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(Revision 2) Experimental investigation of trace element partitioning between amphibole and alkali basaltic melt: towards a more general partitioning model with implications for amphibole fractionation at deep crustal levels

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ABSTRACT

Time-series experiments were carried out in a piston cylinder apparatus conducted at 0.8 GPa and 1030-1080 °C using as starting material a hydrous K-basalt melt to determine the element partition coefficients between amphibole and silicate glass. Major, minor, and trace element compositions of amphibole and glass were determined with a combination of electron microprobe and laser ablation inductively coupled plasma mass spectrometry. Results show that the main mineral phase is calcic amphibole, and the coexisting glass compositions range from basaltic trachyandesite to andesite. We estimated the ideal radius, the maximum partition coefficient and the apparent Young's modulus of the A, M1-M2-M3, and M4-M4' sites of amphibole. The influence of melt and amphibole composition, temperature, and pressure on the partition coefficients between amphiboles and glasses has also been investigated by comparing our data with a literature dataset spanning a wide range of pressures (0.6-2.5 GPa), temperatures (780-1100 °C), and compositions (from basanite to rhyolite). Finally, we modelled a deep fractional crystallization process using the amphibole-melt partition coefficients determined in this study, observing that significant amounts of amphibole crystallization (>30 wt%) well reproduce the composition of an andesitic melt similar to that of the calcalkaline volcanic products found in Parete and Castelvolturno bore-holes (NW of Campi Flegrei, Italy).

Keywords: amphibole; trace element partition coefficient; lattice strain model; Campi Flegrei

INTRODUCTION

The occurrence of amphibole in rocks encompassing the entire range of silica activities in terrestrial igneous suites, coupled with its capacity to incorporate significant concentrations of geochemically important trace elements, underscores the likely importance of this phase in the chemical evolution of both mantle- and crustal-derived magmas (Brenan et al. 1995; Tiepolo et al. 2007). During the last decades, the behavior of trace element partitioning between calcic amphiboles and silicate melts has been investigated at different pressures (0.2-2.7 GPa), temperatures (750-1150 °C), and system compositions (e.g., Nicholls and Harris 1980; Adam et al. 1993; Adam and Green 1994, 2003; Sisson 1994; LaTourrette et al. 1995; Brenan et al. 1995, 1998; Klein et al. 1997; Tiepolo et al. 1999, 2000a, 2020b, 2007; Hilyard et al. 2000a; Zhang et al. 2019). It is widely accepted that the resulting partition coefficients depend on the chemical compositions of mineral and melt phases, pressure, temperature, and H_2O-content of the melt, as well as on the redox conditions (Blundy and Wood 2003; Adam and Green 2006; Aigner-Torres et al. 2007; Severs et al. 2009; van Kan Parker et al. 2010; Hill et al. 2011; Fabbrizio et al. 2021). Moreover, Blundy and Wood (1994) provided a theoretical framework based on the lattice strain model (Brice 1975) for the interpretation of trace element partitioning. So far, it has been applied successfully to trace element partitioning between pyroxene (e.g., Wood and Blundy 1997; Schmidt et al. 1999; Adam and Green 2006; Sun and Liang 2012, 2013; Mollo et al. 2018; Bonechi et al. 2021; Fabbrizio et al. 2021), olivine (e.g., Zanetti et al. 2004; Sun and Liang 2013), garnet (e.g., Draper and van Westrenen 2007; van Westrenen and Draper 2007; Sun and Liang 2013), amphibole (e.g., LaTourrette et al. 1995; Adam and Green 2006; Tiepolo et al. 2007; Wan et al. 2009; Nandedkar et al. 2016; Shimizu et al. 2017; Zhang et al. 2019; Cannaò et al. 2022), phlogopite (e.g., LaTourrette et al. 1995; Schmidt et al. 1999; Fabbrizio et al. 2010), leucite (e.g., Schmidt et al. 1999; Fabbrizio et al. 2008), feldspars (e.g., Icenhower and London 1996; Fabbrizio et al. 2009) and their coexisting melts. Despite numerous investigations on the partition between crystals and melt, there are still some mineral phases, including amphibole, for which data are limited or missing. In this study we provide new data on amphibole major, minor, and trace elements partition coefficients derived from crystallization experiments on a hydrous K-basaltic melt at 0.8 GPa and 1030-1080 °C. In detail, we analysed major and trace elements in amphiboles and glasses of the experimental runs by using an electron microprobe and laser ablation-inductively coupled plasma-mass spectrometry, respectively. We determined the concentrations of large ion lithophile elements, rare earth elements, high field strength elements, and transition metals in experimental phases and then, we used the obtained data to calculate the partition coefficients between amphiboles and glasses. In addition, we estimated the ideal radius, the maximum partition coefficient, and the apparent Young's modulus of the A, M1-M2-M3, and M4-M4’ sites of amphibole. Also, we reviewed the influence of melt and amphibole compositions, temperature, and pressure on the behavior of partition coefficients between amphiboles and glasses by integrating our data with a literature data set (LEPR database and data from Nandedkar et al. 2016, Zhang et al. 2019, and Cannaò et al. 2022) spanning a wide range of pressures (0.6-2.5 GPa), temperatures (780-1100 °C) and compositions (from basanite to rhyolite). Finally, we observed whether a composition approaching the APR16 one is able, through the crystallization of amphibole in a deep differentiation process, to produce an andesite melt with trace element abundances similar to those of the calc-alkaline volcanic products found in Parete and Castelvolturno bore-holes (NW of Campi Flegrei, Italy).

METHODS

Samples’ description

Crystallization experiments were performed by using the end loaded piston cylinder apparatus at the HP-HT Laboratory of the Earth Sciences Department (Sapienza University, Rome, Italy). Experiments were carried out at isobaric conditions of 0.8 GPa, 1030-1080 °C, with an initial H_2O content ≥3 wt%, and durations from 0.25 to 9 hours. Experiments were performed at different duration to observe the variation of trace elements concentration with time in both disequilibrium and equilibrium conditions. We used as starting materials the powder of a natural primitive K-basalt (APR16) and its glass (APR16GL, Table 1), prepared by melting the APR16 powder in a Fe-saturated Pt container for 15 min using a CO/CO_2 gas mixing furnace installed at the Bayerisches Geoinstitut (Bayreuth, Germany) at 1400 °C, atmospheric pressure and oxygen fugacity corresponding to the NNO (nickel-nickel oxide) buffer. The as-fused starting material did not contain crystalline phases, as analysed by both microprobe and SEM image analyses. Then, the obtained glassy starting material was ground in an agate mortar under acetone. The natural primitive K-basalt (APR16 sample) was found as scoria clast in the deposits of the Solchiaro hydromagmatic eruption (~22 ka ago; Morabito et al. 2014) located in Procida Island (Campi Flegrei, Italy). This K-basalt is characterized by 12 vol% of forsteritic olivine and diopsidic clinopyroxene phenocrysts dispersed in a groundmass made of olivine, clinopyroxene, plagioclase, Ti-magnetite, alkali feldspar, and glass (D'Antonio et al. 1999; De Astis et al. 2004). Although amphibole is not present in outcropped products, its stability has been experimentally observed when using APR16 as a starting composition, equilibrated at P = 0.8 GPa when water contents are > 7 wt.% (Bonechi et al. 2017; Perinelli et al. 2019; Bonechi et al. 2020a, 2020b).

Experimental techniques

The detailed experimental procedure is described by Perinelli et al. (2019) and by Bonechi et al. (2020a, 2020b). Here we report the main aspects. Assemblies were 1.25 cm in diameter, and consisted of CaF_2 outer sleeve, graphite furnace, and crushable magnesia spacers were used.

The experimental charges were prepared loading $Au_{75}Pd_{25}$ capsules with ~40 mg of sample powder. In each experiments, we added water in known amounts by using a 1.0 µL microsyringe (Table 2). Loss of H_2O by vaporization during welding was prevented by freezing the crucible with nitrogen. The welded capsule was weighed, stored in a furnace at 110 °C for at least 1 h, and then weighed again to confirm the absence of water leaks. Moreover, to minimize possible loss of H_2 during the experiments the charges were surrounded by pyrophyllite powder (Freda et al. 2001). The temperature was controlled by a factory-calibrated W_3Re_{97}-$W_{25}Re_{75}$ (type D) thermocouple and maintained with an uncertainty of ± 5 °C. For the experimental run-up, we used the "hot piston-out" procedure (Johannes et al. 1971; Presnall et al. 1978) in which the assembly was first cold-pressurized to a value ~10% over the target pressure and then heated to the final run temperature. This technique allows to closely approach the run pressure through the stress relaxation within the assembly upon heating, requiring only minor upward pressure adjustments during the experiment in most cases (Watson et al. 2002). The heating rate was imposed at 150 °C/min. The samples were maintained at the target pressure and temperature for a given duration (nominal duration; Table 2), and then quenched by turning off the power. The temperature drop below 500 °C was of <5 s (average cooling rate of 150 °C/s). All the runs were self-buffered; an estimation of experimental fO_2 was made by using the theoretical model of Barr and Grove (2010), which is based on the temperature-and fO_2-dependent partitioning of Fe between the AuPd capsule and coexisting melt. Thus, we measured the post-run Fe content in the sample-holder as closely as possible to the capsule-sample boundary of a near-liquidus anhydrous experiment. Applying the Barr and Grove (2010) approach the calculated fO_2 were of NNO -0.5 for the near-liquidus run and NNO -0.8 and NNO -1.1 for the longest runs of this study (Bonechi et al. 2020a). As a whole, the estimated range of fO_2 values agree with those estimated for similar furnace assemblages (Conte et al. 2009; Weaver et al. 2013; Perinelli et al. 2019; Bonechi et al. 2020a). Finally, we determined the undercooling (ΔT; Table 2) that is the difference between the liquidus temperature and the nominal temperature of the experiment (Bonechi et al. 2020a, 2020b; Bonechi 2020). For calculations, the liquidus temperature (T_L) of APR16 experiments was taken from Procida K-basalt experimental data (1095 °C; Perinelli et al. 2019, Bonechi et al. 2020a).

Analytical techniques

Textural investigations and major element determinations. Back-scattered electron (BSE) images used to investigate textural aspects of both natural and experimental samples were collected by Scanning Electron Microscopy using a FEI-quanta 400 equipped for microanalysis with an EDAX Genesis system at the Earth Sciences Department, Sapienza University of Rome. Major elements were analysed at the CNR-Istituto di Geologia Ambientale e Geoingegneria di Roma, with a Cameca SX50 electron microprobe equipped with five wavelength dispersive spectrometers. Quantitative analyses were performed using 15 kV accelerating voltage and 15 nA beam current. As standards we employed 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, Periclase for Mg, Apatite for P. Counting times for all elements were 20 s on peak and 10 s on both backgrounds. Light elements (Na, K) were counted first to prevent loss by volatilization. The PAP correction method was used. Minerals were analysed using a beam diameter of 1 μm whereas to minimize alkali loss during glass analysis, the beam was defocused to 15 μm. To evaluate the accuracy of the analyses, repeated analyses of three international secondary standards (Kakanui augite, Icelandic Bir-1, and rhyolite RLS132 glasses from USGS) were made before any series of measurements. The mean precision from the standard value was about 1% for SiO_2, 2% for Al_2O_3, 5% for K_2O, CaO and FeO, and 8-10% for other elements. The analytical precision (2 sigma error) is ≤1% for elements in the concentration range >10 wt% oxide, 5% for elements in the range 2–10 wt% oxide, and better than 10% for elements in the range 0.5-2 wt% oxide. The water contents of experimental glasses were estimated according to the by-difference method (Devine et al. 1995; Humphreys et al. 2006). We are aware that this method is not fully reliable given the estimation is affected by *i*) element concentrations not measured by EMPA and *ii*) surface charge effects (Hughes et al. 2019) leading to an overestimation of H_2O concentration. However, the obtained H_2O values show a good linear correlation (correlation coefficient $R^2 = 0.97$) with those determined by micro-Raman spectroscopy measurements on residual melts of equilibrium experiments performed on the same composition, at the same P, T, and initial hydrous conditions (cf. Perinelli et al. 2019).

Laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS). LA-ICP-MS analyses of the experimental samples were performed at the Department of Physics and Geology, University of Perugia (Italy). The instrumentation consisted of a Teledyne/Photon Machine G2 LA device equipped with a Two-Volume ANU HelEx 2 cell and coupled with a Thermo Fisher Scientific quadrupole-based iCAP-Q ICP-MS. The analyses of amphibole crystals and glasses were performed using a circular laser beam of 12-20 μm diameter, a frequency of 10-15 Hz and a laser density on the sample surface of 3.5 J/cm^2. Oxide formations was checked on the NIST SRM 612 by monitoring and maintaining the ratio ThO/Th ratio below 0.005. The NIST SRM-610 standard reference material was used as calibrant and Ca, previously analysed by EPMA, as internal standard. Under these operating conditions precision and accuracy are better than 10% for most of the elements (Petrelli et al. 2007, 2008, 2016). In detail, at beam sizes equal or larger than 15 μm, precision (measured as one sigma) and accuracy (expressed as relative deviation from the reference value) are of the order of 10% (Petrelli et al. 2016). Accuracy is better or equal to 10% and 13% at beam sizes of 15 and 10 μm, respectively, while when the spatial resolution is increased to 12 μm, accuracy remains better than 15% (Petrelli et al. 2016).

RESULTS

Texture, phase relationships and chemical composition of experimental samples

All the experimental samples investigated in this study, except the APR16-ST1 run, are described in detail in the previous work of Bonechi et al. (2020a) dealing with phase equilibria and crystallization kinetics in the APR16 K-basalt. Here we briefly report a description of the main aspects.

Texture and phase relationships. All the experimental products that for simplicity we have grouped into the C3A (i.e., C3Aa, C3Ab, C3Ad runs) and C3B (C3Ba, C3Bb, C3Bc, C3Bd runs) suites, show a high crystallinity (Fig. 1a, b and Table 2) as a consequence of the imposed undercooling (ΔT = 150-200 °C), that yields strong supersaturation conditions in the K-basaltic melt, enhances the nucleation kinetics in the sample during the early stage of experiments, and affects the phase modal proportions (Bonechi et al., 2020a and reference therein). Amphibole (Amph) occurs in all the experiments as euhedral crystals of ~40 μm in size, along with clinopyroxene (Cpx) + oxide (Ox) ± plagioclase (Plg) ± orthopyroxene (Opx) (Table 2). Both tiny crystals of Cpx and Opx (up to ~5 μm sized) are euhedral in shape, as the larger (~40 μm in size) Ox grains. Subhedral to euhedral plagioclase has dimensions of about 10 μm or less (Bonechi et al. 2020a). Glass is present in all the experimental runs, but it was analysed only in those with glass portions large enough to be examined.

About the APR16-ST1 experiment (Fig. 1c and Table 2), it is similar to the two runs with the longest duration, i.e., C3Ad and C3Bd, in both texture and mineral assemblage. It is formed by abundant Amph showing well-developed crystal face and dimensions up to ~50 μm, combined with idiomorphic Cpx of ~5 μm in size and euhedral Ox (sized up to ~40 μm). Glass pools larger than 60 μm occur within all the capsule. It is also characterized by large (up to 100 μm) and numerous vesicles present throughout the sample as a result of the high amount of water added before the experiment (H_2O_i = 8 wt%), which favored the achievement of saturation conditions (APR16 H_2O solubility ~10 wt%; Perinelli et al. 2019).

Chemical composition. Chemical compositions of Amph are reported in Table S1 of Supplementary Material 2. According to the Hawthorne et al. (2012) classification, all the crystallized Amph is calcic, and its composition varies from magnesiohorneblende and edenite to pargasite and magnesiohastingsite. Cpx compositions are diopsidic ($Wo_{46-48}En39_{-43}Fs_{10-14}$), whereas the orthopyroxene crystals found in the APR16-C3Bc run is enstatitic ($Wo_4En_{73}Fs_{23}$). Oxide crystals are generally hercynites, while in the APR16-C3Aa run Cr-rich spinels also occur. Plagioclase grains occurring in the shortest runs (0.25-3 h) are bytownitic (An_{72}) and labradoritic (An_{62}) in composition. As regards Amph, the calculated Amph-melt Fe-Mg exchange coefficient (i.e., $^{Amph\text{-}liq}K_{DFe\text{-}Mg}$ = $(FeO/MgO)^{Amph}/(FeO/MgO)^{liq}$) for the runs of the C3A and C3B suites varies between ~0.3 and ~1, showing an almost linear decrease with increasing time (Bonechi et al. 2020a) and a non-achievement of equilibrium conditions in many of the experiments. Indeed, only the magnesiohastingsites crystallized in the runs at 9 h (i.e., APR16-C3Ad and APR16-C3Bd with $^{Amph\text{-}liq}K_{DFe\text{-}Mg}$ = 0.34 and 0.40, respectively) attained Amph-liquid equilibrium conditions ($^{Amph\text{-}liq}K_{DFe\text{-}Mg}$ = 0.28 ± 0.11; Putirka

2016). In addition to these, also the magnesiohastingsite crystallized in the run APR16-ST1, carried out for 2 h in saturation conditions (H_2O_i = 8 wt.%; Table 2), achieved Amph-liquid equilibrium conditions ($^{\text{Amph-liq}}K_{\text{DFe-Mg}}$ = 0.32). As regards the other phases, instead, Cpx and Plg result to be always in disequilibrium conditions. Chemical compositions of synthetic glasses, that according to TAS diagram (Le Bas et al. 1986) range from basaltic trachy-andesite to andesite (Fig. S1 of Supplementary Material 1), are reported in Table S2 of Supplementary Material 2.

Trace and REE content

Average compositions of trace elements concentrations analysed by LA-ICP-MS technique in Amph, and coexisting glass are reported in Table 3.

Amphibole. Figure 2 shows the trace elements concentrations in Amph normalized to chondrite C1 after Anders and Grevesse (1989) for LILEs (Large-Ion Lithophile Elements), REEs (Rare Earth Elements), HFSEs (High Field Strength Elements), and TEs (Transition Elements). The abundance of LIL elements (e.g., Rb and Ba) of Amph from all experiments are comparable among them except for Pb which shows significant differences in its content. The chondrite-normalized REE patterns display enrichment of light REE (LREE) over heavy REE (HREE) (i.e., La_N/Yb_N = 3.5-6.2, where the subscript *N* denotes chondrite-normalized values) with a maximum at La_N (~74). All Amph exhibit no Eu anomaly (Eu/Eu* = 0.98-1.06; $Eu/Eu^* = Eu_N/(Sm_N \times Gd_N)^{1/2}$) indicating the absence or scarce crystallization of coexisting plagioclase. Finally, the concentration of tetravalent HFSEs (i.e., Hf, Zr, Ti) is lower than that of pentavalent cations (i.e., Ta and Nb), while as regards TEs, it is possible to see evident troughs at Co and Ni compared to the nearby elements.

Glass. Figure 3 shows the trace elements concentration in the experimental glasses normalized to chondrite C1 after Anders and Grevesse (1989) for LILEs, REEs, HFSEs, and TEs. Generally, all the experimental glasses match the trend of the APR16 sample (Mazzeo et al. 2014) and of the APR16 suite of Bonechi et al. (2021), except for Ni abundances, which are relatively higher. C1-normalized trace element patterns are L-MREE (Light/Middle rare earth element) enriched (La_N = 105-128, La_N/Sm_N = 3.0-4.6, La_N/Yb_N = 5.6-9.5) and nearly flat in the HREE region (Ho_N/Yb_N = 0.7-1.1). All the considered glasses have absent or slightly positive Eu anomaly (Eu/Eu* = 1.01-1.11). Moreover, pentavalent HFSEs (i.e., Ta and Nb) are more abundant than tetravalent cations (i.e., Zr, Hf, Ti).

DISCUSSION

Partition coefficients

Table 4 reports the trace elements Amphibole-melt *D*-values obtained in the present study for the longest experiments of the C3A and C3B suites and for APR16-ST1 run, where amphiboles are in equilibrium with the melt. Unfortunately, due to the impossibility to obtain reliable trace element concentrations of the glasses in the runs with shorter duration and in disequilibrium, we could not quantitively compare the partition coefficients in both disequilibrium and equilibrium conditions. However, the trace element concentrations measured in Amph do not show significant variation except a slight decrease or increase in the ones at equilibrium conditions (i.e., APR16-C3Ad, APR16-C3Bd, APR16-ST1; Table 3 and Fig. S2 of Supplementary Material 1). Qualitatively, this seems to suggest higher Amph-melt *D*-values for incompatible elements (e.g., LILE, REE, HFSE) and lower Amph-melt *D*-values for compatible elements (e.g., TE) in disequilibrium conditions, due to an excessive accumulation or depletion of trace elements, depending on their degree of compatibility or incompatibility, at the crystal-melt interface with a consequent disequilibrium element uptake during crystal growth (Bonechi et al. 2021 and reference therein). Figure 4 shows the partition coefficients between amphibole and melt for LILEs, REEs, HFSEs, and TEs. LILEs are incompatible (e.g., D_{Sr}

≤0.6, D_{Ba} ≤0.5). Noteworthy is the beahviour of lithium that, in agreement with literature data (e.g., D_{Li} = 0.3 in Dostal et al. 1983), results in incompatible behavior in the APR16-ST1 amphiboles but becomes almost compatible in crystals from the APR16-C3Ad (D_{Li} = 0.84) and APR16-C3Bd (D_{Li} = 0.75) runs (Table 4). This contrasting beahviour may have been induced by the different initial H_2O content (H_2O_i) between the APR16-C3Ad/Bd (H_2O_i = 3-4 wt%) and APR16-ST1 (H_2O_i = 8 wt%) experiments, which influenced the kinetic of Amph growth. Indeed, although the ΔT, that is one of the parameters controlling the crystal growth regime, is high for all experiments (Table 2), the H_2O-saturated condition of APR16-ST1 run (ΔT = 100 °C) still allowed for slow Amph growth and selectivity in elements partitioning from the beginning of the experiment, whereas H_2O-undersaturated condition of APR16-C3Ad/Bd experiments (ΔT = ~140-200 °C) probably promoted an initial rapid, disequilibrium growth of Amph and less selectivity in elements partitioning. The experimental duration of APR16-C3Ad/Bd experiments (9 h), may not have been enough for the diffusive re-equilibration of some elements such as lithium, whose abundance in APR16-C3Ad/Bd runs is always higher than in APR16-ST1 one (Table 3). LREEs (e.g., D_{La} ≤0.4) are always more incompatible than MREE and HREEs, which in some cases result to be compatible with Amph (e.g., D_{Tb} in all the considered runs, D_{Sm} to D_{Tm} in APR16-C3Bd, and D_{Sm}, D_{Er} in APR16-ST1). As regards HFSEs, tetravalent and pentavalent-charged cations are always incompatible (D_{Nb} and D_{Ta} ≤0.7; D_{Zr} and D_{Hf} between 0.5 and 0.8), with the exception of Ti. Finally, trace element partition coefficients of TEs (i.e., D_{Co}, D_{Cr}, D_{Ni}, D_{Sc}, and D_V) range from slightly incompatible to highly compatible. In particular, D_V vary between 0.7 and 1.3, whereas D_{Co}, D_{Sc}, D_{Ni}, and D_{Cr} are between 2 and 9.

Lattice strain model (LSM)

At equilibrium, the amph/melt partition coefficient can be quantitatively described by the near-parabolic relationship (Brice 1975; Blundy and Wood 1994; Wood and Blundy 2001):

$$D_j^{crystal-melt} = D_0 exp\left[\frac{-4\pi E N_A}{RT}\left(\frac{r_0}{2}\left(r_{\mathrm{j}} - r_0\right)^2 - \frac{1}{3}\left(r_0 - r_j\right)^3\right)\right] \quad (1),$$

where D_0 is the amphibole-melt partition coefficient for the strain-free substitution; r_0 is the optimum radius for the lattice site; r_{j} is the ionic radius of the element of interest in the appropriate co-ordination taken from Shannon (1976); E is the apparent Young's modulus for the lattice site (GPa); R is the gas constant (8.3144 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$); N_{A} is Avogadro constant and T is the temperature in K. The apparent Young's modulus E controls the tightness of the parabola, and D_0 determines the apex of the parabola with corresponding ideal lattice site r_0.

To apply the lattice strain model (LSM) and fit the experimentally determined trace element partition coefficients, we used the SIMPLE FIT program (Dalou et al. 2018), a lattice strain model fit by a differential-evolution-constrained algorithm (Storn and Price 1997) adapted to be error weighted. In presence of a small number of measured trace elements, the program failed to produce good fits. Therefore, following Dalou et al. (2018), we reduced the parameter space from the default range ($\mathrm{D_0}$ min and/or $\mathrm{D_0}$ max; E min and/or E max; $\mathrm{r_0}$ min and/or $\mathrm{r_0}$ max) to overcome this limitation. Best-fit parabolas determined for monovalent, divalent, trivalent, and tetravalent cations are plotted in Figure 5. Fit parameters E, D_0, and r_0 and related errors for monovalent, divalent, trivalent, and tetravalent cations in A, M1-M2-M3, and M4-M4' sites are reported in Table 5.

Onuma diagrams for monovalent, divalent, trivalent, and tetravalent cations

The partitioning behaviour for cations ($\mathrm{D_i}$) with the same valence is conveniently shown in Onuma diagrams (Onuma et al. 1968) as a function of the ionic radius, indicating which elements are compatibles/incompatibles in a given site or which ones are fractionated between two distinct sites. The parabolic fits of monovalent cations indicate that they are incorporated in the larger A-site permitting a very good constraining of its lattice strain parameters, especially for APR16-ST1 run. The best fits for the monovalent cations of the runs APR16-C3Ad and APR16-C3Bd were obtained by fixing the E value equal to that determined by the fit of APR16-ST1.

The larger divalent elements (Ca, Sr, Pb, Ba) enter the XII-fold A-site, whereas smaller cations enter into the M4-site with Mg, Co, Fe, Mn that seem to be fractionated between the VIII-fold and the VI-fold sites, Ni enters exclusively into the smaller VI-fold site. However, given that cations entering in the M4 sites plot only on the right-limb of the parabola it is not possible to fully constrain these fits. Also, the limited amount of data for the larger divalent cations prevented us from deriving the parabolic fits for these elements (Fig. 5). The parabolic distribution of the trivalent (i.e., REE, Sc, Cr, and Al) partition coefficients indicates that amphiboles crystallized close to equilibrium conditions (Fig. 5). One of the three structurally distinct octahedral (VI-folds) sites, M1, M2, or M3 hosts Sc, Cr, and Al whereas the REEs enter all in the larger VIII-fold M4 and M4’ sites. Given the apexes of the parabolic fits in all the runs are located near the ionic radius of Gd, the REEs should preferentially occupy the M4’ site (Bottazzi et al. 1999; Tiepolo et al. 2000b). Europium partition coefficients fall on the parabolas of the REE showing that all Eu is trivalent. Finally, tetravalent cations are fractionated between the VIII-fold (U, Th) and the VI-fold sites (Ti, Zr, Hf), while pentavalent cations (i.e., Nb, Ta, V) enter the small VI-fold site.

Comparison with the parameterized lattice strain model for REE of Shimizu et al. (2017)

Shimizu et al. (2017) used previous published experimental REE and Y partitioning data between amphibole and silicate melt, the lattice strain model, and nonlinear least-squares regression method to parameterize key partitioning parameters in the lattice strain model for REEs as a function of pressure, temperature, and both amphibole and melt compositions. We compared our D_{REE} with those obtained applying the model (Hybrid mode using mineral and melt chemistry) of Shimizu et al. (2017). As shown in Figure 6, $^{\text{Amph-glass}}D_{\text{REE}}$ predicted by Shimizu et al. (2017) correlates quite well with those measured in this study (R^2 = 0.68-0.74). In particular, the most compatible elements show a good agreement with the Shimizu et al. model while the elements that most differ from the model are the most incompatible ones (e.g., La, Ce). This deviation can be explained considering the analytical difficulties in measuring these incompatible elements due to possible micro/nano inclusion of glass and/or the limited spot size. Moreover, the combination of the small spot size (12 μm), used for the measurement of the trace element concentrations, with the potential presence of defect substitutions, kinetic effects and boundary layers in the melt can have a significant effect on the measurement error of the most incompatible elements making their analytical determination extremely difficult or impossible (Fabbrizio et al. 2021) .

Influence of melt composition, pressure, and temperature on trace element partitioning

To determine the main influencing variables affecting the partition coefficients (e.g., melt composition, Amph composition, temperature, pressure), we performed multiple linear regression analyses using our data joint to those of a database of existing experimental amphibole-melt partition coefficients (LEPR database and data from Nandedkar et al. 2016, Zhang et al. 2019, and Cannaò et al. 2022) spanning a wide range of conditions (0.6-2.5 GPa, 780-1100 °C; Table S3 of Supplementary Material 2) and starting compositions from basalt to rhyolite (Fig. S1 of Supplementary Material 1). The experiments crystallized calcic amphiboles in the range pargasite-edenite-hastingsite-magnesiohastingsite-magnesiohorneblende (Fig. S3 of Supplementary Material 1). In the regression analysis, the natural logarithms of $^{\text{Amph/L}}D$ (ln$D$) were treated as independent variables while melt composition (X_{nf}/X), Amph composition ($\text{Mg\#}_{\text{Amph}}$), P, and T were considered as dependent variables. X_{nf}/X is defined as the sum of the molar fractions of network-forming cations (X_{nf}, i.e., Si and the fraction of Al balanced by alkalis) normalized to the sum of all cations on a molar basis (X; Tiepolo et al. 2000b), while

$Mg\#_{Amph}$ is defined as $Mg/(Mg+Fe^{2+}+Fe^{3+})$. Instead of the NBO/T value (i.e., NBOs are the non-bridging oxygen atoms and T are the cations in tetrahedral coordination) that is usually used to express the structural organization of a melt and requires the knowledge of the H_2O content and the Fe^{2+}/Fe^{3+} ratio of the melt, we decided to use the parameter X_{nf}/X because it allows making a wider comparison with the literature data for many of which H_2O content and Fe^{2+}/Fe^{3+} ratio data are missing. We obtained a fine correlation ($R^2 > 0.8$) for Fe, Ho, Tb, and Tm (Figure 7 and Supplementary Material 3), whose partition coefficients are greatly influenced by X_{nf}/X, T and $Mg\#_{Amph}$. Particularly, Fe ($R^2 = 0.83$ and SEE = ± 18), Ho ($R^2 = 0.87$ and SEE = ± 4) and Tm ($R^2 = 0.86$ and SEE = ± 3) are affected by X_{nf}/X, T and $Mg\#_{Amph}$, while Tb ($R^2 = 0.91$ and SEE = ± 2) by X_{nf}/X and $Mg\#_{Amph}$. For Ca, Ce, Dy, Er, Eu, Gd, K, Lu, Mg, Mn, Nb, Nd, Pr, Sm, Ti, Yb (Supplementary Material 3) we obtained satisfactory correlation (R^2 = 0.7-0.8) observing, also in this case, the main influence of X_{nf}/X followed by $Mg\#_{Amph}$, P, and T. Finally, we observed a moderate correlation (R^2 = 0.6-0.7) for Al, Hf, La, Ta, Zr (Supplementary Material 3) while for the remaining elements (e.g., Ba, Cr, Na, Ni, Rb, Sr) we did not observe a clear trend ($R^2 < 0.5$). As regards Pb, Th and U, instead, we noted the influence of X_{nf}/X, T and P, without finding any good correlations ($R^2 \sim 0.5$; Supplementary Material 3). We noticed, indeed, that our runs and those of Zhang et al. (2019) show higher D_{Pb}, D_{Th}, and D_U than those of the other data considered in the comparison. The observed variation may also be related either to melt polymerization either to the effect of the redox conditions on the oxidation state of U (Tiepolo et al. 2007). Whether or not the significant increase in ${}^{Amph/L}D_i$ for Pb, Th, and U is related to variations of melt structure, oxide phases crystallization or oxygen fugacity is beyond the scope of this study.

Melt composition. The influence of melt composition on partitioning is essentially related to its degree of polymerization: the higher the structural organization of the melt, the lower the probability of hosting those cations not fitting tetrahedral coordination due to their ionic radius and charge (Tiepolo et al. 2007). As shown in Supplementary Material 3, at X_{nf}/X ranging between 0.5 and 0.8, the relation between ${}^{\mathrm{Amph/L}}D_{\mathrm{REE}}$ and melt composition is approximately linear as observed in Tiepolo et al. (2000b). As regards HFSE, ${}^{\mathrm{Amph/L}}D_{\mathrm{Ti}}$ is exponentially correlated with melt composition (Supplementary Material 3). As observed also in the work of Tiepolo et al. (2007), at higher X_{nf}/X values (>0.6) the variation of ${}^{\mathrm{Amph/L}}D_{\mathrm{Ti}}$ with melt composition is stronger, and two separate trends can be distinguished. The first trend is similar to that observed for REE (Dy and Yb). The second trend, defined by the samples from Hilyard et al. (2000), Tiepolo et al. (2000a), Xiong et al. (2005), and Liu et al. (2015), in agreement with what previously observed in the work of Tiepolo et al. (2007), suggests the prevalence of structural control on ${}^{\mathrm{Amph/L}}D$ for Ti^{4+} over that of the melt. A similar strong crystal structure control has been observed on ${}^{\mathrm{Amph/L}}D_{\mathrm{Ca}}$, ${}^{\mathrm{Amph/L}}D_{\mathrm{Fe}}$, ${}^{\mathrm{Amph/L}}D_{\mathrm{K}}$, ${}^{\mathrm{Amph/L}}D_{\mathrm{Mg}}$.

Pressure. The role of pressure on the ${}^{\mathrm{Amph/L}}D$ of the LIL elements was specifically investigated by Adam and Green (1994) and Dalpé and Baker (2000). Dalpé and Baker (2000) noted that ${}^{\mathrm{Amph/L}}D$ for the elements with ionic radii farther from the r_0 of the A-site are much more strongly affected by pressure than those with ionic radius closer to the r_0. The dependence of ${}^{\mathrm{Amph/L}}D$ for Rb on pressure is much stronger than that of Na or K (Dalpé and Baker 2000). However, in this study, as possible to see for Ba in Supplementary Material 3, no obvious correlation between LILE and pressure can be noted. The effect of pressure on the overall variation of the ${}^{\mathrm{Amph/L}}D_{\mathrm{REE}}$ was investigated by Adam and Green (1994). These authors showed that ${}^{\mathrm{Amph/L}}D$ for Lu and Sm decrease by up to a factor of about two with increasing pressure from 0.5 to 2.0 GPa. We observed a similar beahviour with a decrease of D_{REE} (La, Ce, Eu, Nd, Sm) with increasing pressure from 0.5 to 3 GPa in the comparison of our data with the database of existing experimental amphibole-melt partition coefficients (Supplementary Material 3). Adam and Green (2003) showed that the negative correlation observed between D_{REE} and pressure is not predicted by the thermodynamic model of Wood and Blundy (1997) and concluded that variations in ${}^{\mathrm{Amph/L}}D_{\mathrm{REE}}$ mostly depend on the volume-reducing substitutions occurring at the octahedra and the tetrahedra, which increase the activities of +3 and +4 ions, and decrease those of +1 ions, in sites with

VIII-fold co-ordination as pressure increases. A specific study on the influence of pressure on the $^{Amph/L}D_{HFSE}$ was carried out by Adam and Green (1994), who documented a decrease of the $^{Amph/L}D_{Ti}$ by a factor of 2 with increasing pressure from 0.5 to 2.0 GPa. According to this observation, we noted for the dataset considered, a decrease of D_{Ti}, D_{Zr}, and D_{Hf} with increasing pressure up to ~3 GPa for the considered data set.

Temperature. Adam and Green (1994) observed that *D*-values for Ti and REE are relatively insensitive to changes in temperature contrasting with the results of many previous studies (e.g., Nicholls and Harris 1980; Ray et al. 1983; Green and Pearson 1985). The reason for this is not immediately obvious but may be related to the complex inter-element substitutions which occur between crystallographic sites as temperature varies. Even the recent studies of Li et al. (2017) and Shimizu et al. (2017) observed the influence of temperature on trace element partitioning. Particularly, Li et al. (2017) observed a decrease of D_{Ti} and D_{Nb} with increasing temperature, while Shimizu et al. (2017) noticed that D_0 for REE negatively correlates with temperature. However, to date, the influence of temperature on amphibole/melt trace element partitioning has been found only in a few experimental works in the literature probably due to the relatively small thermal stability field of the amphibole and/or the relation between temperature and melt polymerization. Noteworthy, in the runs of this study we identified the influence of temperature on the partitioning of several trace elements between amphibole and melt, which can be well observed considering the D_0 values reported in Table 5. As regards the divalent cations, we noted that D_0 increases with decreasing T in M1-M2-M3 site while it decreases with decreasing T in M4-M4' one (Fig. 8a). This trend suggests that the decrease in T favors the entry of Mn, Fe, Co, Mg in VI-fold coordination into the M1-M2-M3 site. As regards the trivalent cations, we noted that D_0 decreases with decreasing T in M1-M2-M3 site while it increases with decreasing T in M4-M4' one (Fig. 8b). In this case, REEs are favored with respect to Al, Cr, Sc as the T decreases, in agreement with what was observed by Shimizu et al. (2017). Finally, as regards tetravalent cations (Ti, Hf, Zr), D_0 tends to decrease with increasing T in M1-M2-M3 site (Fig. 8c), agreeing with what was previously observed for D_{Ti} in the work of Li et al. (2017).

The trends of the D_0 for divalent, trivalent, and tetravalent cations in M1-M2-M3 and M4-M4' sites as a function of temperature, observed in Figure 8, are well in agreement with the trends of the respective D_i considered in the multiple linear regression (Supplementary Material 3). For instance, we noted a positive correlation for D_{Al} (trivalent in M1-M2-M3), and a negative correlation for D_{Fe}, D_{Mg} (divalent in M1-M2-M3), D_{Dy}, D_{Eu}, D_{Ho}, D_{Nd} (trivalent in M4-M4'), and D_{Ti}, D_{Hf} (tetravalent in M1-M2-M3).

IMPLICATIONS

A unique aspect of the investigated composition (a primitive K-basalt from the Campi Flegrei Volcanic District) lies in the compositional evolution of its experimental liquids as a function of the amount of water in the melt, which covers the field of basalt, trachybasalt, and shoshonite for water content <3 wt%, and that of basaltic andesite and andesite for water content >4 wt% (Perinelli et al. 2019), approaching in term of major elements those of the 2 Ma old, calc-alkaline volcanic products found in Parete and Castelvolturno bore-holes (north-west of Campi Flegrei; Beccaluva et al. 1991 and references therein) (Fig. S4 of Supplementary Material 1). The trace element compositions of the experimental residual glasses, on the other hand, do not correspond to those of the calc-alkaline rocks of Campi Flegrei. This difference is not surprising because geochemical models of magmatic suites deriving from metasomatic mantle sources should be computed on co-magmatic end-members (e.g., Gaeta et al. 2016, 2021) and ~2 Ma separate the APR16 basalt from the old calc-alkaline rocks of Campi Flegrei. The presence of tephra dated at 2.214 ± 0.034 Ma and rich in amphibole with relative high Mg# (60-64; Florindo et al. 2021; Fig. S5 of Supplementary Material 1) indicates, on the other hand, the importance of the amphibole in the pre-eruptive systems of the volcanic districts of the circum-Tyrrhenian region.

We used submarine basalt to trachybasalt compositions from the Pontine archipelago area to model the trace element abundances due to the fractional crystallization of amphibole. These rocks have been interpreted to be the primitive/intermediate lithologies representing parental compositions for the >1 Ma, peralkaline felsic rocks outcropping in the western Pontine Islands (Conte et al. 2016, 2020). In addition, the Pontine submarine lithotypes share orogenic trace element signatures exhibited by the calc-alkaline volcanic products of the Campi Flegrei. This and the results obtained from H_2O-saturated experiments on APR16 prompted us to test the hypothesis whether a composition similar to those submarine basalts, approaching that of APR16 (i.e., SiO_2 = 49.31-50.31 wt%, Na_2O+K_2O = 3.81-5.39 wt%, Mg# = 0.72-0.64; Conte et al. 2016, 2020), is able of producing andesites with the trace elements abundances such as those recovered in the Parete and Castelvolturno bore-holes by a differentiation process that involves the crystallization of amphibole. Thus, using as parental magma the trace element composition of submarine TD4B basalt (Conte et al. 2016), we calculated the concentration of selected elements in residual melts due to crystal-liquid fractionation process (FC). To model the FC process, we used the Excel© spreadsheet program ‘‘FC-AFC-FCA and mixing modeler” (Ersoy and Helvaci 2010) considering: *i*) a fractionate mineral assemblage formed by amphibole + clinopyroxene + oxides in proportion as in the experiments producing an andesitic residual melt (Table 2), *ii*) the partition coefficients amphibole-melt determined in this study, *iii*) the partition coefficients clinopyroxene-melt from the longest experiments determined by Bonechi et al. (2021). Modelling results indicate that the pattern of natural andesite, is well reproduced for a calculated residual liquid fraction of 44% (Fig. 9), a value close to the experimental 40% (Table 2), with the exception of Cs and Rb. As for Cs and Rb, the fractionation behavior of these elements cannot be accurately modelled starting from TD4B basalt composition. This result could be due either to the mobility and the incompatibility (*D* <1) of these elements either to the presence of a parental magma with different Cs and Rb concentrations.

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Figures captions

Figure 1. Backscattered images of experimental samples. Details of the experimental conditions are reported at the bottom of each image. Amph shows euhedral habit and maximum size of ~40 μm; pyroxene and oxide show euhedral habit with sizes up to ~5 μm and 40 μm, respectively. In Figure 1a some tiny quench crystals are present. Black holes with size ≤5 μm are saturation bubbles. Abbreviation: Amph: amphibole; Px: pyroxene; Ox: oxide; Gl: glass.

Figure 2. C1-normalized (Anders and Grevesse 1989) trace elements abundances for synthetic amphiboles. C3A suite (1080 °C) is reported in green, C3B (1030 °C) in light blue and APR16-ST1 (1050 °C) in blue. Symbols indicate different experimental dwell time: circle 0.15 h, asterisk 2 h, triangle 3 h, diamond 6 h and square 9 h.

Figure 3. C1-normalized (Anders and Grevesse 1989) trace elements abundances for analysed synthetic glasses. Symbols are as in Figure 2. Red crosses indicate data for the APR16 natural samples from Mazzeo et al. (2014). For comparison we reported C1-normalized trace elements abundances for synthetic glasses of Bonechi et al. (2021), indicated with the yellow field.

Figure 4. Calculated $^{\mathrm{Amph/Glass}}D$ values for trace elements in experimental samples. Symbols are as in Figure 2.

Figure 5. Onuma diagrams for amphibole-liquid partition coefficients for mono-, di-, tri-, and tetravalent cations versus ionic radii (in Å; Shannon 1976) for VI-, VIII- and XII-fold coordinated sites along with the results of the lattice strain fits in A, M1-M2-M3, M4-M4' sites for samples (a) APR16-C3Ad (1080 °C), (b) APR16-C3Bd (1030 °C), (c) APR16-ST1 (1050 °C). The dotted curves represent the fits of the lattice strain model to $^{\mathrm{Amph/Glass}}D_{\mathrm{i}}$ values while symbols represent measured $^{\mathrm{Amph/Glass}}D_{\mathrm{i}}$ values. Cations are indicated as follow: monovalent in orange, divalent in green, trivalent in light blue, tetravalent in yellow and pentavalent in purple. Cations in site-A are indicated with triangles, in site M4-M4' with circles and in site M1-M2-M3 with squares. Empty symbols indicate elements not considered in the fits of the LSM.

Figure 6. (a) Amphibole-melt REE partition coefficients calculated in this study and those calculated using the model of Shimizu et al. (2017). Symbols are as in Figure 2. Solid lines indicates partition coefficients calculated in this study while dashed lines those obtained with the model. (b) Comparison between the experimentally measured partition coefficients to those predicted using the model of Shimizu et al. (2017). The solid line represents 1:1 ratio, and dashed lines represent 2:1 and 1:2 ratios.

Figure 7. Calculated and predicted $\ln D_{Tb}$ is compared for the available database of existing experimental amphibole-melt partition coefficients (LEPR database and data from Nandedkar et al. 2016, Zhang et al. 2019, and Cannaò et al. 2022; Table S3 of Supplementary Material 2 and Supplementary Material 3). Solid and dashed grey lines are 1:1, 1:2 and 2:1 lines, while green dashed line is the regression line. Embedded table reports the parameters and related errors obtained from the regression analysis. For creating the model and to avoid over-fitting of the data the t-stat (calculated as the ratios between the coefficients and their standard errors and thus representing a measure of the precision with which the regression coefficients are measured; e.g., Rawlings et al. (1998)) were checked for all variables, looking for the t-stat ≥ 5, and the P-value (a measure of how the overall result of the regression is statistically significant; e.g., Rawlings et al. (1998)) was checked in order to achieve the maximum value similarly to the approach used in Putirka et al. (2003).

Figure 8. Diagrams showing the variation in the strain-free partition coefficient (D_0) for the amphibole as function of temperature for divalent (a), trivalent (b) and tetravalent (c) cations in VI-fold coordinated M1-M2-M3 site and in VII-fold coordinated M4-M4' site. Symbols are as in Figure 5. Arrows indicate the trends observed for D_0 as function of temperature variation.

Figure 9. Primitive Mantle normalized (McDonough and Sun 1995) trace elements patterns of TD4B basalt (Conte et al. 2016) and the predicted composition of differentiated melts obtained after 56% of fractional crystallization of TD4B basalt assumed as primitive parental melt of andesitic magma of Campi Flegrei (sample from Parete borehole; Beccaluva et al. 1991). The reported degree of fractionation (FC) reflects the crystallized phase assemblage and proportions determined for run APR16-C3Bd (amphibole (35) + clinopyroxene (24) + oxide (1)) that produced andesitic residual glass. The modelled compositions were calculated by using the Excel® spreadsheet program of Ersoy and Helvaci (2010).

Tables captions

Table 1 Composition (wt%) of APR16 rock sample and APR16GL starting material

Table 2 Experimental run conditions, melt water contents, phases assemblage and proportions in run products

Table 3 Major and trace element concentrations (ppm) for synthetic amphibole crystals and glasses

Table 4 Major and trace elements partition coefficients between amphibole and glass for experimental samples

Table 5 Best fits for E, r_0 and D_0 obtained by regression of amphibole/glass partition coefficients of monovalent, divalent, trivalent and tetravalent cations in A, M1-M2-M3, M4-M4' sites

Supplementary materials

Supplementary Material 1 contains supplementary figures

Supplementary Material 2 contains supplementary tables

Supplementary Material 3 contains multiple linear regression analyses

Figure 1

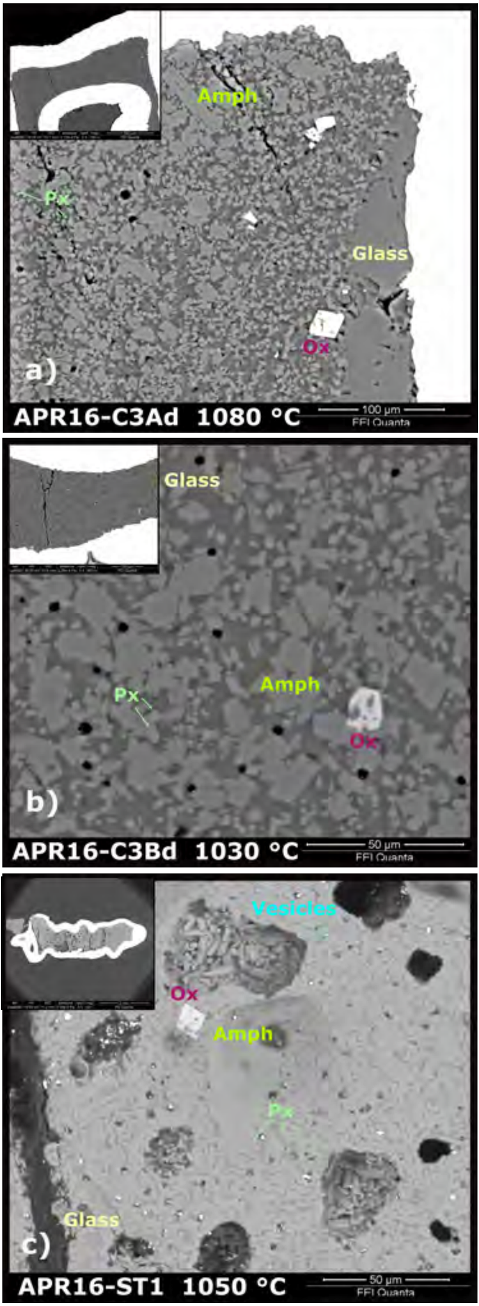

Amph
Px
Glass
Ox
a)
APR16-C3Ad 1080 °C
100 µm
FEI Quanta
Glass
Px
Amph
Ox
b)
APR16-C3Bd 1030 °C
50 µm
FEI Quanta
Vesicles
Ox
Amph
Px
Glass
c)
APR16-ST1 1050 °C
50 µm
FEI Quanta

Figure 2

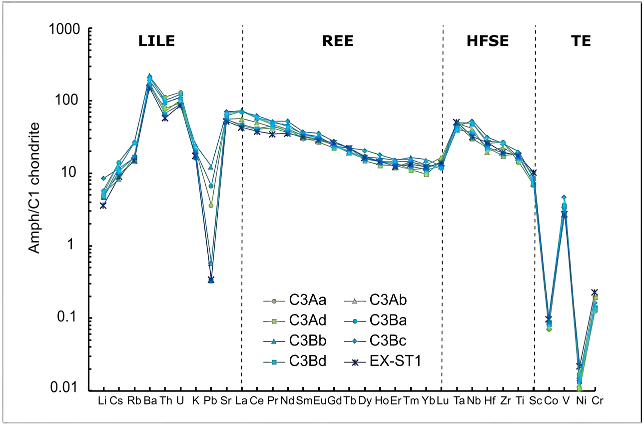

LILE
REE
HFSE
TE
1000
100
10
1
0.1
0.01
Amph/C1 chondrite
Li Cs Rb Ba Th U K Pb Sr La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Ta Nb Hf Zr Ti Sc Co V Ni Cr
C3Aa
C3Ab
C3Ad
C3Ba
C3Bb
C3Bc
C3Bd
EX-ST1

Figure 3

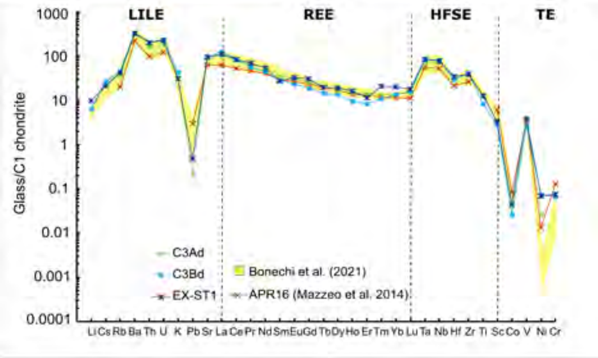
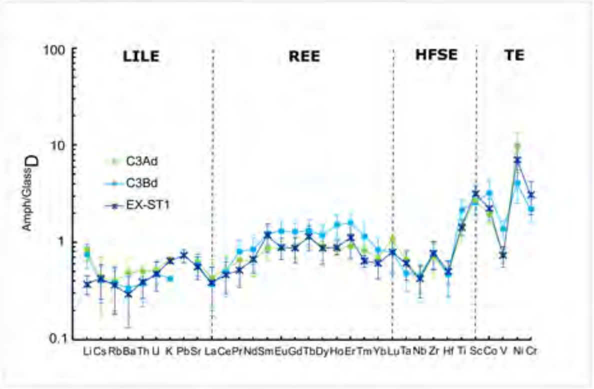

LILE
REE
HFSE
TE
Glass/C1 chondrite
1000
100
10
1
0.1
0.01
0.001
0.0001
Li Cs Rb Ba Th U K Pb Sr La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Ta Nb Hf Zr Ti Sc Co V Ni Cr
C3Ad
C3Bd
EX-ST1
Bonechi et al. (2021)
APR16 (Mazzeo et al. 2014)

Figure 4


100
10
1
0.1
$^{Amph/Glass}D$
LILE
REE
HFSE
TE
C3Ad
C3Bd
EX-ST1
Li Cs Rb Ba Th U K Pb Sr La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Ta Nb Zr Hf Ti Sc Co V Ni Cr

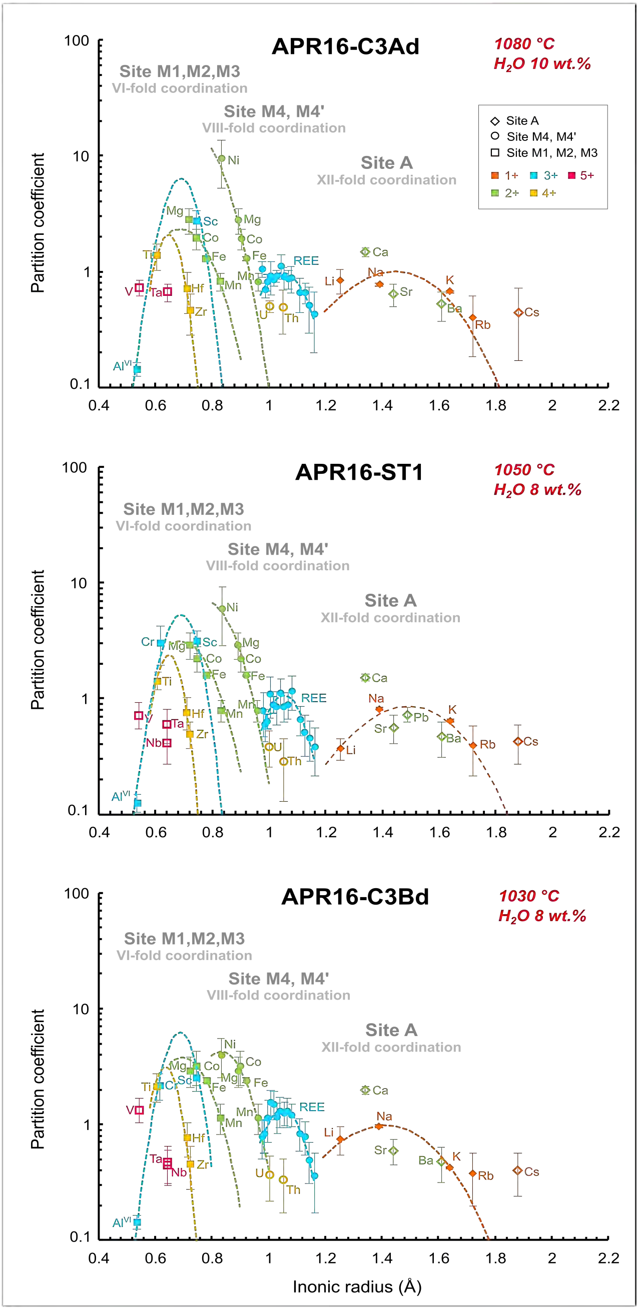
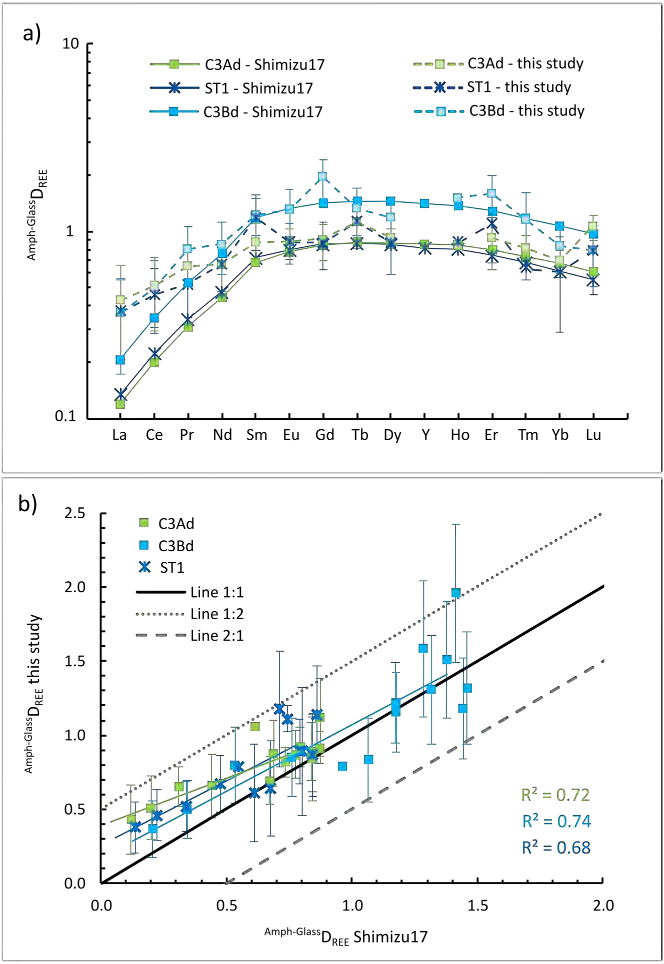
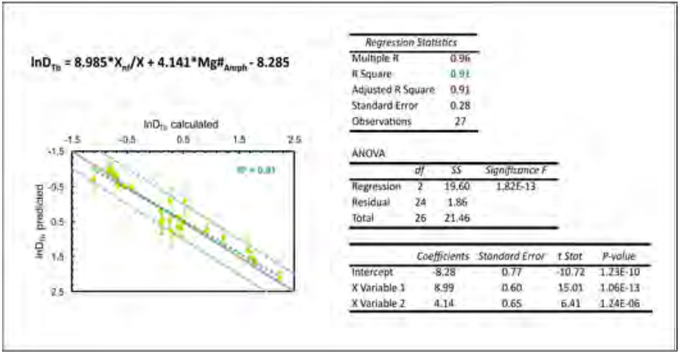

APR16-C3Ad
1080 °C
H_2O 10 wt.%
Site M1,M2,M3
VI-fold coordination
Site M4, M4'
VIII-fold coordination
Site A
XII-fold coordination
◇ Site A
○ Site M4, M4'
☐ Site M1, M2, M3
🟧 1+ 🟦 3+ 🟥 5+
🟩 2+ 🟨 4+
Ni
Mg
Sc
Mg
Co
Co
Ti
Fe
Fe
REE
Ca
Li
Na
K
Mn
Mn
V
Ta
Hf
Sr
Zr
U
Th
Ba
Rb
Cs
Al^{VI}
Partition coefficient
100
10
1
0.1
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
APR16-ST1
1050 °C
H_2O 8 wt.%
Site M1,M2,M3
VI-fold coordination
Site M4, M4'
VIII-fold coordination
Site A
XII-fold coordination
Ni
Cr
Mg
Sc
Mg
Co
Co
Fe
Fe
Ti
REE
Ca
Na
Mn
Mn
K
V
Hf
Sr
Pb
Ta
Zr
Ba
Nb
U
Rb
Cs
Li
Th
Al^{VI}
Partition coefficient
100
10
1
0.1
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
APR16-C3Bd
1030 °C
H_2O 8 wt.%
Site M1,M2,M3
VI-fold coordination
Site M4, M4'
VIII-fold coordination
Site A
XII-fold coordination
Ni
Mg
Co
Co
Mg
Ti
Cr
Sc
Fe
Fe
Ca
V
REE
Mn
Mn
Na
Li
Hf
Sr
Ta
Ba
K
Nb
Zr
Rb
Cs
U
Th
Al^{VI}
Partition coefficient
100
10
1
0.1
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
Inonic radius (Å)

Figure 6


a)
10
1
0.1
$^{\mathrm{Amph\text{-}Glass}}D_{\mathrm{REE}}$
C3Ad - Shimizu17
ST1 - Shimizu17
C3Bd - Shimizu17
C3Ad - this study
ST1 - this study
C3Bd - this study
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Y
Ho
Er
Tm
Yb
Lu
b)
2.5
2.0
1.5
1.0
0.5
0.0
$^{\mathrm{Amph\text{-}Glass}}D_{\mathrm{REE}}$ this study
C3Ad
C3Bd
ST1
Line 1:1
Line 1:2
Line 2:1
$R^2 = 0.72$
$R^2 = 0.74$
$R^2 = 0.68$
0.0
0.5
1.0
1.5
2.0
$^{\mathrm{Amph\text{-}Glass}}D_{\mathrm{REE}}$ Shimizu17



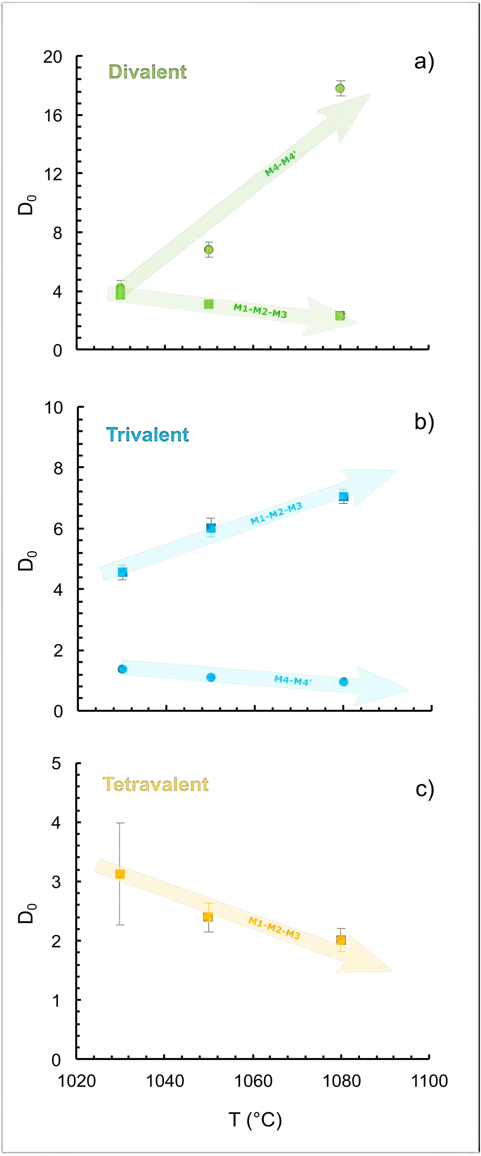
$$\ln D_{Tb} = 8.985 * X_{nf}/X + 4.141 * Mg\#_{Amph} - 8.285$$

Regression Statistics	
Multiple R	0.96
R Square	0.91
Adjusted R Square	0.91
Standard Error	0.28
Observations	27

ANOVA

	df	*SS*	*Significance F*
Regression	2	19.60	1.82E-13
Residual	24	1.86	
Total	26	21.46	

	Coefficients	*Standard Error*	*t Stat*	*P-value*
Intercept	-8.28	0.77	-10.72	1.23E-10
X Variable 1	8.99	0.60	15.01	1.06E-13
X Variable 2	4.14	0.65	6.41	1.24E-06


a)
Divalent
M4-M4'
M1-M2-M3
b)
Trivalent
M1-M2-M3
M4-M4'
c)
Tetravalent
M1-M2-M3
D$_0$
0
4
8
12
16
20
0
2
4
6
8
10
0
1
2
3
4
5
1020
1040
1060
1080
1100
T (°C)

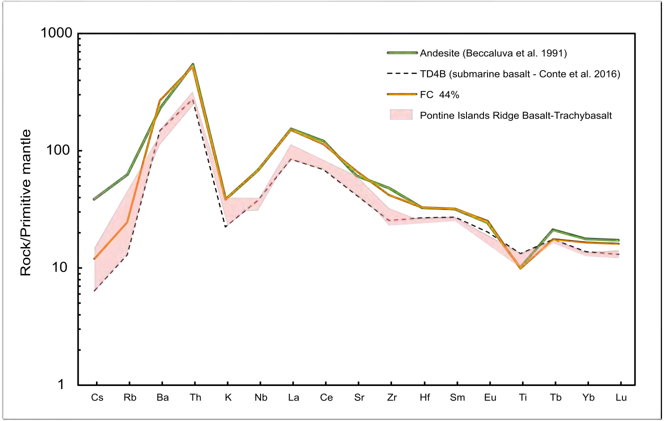

1000
100
10
1
Rock/Primitive mantle
Cs
Rb
Ba
Th
K
Nb
La
Ce
Sr
Zr
Hf
Sm
Eu
Ti
Tb
Yb
Lu
Andesite (Beccaluva et al. 1991)
TD4B (submarine basalt - Conte et al. 2016)
FC 44%
Pontine Islands Ridge Basalt-Trachybasalt

Table 1 Composition (wt%) of APR16 rock sample and APR16GL starting material

Sample	APR16	APR16GL
SiO_2	48.89	49.3 (0.46)
TiO_2	1.23	1.33 (0.03)
Al_2O_3	15.65	15.31 (0.14)
FeO_{tot}	8.08	7.79 (0.13)
MnO	0.14	0.14 (0.05)
MgO	8.89	9.31 (0.07)
CaO	11.64	12.02 (0.09)
Na_2O	2.88	2.86 (0.05)
K_2O	1.52	1.60 (0.02)
P_2O_5	0.31	0.55 (0.02)
Total	99.23	99.31 (0.29)$^{\gamma}$
L.O.I.	0.61	-
Mg# *	0.66	0.68

*[$MgO/(MgO+FeO_{tot})$] molar, assuming all Fe^{2+} and Fe^{3+} as FeO_{tot}. Chemical composition of APR16 is from D'Antonio et al. (1999); APR16GL composition is from Perinelli et al. (2019). $^{\gamma}$ For APR16GL the analysis is normalized to 100 but the original total is reported. Standard deviation is reported in parenthesis.

Table 2 Experimental run conditions, melt water contents, phases assemblage and proportions in run products

Run #	T (°C)	T_L (°C)	ΔT (°C)	Time (h)	H_2O_i (wt%)	Phases	H_2O_f EPMA (wt%)	Σr^2	% ΔFe§
APR16-C3Aa*	1080	1218	138	0.25	4	Gl + Amph + Cpx + Plg + Ox			
APR16-C3Ab*	1080	1218	138	3	4	Gl + Amph + Cpx + Plg + Ox	7.5		
APR16-C3Ad	1080	1233	153	9	3.3	Gl(55) + Amph(24) + Cpx(20) + Ox(1)	10.2	0.41	-1
APR16-C3Ba*	1030	1224	194	0.25	3.8	Gl + Amph + Cpx + Plg + Ox	10.6		
APR16-C3Bb*	1030	1225	195	3	3.7	Gl + Amph + Cpx + Plg + Ox	9.5		
APR16-C3Bc*	1030	1232	202	6	3.4	Gl + Amph + Cpx + Opx + Ox			
APR16-C3Bd	1030	1216	186	9	4.2	Gl(40) + Amph(35) + Cpx(24) + Ox(1)	8.3	0.18	-1
APR16-ST1	1050	1150	100	2	8	Gl(51) + Amph(36) + Cpx(13) + Ox(1)	8.1	0.31	

Gl = glass; Amph = amphibole; Cpx = clinopyroxene; Opx = orthopyroxene; Plg = plagioclase; Ox = oxide minerals. ΔT is the difference between the liquidus temperature and the nominal temperature of the experiment. T_L is the liquidus temperature (°C) determined on the basis of phase relations experimental data from Perinelli et al. (2019). H_2O_f EPMA = water content in the melt determined by the by-difference calculation method (respect to the total of EMP analyses); % Percent 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. Σr^2 values from mass balance calculation. *Crystals too small for analysis and not considered for mass balance calculations.

Table 3 Major and trace element concentrations (ppm) for synthetic amphibole crystals and glasses

Run#	APR16-C3Aa	APR16-C3Ab	APR16-C3Ad	APR16-C3Ba	APR16-C3Bb	APR16-C3Bc	APR16-C3Bd	APR16-ST1
Phase	Amph glass	Amph glass	Amph glass	Amph glass	Amph glass	Amph glass	Amph glass	Amph glass
Na*	18472 (838)	16766 (307)	16469 (351)	14763 (265)	13353 (302)	10831 (452)	17211 (513)	16840 (433)
			21514 (213)				17730 (231)	20698 (211)
K*	11456 (102)	11124 (52)	11207 (103)	11207 (98)	13448 (92)	10709 (232)	8965 (272)	9630 (312)
			16769 (206)				21168 (209)	15025 (204)
Ca*	80121 (5800)	82051 (6100)	83337 (5980)	84409 (4800)	86196 (6400)	88912 (5100)	84909 (5150)	90556 (4350)
			56892 (3850)				43026 (3105)	59608 (3400)
Fe*	82005 (4451)	65526 (2350)	59774 (2310)	71123 (1890)	66537 (1930)	76952 (2100)	70812 (2250)	68635 (1850)
			46327 (950)				29382 (890)	42285 (850)
Mg	51270 (4251)	55950 (3402)	71267 (16478)	57857 (3171)	56380 (1819)	79820 (18651)	56740 (13767)	77962 (14804)
			25466 (2086)				19200 (3389)	26575 (4189)
Al	83550 (13055)	75983 (5265)	79183 (11744)	87900 (2712)	89100 (1880)	100340 (5010)	79311 (15056)	79892 (10591)
			100157 (5379)				103500 (35003)	109100 (18949)
Mn	1269 (112)	1199 (79)	1048 (173)	1373 (93)	1355 (23)	1557 (142)	1153 (197)	1048 (139)
			1283 (46)				995 (135)	1381 (207)
Ti	6426 (788)	7453 (904)	8157 (2071)	7266 (195)	7280 (86)	8838 (2971)	7906 (2131)	7787 (1151)
			5949 (324)				3633 (239)	5452 (509)
Zr	107 (19)	90 (4)	69 (26)	105 (3)	106 (1)	101 (9)	75 (24)	77 (16)
			149 (15)				163 (40)	154 (24)
Nb	12 (2)	10.1 (0.6)	7.4 (3.3)	12 (1)	11.9 (0.4)	13 (2)	8 (2)	8 (2)
			17.6 (1.4)				20 (5)	19 (4)
Hf	2.9 (0.6)	2.1 (0.3)	2.3 (0.9)	2.7 (0.4)	2.7 (0.6)	3.3 (0.4)	2.4 (0.8)	2.7 (0.5)
			3.2 (0.3)				3.04 (0.01)	3.6 (0.9)
Ta	0.71 (0.14)	0.7 (0.1)	0.66 (0.11)	0.7 (0.1)	0.7 (0.1)	0.6 (0.1)	0.6 (0.2)	0.7 (0.1)
			0.99 (0.05)				1.2 (0.1)	1.2 (0.3)
Th	3.32 (0.86)	2.1 (0.3)	2.31 (0.94)	3.0 (0.2)	2.8 (0.1)	2.7 (0.5)	1.9 (0.9)	1.7 (0.8)
			4.7 (0.4)				5.8 (0.3)	5.9 (1.6)
U	1.06 (0.28)	0.82 (0.08)	0.75 (0.05)	1.0 (0.1)	0.9 (0.1)	0.9 (0.1)	0.7 (0.3)	0.7 (0.2)
			1.5 (0.1)				1.9 (0.4)	1.8 (0.4)

Rb	61 (16)	40 (3)	34 (18)	62 (11)	61 (3)	38 (7)	39 (17)	35 (14)
			86 (7)				103 (20)	87 (18)
Sr	518 (107)	435 (32)	429 (91)	484 (96)	539 (15)	555 (43)	422 (88)	407 (80)
			679 (24)				708 (103)	733 (136)
Cs	2.7 (0.8)	1.6 (0.4)	1.8 (0.1)	2.7 (0.4)	2.3 (0.1)	2.2 (0.1)	2.0 (0.7)	1.7 (0.5)
			4.1 (0.5)				5 (1)	4 (1)
Ba	507 (125)	414 (37)	377 (104)	491 (100)	523 (11)	450 (61)	376 (111)	354 (93)
			729 (56)				791 (139)	761 (164)
Pb	9 (5)	1.4 (0.7)	bdl	17 (9)	31 (23)	1.44 (*0.36*)	0.83 (0.18)	0.85 (0.13)
			0.51 (0.07)				bdl	1.17 (0.03)
Sc	40 (5)	42 (3)	50 (10)	43 (3)	43 (1)	50 (5)	41 (7)	60 (9)
			18 (2)				16 (3)	19 (3)
V	189 (18)	208 (23)	163 (26)	209 (12)	210 (2)	264 (61)	198 (39)	154 (30)
			223 (3)				146 (18)	212 (31)
Cr	337 (41)	355 (30)	525 (173)	377 (15)	375 (7)	436 (68)	381 (96)	612 (208)
			bdl				175 (9)	200 (28)
Co	36 (8)	38 (3)	44 (8)	45 (4)	46 (2)	52 (18)	42 (12)	49 (10)
			23 (2)				13 (2)	22 (3)
Ni	119 (37)	135 (16)	184 (70)	148 (22)	165 (16)	167 (66)	149 (52)	241 (75)
			13 (4)				37 (5)	40 (17)
La	16.7 (3.3)	13.3 (0.7)	11 (5)	17 (1)	17 (1)	16 (1)	11 (5)	10 (4)
			25 (1)				30 (8)	26 (5)
Ce	34 (4)	30 (1)	25 (10)	35 (1)	35 (1)	37 (4)	25 (9)	23 (7)
			48 (1)				50 (7)	50 (10)
Pr	4.2 (0.8)	3.8 (0.3)	3.8 (0.8)	4.4 (0.3)	4.6 (0.1)	4.6 (0.4)	4 (1)	3 (1)
			48 (1)				5 (1)	6 (1)
Nd	18.4 (2.9)	18.5 (1.3)	16.2 (5.2)	21 (2)	19.8 (1.7)	23.7 (2.9)	17 (4)	16 (3)
			25 (1)				20 (4)	24 (5)
Sm	4.4 (0.5)	4.8 (0.5)	4.5 (1.0)	5 (1)	5.1 (0.7)	5.5 (1.5)	5 (1)	5 (1)
			5.2 (0.5)				4.1 (0.4)	4 (1)
Eu	1.6 (0.3)	1.6 (0.3)	1.5 (0.2)	1.8 (0.4)	1.8 (0.3)	2.0 (0.4)	1.7 (0.4)	1.6 (0.3)
			1.7 (0.4)				1.3 (0.2)	1.8 (0.3)
Gd	4.9 (0.9)	4.8 (0.5)	4.4 (0.9)	4.6 (0.8)	4.9 (0.4)	5.4 (1.6)	4.7 (1.1)	5.2 (1.2)
			4.9 (0.4)				3.7 (0.1)	6 (1)

Tb	0.7 (0.1)	0.7 (0.1)	0.8 (0.2)	0.8 (0.1)	0.7 (0.1)	0.8 (0.2)	0.7 (0.2)	0.8 (0.2)
			0.74 (0.04)				0.53 (0.01)	0.7 (0.1)
Dy	3.8 (0.5)	3.9 (0.9)	3.6 (0.2)	4.2 (0.6)	4.1 (0.5)	5.0 (0.8)	3.8 (1.1)	4 (1)
			3.9 (0.4)				3.22 (0.01)	4.6 (0.9)
Ho	0.8 (0.1)	0.8 (0.2)	0.7 (0.1)	0.8 (0.1)	0.9 (0.1)	1.0 (0.1)	0.8 (0.2)	0.8 (0.1)
			0.85 (0.05)				0.53 (0.06)	0.9 (0.1)
Er	2.2 (0.5)	1.93 (0.32)	2.02 (0.62)	2.3 (0.2)	2.4 (0.2)	2.4 (0.8)	2.1 (0.5)	2.0 (0.4)
			2.2 (0.2)				1.32 (0.13)	1.8 (0.6)
Tm	0.27 (0.05)	0.34 (0.03)	0.27 (0.03)	0.35 (0.01)	0.4 (0.1)	0.37 (0.13)	0.3 (0.1)	0.32 (0.04)
			0.33 (0.04)				0.26 (0.04)	0.50 (0.03)
Yb	1.88 (0.32)	2.1 (0.3)	1.6 (0.1)	1.96 (0.04)	2.5 (0.5)	2.11 (0.27)	1.83 (0.43)	1.97 (0.47)
			2.3 (0.3)				2.2 (*0.5*)	3.2 (*0.7*)
Lu	0.35 (0.08)	0.4 (0.1)	0.37 (0.02)	0.34 (0.03)	0.3 (0.1)	0.29 (0.06)	0.3 (0.1)	0.34 (0.12)
			0.35 (0.05)				0.38 (0.05)	0.43 (*0.08*)

Notes: Amph = amphibole; standard deviation is reported in brackets. *Data from EPMA.
For single analysis Int2SE (i.e., analytical error) is reported also in brackets but in italic; bdl = below detection limit.

Table 4 Major and trace elements partition coefficients between amphibole and glass for experimental samples

Run#	APR16-C3Ad	APR16-C3Bd	APR16-ST1
Na*	0.77 (0.02)	0.97 (0.03)	0.81 (0.02)
K*	0.67 (0.01)	0.42 (0.01)	0.64 (0.02)
Ca*	1.46 (0.12)	1.97 (0.16)	1.52 (0.10)
Fe*	1.29 (0.05)	2.41 (0.12)	1.62 (0.05)
Mg	2.79 (0.69)	2.95 (0.88)	2.93 (0.77)
Al	0.79 (0.12)	0.76 (0.29)	0.73 (0.17)
Al^{IV}	0.64	0.60	0.61
Al^{VI}	0.14	0.15	0.12
Mn	0.82 (0.14)	1.16 (0.25)	0.79 (0.16)
Li	0.84 (0.20)	0.75 (0.21)	0.37 (0.08)
Ti	1.37 (0.36)	2.16 (0.60)	1.43 (0.25)
Zr	0.46 (0.18)	0.46 (0.19)	0.50 (0.13)
Nb	0.42 (0.14)	0.45 (0.15)	0.42 (0.15)
Hf	0.71 (0.28)	0.78 (0.25)	0.77 (0.24)
Ta	0.67 (0.12)	0.48 (0.17)	0.61 (0.20)
Th	0.49 (0.20)	0.34 (0.16)	0.29 (0.16)
U	0.50 (0.05)	0.37 (0.16)	0.39 (0.13)
Cs	0.44 (0.27)	0.40 (0.16)	0.43 (0.16)
Rb	0.40 (0.21)	0.38 (0.18)	0.40 (0.18)
Sr	0.63 (0.14)	0.60 (0.15)	0.56 (0.15)
Ba	0.52 (0.15)	0.48 (0.16)	0.47 (0.16)
Pb			0.73 (0.11)
Sc	2.73 (0.62)	2.56 (0.65)	3.16 (0.69)
V	0.73 (0.12)	1.36 (0.32)	0.73 (0.18)
Cr		2.18 (0.56)	3.06 (1.12)
Co	1.93 (0.38)	3.23 (1.05)	2.23 (0.55)
Ni	9.42 (4.15)	4.03 (1.51)	6.03 (3.17)
La	0.43 (0.23)	0.37 (0.19)	0.38 (017)
Ce	0.51 (0.22)	0.50 (0.19)	0.46 (0.17)
Pr	0.66 (0.13)	0.80 (0.26)	0.52 (0.17)
Nd	0.66 (0.21)	0.85 (0.26)	0.67 (0.19)
Sm	0.88 (0.22)	1.22 (0.27)	1.18 (0.39)
Eu	0.87 (0.16)	1.31 (0.37)	0.89 (0.22)
Gd	0.89 (0.20)	1.27 (0.47)	0.87 (0.25)
Tb	1.12 (0.26)	1.32 (0.38)	1.14 (0.33)
Dy	0.92 (0.11)	1.18 (0.34)	0.87 (0.28)
Ho	0.85 (0.10)	1.51 (0.41)	0.89 (0.15)
Er	0.92 (0.29)	1.58 (0.40)	1.11 (0.43)
Tm	0.82 (0.13)	1.15 (0.46)	0.64 (0.09)
Yb	0.69 (0.10)	0.84 (0.27)	0.61 (0.19)
Lu	1.06 (0.16)	0.79 (0.28)	0.79 (0.32)

Table 5 Best fits for E, r_0 and D_0 obtained by regression of amphibole/liquid partition coefficients of monovalent, divalent, trivalent and tetravalent cations in A, M1-M2-M3, M4-M4’ sites

		APR16-C3Ad	APR16-ST1	APR16-C3Bd
Monovalent	**A**			
	D_0	0.97±0.20	0.86±0.06	0.98±0.11
	r_0	1.449±0.049	1.495±0.008	1.419±0.030
	E	*30±4*	30±4	*30±4*
Divalent	**M1, M2, M3**			
	D_0	2.32±0.14	3.11±0.09	3.77±0.30
	r_0	0.689±0.006	0.686±0.008	0.697±0.013
	E	209±5	200±1	247±37
	M4, M4'			
	D_0	17.77±0.51	6.84±0.53	4.24±0.47
	r_0	0.709±0.002	0.776±0.008	0.834±0.015
	E	202±2	227±20	259±48
Trivalent	**M1, M2, M3**			
	D_0	7.08±0.09	6.04±0.28	4.56±0.25
	r_0	0.689±0.004	0.688±0.002	0.688±0.004
	E	785±12	805±10	696±27
	M4, M4'			
	D_0	0.9550±0.0002	1.1004±0.0018	1.3541±0.0634
	r_0	1.0514±0.0001	1.0558±0.0007	1.0511±0.0006
	E	200±1	299±4	303±17
Tetravalent	**M1, M2, M3**			
	D_0	2.004±0.194	2.39±0.24	3.12±0.86
	r_0	0.6475±0.0038	0.6477±0.0034	0.6368±0.0117
	E	1195±143	1247±137	1181±429

Note: D_0: strain-compensated partition coefficient. E: Young Modulus of the lattice site (GPa). r_0: optimum site radius (Å). D_0, r_0 and E were calculated using the SIMPLE program (Dalou et al. 2018). E values of the monovalent cations (reported in italic) for APR16-C3Ad and APR16-C3Bd runs have been set equal to that determined for run APR16-ST1.