16 and CM42 whole rocks, respectively) could explain the different K$_2$O contents in amphiboles, this cannot justify the aforementioned differences in Mg# (0.63 and 0.69, APR16 and CM42 whole rocks, respectively). Our experiments show that amphibole crystallizes at about 150 °C below the liquidus temperature, after olivine, pyroxenes and oxides crystallization significantly modifying the bulk chemistry of coexisting melt. In this context, identifying which chemical component exerts a primary control on amphibole stability on the base of starting material compositions is not straightforward (Figure 8a-c). However, some considerations can be attempted as follows. Interestingly, we find that amphibole crystallizing at higher temperature (i.e., 1050 °C; Figure 9b) is in equilibrium with a melt (i.e.,

![Figure 9](https://example.com/figure9.png)

Figure 9. Experimental glasses of the samples APR16, CM42 and MF reported in the T °C vs H$_2$O$_i$ (a), Na$_2$O vs Mg# (b), Na$_2$O/K$_2$O vs H$_2$O$_i$ (c) and K$_2$O vs Mg# (d) diagrams.
CM42-1 melt) characterized by a lower Mg\# and sodium content (Mg\#0.52 and Na\textsubscript{2}O \approx 2 wt\%) with respect to that crystallizing at lower temperature (i.e., 1000 °C; Figure 9a) from APR16-W13 melt (Mg\#0.56 and \textasciitilde 4 wt\% Na\textsubscript{2}O). Despite the activity of sodium is generally considered of paramount importance for amphibole stability in arc magmas (e.g. Cawthorn and Ohara, 1976; Martin, 2007; Nandedkar et al., 2014 and references therein), our experiments, according to those realized on similar compositions (e.g., Pilet et al., 2010 and Melekhova et al., 2015), underline that the increase of Na\textsubscript{2}O/K\textsubscript{2}O ratio (up to 2.04 in our experiments; see Table S8 for comparison with literature data) is actually more effective in stabilizing amphibole than the absolute sodium content in the melt. The diagrams in Figure 9a-c show that the amphibole crystallization at 1050 °C in the CM42 magma is associated with the increase of water and Na\textsubscript{2}O/K\textsubscript{2}O ratio, but not with the variation of sodium content in the melt. Pilet et al (2010) show that K\textsubscript{2}O in amphiboles increases with increasing Mg\# and/or temperature. High temperature would indeed promote the increase of K\textsubscript{2}O accompanied by a decrease of Na\textsubscript{2}O (and then a decrease of Na\textsubscript{2}O/K\textsubscript{2}O ratio), due to an isomorphous exchange of K for Na in the A site of amphibole. On the other hand, the increasing Fe component in the amphibole would favor the Na substitution (increase Na\textsubscript{2}O/K\textsubscript{2}O ratio in Amph). Thus, we consider the effects of liquid composition (i.e., degree of differentiation) to prevail on those of temperature for our amphiboles crystallized at constant pressure, as suggested by Pilet et al. (2010). The comparison of phase relations obtained at 800 MPa on the CM42 composition with those obtained with both Rhyolite-MELTS modelling and experiments on the MF leucite-basanite composition (Figure 8c), confirms that Na\textsubscript{2}O/K\textsubscript{2}O ratio in magmas plays a role on amphibole stability. According to Rhyolite-MELTS, amphibole never crystallizes from the MF (Figure 8c), irrespective of the absolute amount of sodium in the melt. Experimental glasses reported by Conte et al. (2009) for the 1000 MPa hydrous experiments on the MF show Na\textsubscript{2}O contents comparable to those obtained in the present study on CM42 (Na\textsubscript{2}O \approx 2 wt\%; Figure 9b), however, their Na\textsubscript{2}O/K\textsubscript{2}O ratios are lower than ours (<0.8 compared to \textasciitilde 0.9, respectively; Figure 9c). Thus, the near-primary ultrapotassic character of the MF composition (high Mg\#=0.75) favors the early crystallization (i.e. at 1200 °C) of phlogopite rather than amphibole in the experimental runs.

On the other hand, the occurrence of amphiboles in the lava flows of the Colli Albani Volcanic District (6-11 wt\% K\textsubscript{2}O; Gaeta and Freda, 2001; Gozzi et al., 2014; Gaeta et al., 2016) indicates that the inhibition of amphibole crystallization in ultrapotassic magmas is not caused by the high activity of potassium but, according to our experiments, it depends on the low Na\textsubscript{2}O/K\textsubscript{2}O ratios of magmas.

CONCLUSIONS

An alkaline (sample APR16) and a calc-alkaline (sample CM42) primitive basaltic liquids from the Phlegraean Volcanic District (South Italy) and the Capo Marargiu Volcanic District (Sardinia, Italy) are experimentally crystallized at deep crustal pressures under hydrous conditions. The experiments aim to investigate the effects of alkali on the stability of amphibole during the early stages of fractionation in alkaline/calc-alkaline magmas. Clinopyroxene is always present; orthopyroxene crystallizes in the calc-alkaline composition for H\textsubscript{2}O contents <5 wt% and, unexpectedly, it also occurs in the alkaline composition. Amphibole stability is achieved in the calc-alkaline composition at 1050 °C and \textasciitilde 5 wt% H\textsubscript{2}O in the melt, while its crystallization is restricted at lower temperature (i.e. 1000 °C) in the alkaline composition. This is unexpected by virtue of the relatively high Na\textsubscript{2}O content in the experimental alkaline glasses, which is thought to favor amphibole crystallization under a wider range of physico-chemical conditions. Therefore, we interpret amphibole crystallization in our experiments as being mostly controlled by the Na\textsubscript{2}O/K\textsubscript{2}O ratio of the residual melt rather than by its absolute sodium content. The comparison of our results with those obtained from Rhyolite-MELTS simulations and experiments on ultrapotassic compositions from literature demonstrated at deep crustal level, the crystallization of amphibole from primitive liquids depends not only on the water contents but also on of the Na\textsubscript{2}O/K\textsubscript{2}O that should be \textasciitilde 0.9.

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APPENDIX

Supplemental material is available for downloading at the journal site.

REFERENCES

Alonso-Perez R., Müntener O., Ulmer P., 2009. Igneous garnet
and amphibole fractionation in the roots of island arcs: experimental constraints on andesitic liquids. Contributions to Mineralogy and Petrology 157, 541-558.


D’Antonio M., Civetta L., Di Girolamo P., 1999. Mantle source heterogeneity in the Campanian Region (South Italy) as inferred from geochemical and isotopic features of mafic volcanic rocks with shoshonitic affinity. Mineralogy and Petrology 67, 163-192.


Tecchiato V., Gaeta M., Mollo S., Perinelli C., Scarlato P., 2015. High porphyritic calc-alkaline basalts from the Cenozoic Capo
Marargiu Volcanic District (Sardinia, Italy). Goldschmidt Conference, 16-21 August, Prague, Czech Republic.

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