

HIGH PRESSURE EXPERIMENTS ON KINETIC AND RHEOLOGICAL PROPERTIES OF PRIMITIVE ALKALINE MAGMAS: CONSTRAINTS ON DEEP MAGMATIC PROCESSES AT THE CAMPI FLEGREI VOLCANIC DISTRICT

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Defining the timescales of magma storage and ascent beneath active volcanoes is a fundamental tool in volcanological investigation of the last decade to constrain pre-eruptive magmatic processes and magma chamber dynamics, since it is able to provide the basis for volcanic hazard assessment. This Ph.D. project focuses on the investigation of the deep portion of the Campi Flegrei Volcanic District (CFVD; Italy) plumbing system (crustal-mantle boundary; ~25 km of depth), in correspondence of which the presence of a possible crystallization zone has been hypothesized on the basis of melt inclusion studies, seismic data interpretations, gravimetric and petrological modelling, and experimental data. The CFVD, which includes the Campi Flegrei and the islands of Ischia and Procida, represents one of the most active volcanic areas in the Mediterranean region and one of the most dangerous volcanic complexes on Earth owing to the intense urbanization of the area. Many petrological, geochemical and geophysical surveys were carried out in the Campania Active Volcanic Area that have helped to define the main architecture and the development of the sub-volcanic system. Nevertheless, the dynamic processes that operate during the earliest, deepest differentiation steps of primitive magmas that fed all Campi Flegrei eruptions are poorly constrained, yet. The knowledge of the dynamics and residence as well as ascent timescales of magma at deep levels, indeed, may be the key to understand the triggering mechanisms of volcanic eruptions and are essential for understanding the rates at which magmas are supplied to volcanic complexes. In this work, the investigation of the kinetic and rheological properties of a K-basaltic magma at Moho depth, together with the partitioning of trace elements between crystal and melts, has allowed to fill some gaps relative to the knowledge of the deep portion of the Campi Flegrei Volcanic District plumbing system, providing magma residence time and ascent timescales, and models for deep magmatic differentiation processes.

INTRODUCTION

It has been known for long time that the timescale of magma formation, storage and ascent beneath active volcanoes is the key to constrain pre-eruptive magmatic processes and magma chamber dynamics, which provide the basis for volcanic hazard assessment (*e.g.*, Morgan *et al.*, 2006; Saunders *et al.*, 2012; Petrone *et al.*, 2016). Estimates of these timescales and knowledge of magmatic processes can be obtained by several methods (Costa *et al.*, 2020, and reference therein), among which the investigation of: *i*) kinetics of crystal nucleation and growth; *ii*) dissolution kinetics; *iii*) rheological properties; *iv*) partitioning of trace elements between crystals and melts.

i): The kinetics of crystal nucleation and growth are fundamental for the interpretation of rock textures in terms of thermal history of a magma during its ascent to the surface and to constrain timescales of magmatic processes. Indeed, deep-level ascent rates may be the key to understand the triggering mechanisms of volcanic eruptions and are essential for understanding the rates at which magmas are supplied to volcanic complexes (Armienti *et al.*, 2013; Perinelli *et al.*, 2018). In this regard, the experimental approach is used to reproduce natural processes on a small scale as reliably as possible. The performance of experiments together with a series of assumptions targeted at constraining the countless variables present in nature, provides fundamental data for developing petrological models aimed at interpreting and predicting what happens in nature.

In this work clinopyroxene and amphibole growth rates were investigated in detail, since they are the predominant phases under the studied conditions (see next section “Choice of the experimental conditions”). Clinopyroxene, indeed, is a common phenocryst in basaltic systems and, due to its wide crystallization range, it may contain the most complete record of evolutionary history of a magma. Amphibole, instead, is a typical phase

of mafic to felsic hydrous magmas (*e.g.*, Davidson *et al.*, 2007, and reference therein) through which it was possible to qualitatively and quantitatively infer magmatic crystallization pressure and temperature as well as magma storage, mixing and ascent processes (*e.g.*, Zhang *et al.*, 2017, and reference therein). However, to date, experimental studies of clinopyroxene crystallization kinetics in primitive alkaline compositions are few and limited to low pressure conditions (≤ 0.5 GPa; *e.g.*, Orlando *et al.*, 2008; Arzilli & Carroll, 2013; Pontesilli *et al.*, 2019), as well as the investigations on the kinetics of amphibole crystallization, that are all addressed to investigate calc-alkaline rocks affinity (*i.e.*, Simakin *et al.*, 2009; Shea & Hammer, 2013; Zhang *et al.*, 2019). In this work, the cooling rate and the deep-level ascent rates of K-basaltic magmas were evaluated by combining the clinopyroxene growth rate determined by high-pressure crystallization experiments with data from crystal size distribution analyses and thermobarometry of clinopyroxenes occurring in the most primitive scoria clasts of the CFVD. The aim, indeed, was to investigate the CFVD magmas transport at Moho-lower crust depth and provide an estimate of magma recharge of the deep reservoirs.

ii): Similarly, knowledge of dissolution kinetics of minerals is important to provide constraints on crystal residence times and magma chamber dynamics. Dissolution is a fundamental process in igneous petrology and it often occurs, for instance, during xenolith and/or xenocryst digestion by magma assimilation and transport processes (*e.g.*, Edwards & Russell, 1998). Among the studies available in the literature regarding the dissolution of minerals in silicate melts, those focusing on clinopyroxene dissolution are few and sparse (Chen & Zhang, 2009, and reference therein) and only those by Scarfe *et al.* (1980) and Brearley & Scarfe (1986) report data on clinopyroxene dissolution in alkali basaltic compositions. The clinopyroxene dissolution rates calculated in this work were employed to determine the dissolution times of phenocrysts from the Campi Flegrei caldera, since the omission of the effect of the dissolution of the crystals, could lead to an underestimation of the residence times.

iii): Evidence that the re-activation of volcanic areas is supported by an input of deeply formed magmatic batches, implies that the eruptive style at surface is influenced by the physical and chemical conditions of magmas at depths of the upper mantle. In the case of Campi Flegrei, several studies have pointed out the geochemical and seismic signature for the presence of mantle-derived magmas, the rheological properties of which remained unexplored so far. Experimental studies have provided the pressure dependence of viscosity first by performing quench experiments in multi anvil and piston cylinder (Kushiro *et al.*, 1976) although limited to viscosities > 1 Pa·s. More recent experimental studies performed at high pressure and temperature representative of mantle regions by means of *in situ* radiographic techniques combined with high-pressure apparatus have allowed to explore a wider range of silicate melt compositions like basaltic (Sakamaki *et al.*, 2013), trachy-andesitic (Suzuki *et al.*, 2005), albitic (Suzuki *et al.*, 2002) and dacitic (Tinker *et al.*, 2004) melts. To date, experimental studies on the rheological properties of magmas of interest for the CFVD investigate only differentiated compositions from latites to trachytes at low (< 0.5 GPa) and atmospheric pressure (Misiti *et al.*, 2011, and reference therein). Viscosity data measured in this work were used to model *i*) the mobility and migration rate of APR16 K-basaltic melt at upper mantle conditions corresponding to a scenario of new batches of magma that form in the mantle source and move upward creating the conditions of re-filling of the chamber at crustal depths, and *ii*) the flow regime and magma ascent rate from deep to shallow reservoirs, and up to the surface.

iv): Finally, a central factor in the evolution of an igneous body is the partitioning of elements between the melt and the crystallizing minerals. The study of the factors influencing the partitioning coefficients is of paramount importance since the latter are frequently used in petrological and geochemical studies to better understand magmatic processes, like fractional or equilibrium crystallization, assimilation, and partial melting (*e.g.*, Mollo *et al.*, 2016). Trace elements partitioning results to be controlled by several parameters like temperature and pressure (*e.g.*, Blundy & Wood, 2003; Sun & Liang, 2012; Mollo *et al.*, 2018), mineral composition (*e.g.*, Blundy & Wood, 1994; Mollo *et al.*, 2016), melt composition (*e.g.*, Bennett *et al.*, 2004, and reference therein), redox conditions (*e.g.*, Cartier *et al.*, 2014), and kinetic effects (*e.g.*, Arzilli *et al.*, 2018, and reference therein). Among these latter only few are relative to clinopyroxene (Shimizu, 1981; Lofgren *et al.*, 2006; Mollo *et al.*, 2013). In this work, trace element partition coefficients between clinopyroxene and K-basaltic melts

were investigated aiming to *i*) provide clinopyroxene-melt partition coefficient experimental data for primitive compositions in the CFVD area, *ii*) understand the role of the crystallization kinetics on trace elements partitioning behaviour relevant for deep magmatic reservoirs, and *iii*) model deep differentiation of primitive parental K-basaltic magmas of the CFVD.

CHOICE OF THE EXPERIMENTAL CONDITIONS

Pressure

The main pressure investigated in this work (0.8 GPa) is representative of the crustal-mantle boundary in the Phlegraean area (~25 km of depth; Di Stefano *et al.*, 2011). At that depth, the presence of a possible crystallization zone was hypothesized on the basis of the results of melt inclusion studies (*e.g.*, Moretti *et al.*, 2013), seismic data interpretations (Chiarabba *et al.*, 2008, and reference therein), gravimetric and petrological modelling (Fedi *et al.*, 2018) and experimental data (Perinelli *et al.*, 2019). Moreover, in this work pressures between 0.7 and 7 GPa are considered to investigate the mobility of the APR16 K-basaltic melt from the mantle region to the deep reservoir.

Temperature and water content

Temperature and water amount of the experimental runs of this work ($T = 1030\text{--}1250\text{ }^{\circ}\text{C}$ and $\text{H}_2\text{O}_i = 0\text{--}4\text{ wt.}\%$) have been chosen to have clinopyroxene as the only crystallized phase when possible (anhydrous conditions), otherwise as liquid phase in the presence of other mineral phases (hydrous conditions), based on the $T\text{--}\text{H}_2\text{O}_i$ content projections of Perinelli *et al.* (2019), where phase relations of the APR16 and APR16GL compositions (*i.e.*, the natural and glassy starting materials used in the experiments) are shown in Fig. 1. As shown in the $T\text{--}\text{H}_2\text{O}_i$ diagram of Perinelli *et al.* (2019), indeed, the liquidus temperature is at about $1300\text{ }^{\circ}\text{C}$ in the NWA (no water added) runs and below $1150\text{ }^{\circ}\text{C}$ for H_2O_i contents higher than 8 wt.%. In the NWA runs, clinopyroxene is the liquidus phase ($1270\text{--}1295\text{ }^{\circ}\text{C}$) followed by olivine and oxide (Cr-spinel) at $1250\text{ }^{\circ}\text{C}$ and by plagioclase at $1190\text{--}1235\text{ }^{\circ}\text{C}$. In the damp runs, *i.e.*, 1.5–3 wt.% H_2O_i , olivine begins to crystallize reaching a degree of crystallization ($\leq 15\text{ wt.}\%$) lower than that at NWA conditions ($\geq 20\text{ wt.}\%$). In the wet runs, *i.e.*, 4–6 wt.% H_2O_i , olivine joints clinopyroxene at $1150\text{ }^{\circ}\text{C}$ and it is replaced by orthopyroxene coexisting with oxide at $1100\text{ }^{\circ}\text{C}$. By lowering the temperature ($T = 1080\text{ }^{\circ}\text{C}$), amphibole becomes stable and the resulting mineral assemblage for temperatures down to $1000\text{ }^{\circ}\text{C}$ is composed by Cpx + Amph + Ox + Opx. Notably, in the hydrous runs at 1030 and $1080\text{ }^{\circ}\text{C}$ the predominant crystallization of Amph compared to that of Cpx allowed to estimate its growth rate. Differently, temperatures of the experimental runs are superliquidus temperatures ($1300\text{--}1350\text{ }^{\circ}\text{C}$ and $1300\text{--}2000\text{ }^{\circ}\text{C}$, respectively). As regards dissolution kinetics, they were necessary to avoid the occurrence of the crystallization process which would disturb the diffusion and dissolution processes (Chen & Zhang, 2009); as regards rheological properties, instead, they were necessary to perform falling-sphere viscosity measurement via ultrafast imaging (Kono *et al.*, 2014).

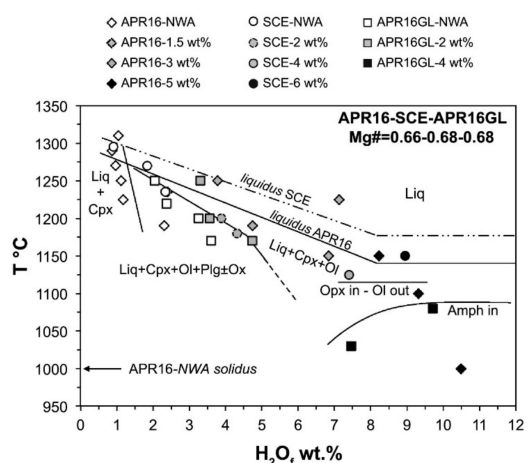


Fig. 1 - T vs. H_2O_i in melt phase diagram showing experimental saturation curves (dashed when estimated), phase assemblages and stability fields for APR16, APR16GL and SCE compositions. The diagram combines the results from NWA, damp and wet experiments of Perinelli *et al.* (2019). NWA solidus temperature of APR16 composition is from Bonechi *et al.* (2017). Liq: liquid; Cpx: clinopyroxene; Ol: olivine; Plg: plagioclase; Opx: orthopyroxene; Amph: amphibole. Error bars are smaller than symbol size. After Perinelli *et al.* (2019).

RESULTS AND DISCUSSION

In this work, the investigation of the kinetic and rheological properties of a primitive K-basaltic magma in the deep portion of the CFVD plumbing system allowed to improve the knowledge of the pre-eruptive magmatic processes and magma chamber dynamics, and to provide estimates of magma residence and ascent timescales.

Kinetics of crystals nucleation, growth and dissolution

As regards the kinetic properties at 0.8 GPa, 1170-1250 °C and $H_2O < 4$ wt.%, clinopyroxene growth rate results to be strongly affected by time, with average values that vary from 10^{-7} to 10^{-8} $cm \cdot s^{-1}$ from the shortest (0.25 h) to the longer-lasting (6-9 h) experiments (Fig. 2). The growth rates calculated in the run performed using natural starting material with pre-existing nuclei are higher than those calculated in the runs performed using the vitrified starting material, while the nucleation rates show the opposite behavior with lower values for the run containing pre-existing nuclei. These differences are due to the structural similarities between the pre-existing nuclei and the nucleating phases that concentrate the supply of chemical elements in the liquid surrounding the new growing crystals, limiting in this way the formation of new nucleation sites (Bonechi, 2020).

At 0.8 GPa, 1030-1080 °C and $H_2O > 4$ wt.%, the growth rate of amphibole, which is the dominant phase, decreases from $1.5 \cdot 10^{-7}$ to $2.9 \cdot 10^{-8}$ $cm \cdot s^{-1}$ with increasing time (from 0.25 to 9 h). Comparison between amphibole and clinopyroxene growth rates provides evidence for the faster growth of amphibole with respect to clinopyroxene, which is due to chemical and structural similarities between these minerals that cause a “kinetic competition” (Fig. 3). This “kinetic competition” and consequently the different growth rates observed for the coexisting clinopyroxene and amphibole, could be attributed to a different element diffusivity; however, further targeted experiments are needed to firmly support this assumption. This competition also explains why the growth rates of clinopyroxene calculated in the high water content runs ($H_2O_f > 4$ wt.%) turn out to be lower than those calculated in the low water content runs ($H_2O_f < 4$ wt.%). In fact, crystal growth rates should be higher in the presence of high amount of water given its depolymerizing effect on the melt. By the comparison with growth rate data available in the literature, viscosity, composition, undercooling and cooling rate are the factors that mostly affect crystal growth rate, while pressure appears to have no influence on it (Fig. 4). The experimental Cpx growth rate combined with data from CSD and thermobarometry of CFVD

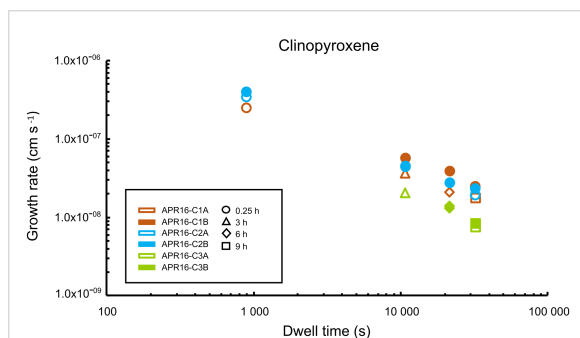


Fig. 2 - Relation between Cpx growth rate (G_L) and experimental duration (t). The duration of the runs is indicated with different symbols: circle for 0.25 h runs, triangle for 3 h runs, diamond for 6 h runs and square for 9 h runs. Series are indicated with different colours: red for APR16-C1, light blue for APR16-C2 and green for APR16-C3. Within each series, each subseries is indicated with full (runs at lower temperature) and empty (runs at higher temperature) symbols. Error bars are not shown since they are inside the symbols. After Bonechi *et al.* (2020a).

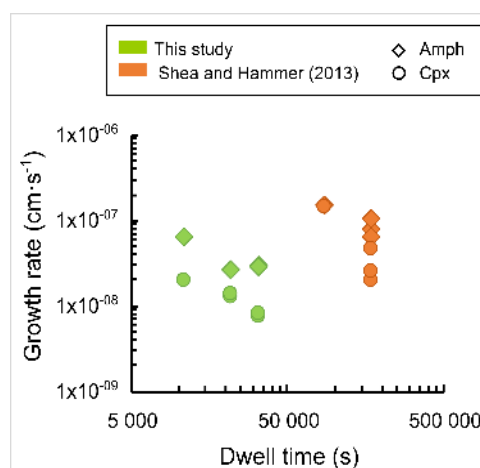


Fig. 3 - Clinopyroxene and amphibole growth rate vs. dwell time (s) diagram, showing the faster growth of amphibole (diamonds) relatively to coexisting clinopyroxene (circles). Literature data (orange symbols) from Shea & Hammer (2013) are in agreement with our observation. After Bonechi *et al.* (2020b).

clinopyroxenes suggests that recharge by primitive magmas in the deep CFVD reservoirs occurs with a relatively high ascent rate ($\sim 0.5 \cdot 10^{-4} \text{ m} \cdot \text{s}^{-1}$). The estimated recharge rate ($0.2\text{-}2 \text{ km}^3 \cdot \text{y}^{-1}$ in absence of pre-existing nuclei or $1\text{-}10 \text{ km}^3 \cdot \text{y}^{-1}$ in presence of pre-existing nuclei) suggests that a deep reservoir of primitive parental magma similar to those had feeding the Campanian Ignimbrite eruption (39 ka), could be formed in a time interval ranging from 104 to 105 years (absence of pre-existing nuclei) or 103 to 104 years (presence of pre-existing nuclei).

Moreover, in the dissolution-crystallization experiment, the formation of overgrowth rims and new cpx crystals with different textures and compositions suggests that injection of basaltic melts in a cold magma chamber may produce crystals with inverse or oscillatory zonation. This disequilibrium crystallization process is also related to the dissolution of pristine crystals resident in the magma reservoir. The growth rate ($1.35 \cdot 10^{-6} \text{ cm} \cdot \text{s}^{-1}$) extrapolated from this dissolution-crystallization experiment, confirms that chemical dynamic conditions favour an increase in the crystal growth rate. Finally, the application of the calculated experimental dissolution rates to products of Agnano-Monte Spina eruption (4100 BP, Campi Flegrei), results in maximum cpx dissolution time-scales of $\sim 40 \text{ h}$, and that the effect of crystal dissolution may be relevant to estimate magma residence times whether significant dissolution occurs during magma mixing processes. Indeed, if magma mixing is accompanied by crystal dissolution, then it is likely that most of retrieved residence times are potentially underestimated.

Rheological properties

Measured viscosities ($\sim 0.3\text{-}2 \text{ Pa} \cdot \text{s}$) along with modelled rock parameters (*e.g.*, permeability, porosity and mineral grain size) show that magmas underneath Campi Flegrei are characterized by a mobility ($0.3\text{-}3 \text{ g cm}^3 \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$) and a migration velocity ($3\text{-}32 \text{ m} \cdot \text{y}^{-1}$) higher than those of basalts from mid-ocean ridges. Moreover, despite the magma migration underneath a volcano is usually accompanied by geophysical precursors (*e.g.*, volcano-tectonic earthquakes, tremors, and deformations), these signals alone are not enough to forecast volcanic eruptions. In this context, the viscosity measured at the lowest pressure (0.7 GPa ; \sim the depth of deep reservoir), corrected for temperature, water and crystals contents, was used to estimate magma ascent rate and time from the deep reservoir ($\sim 25 \text{ km}$ depth) to the shallower reservoir located at $\sim 8 \text{ km}$ depth (path 1), and from the deep reservoir to the surface (path 2). For both paths, it has been estimated an ascent velocity of 36 and 33 m/s for dry and hydrous conditions, respectively. For the path 1, the magma ascent times are in the order of 7.9 min (dry) and 8.4 min (hydrous), while for the path 2, they are 11.7 min (dry) and 12.4 min (hydrous).

Partitioning of trace elements between crystals and melts

Partition coefficient data derived from synthetic clinopyroxenes in equilibrium and in disequilibrium with a primitive K-basaltic composition from the CFVD were provided since their usefulness in petrological and geochemical studies to better understand magmatic processes, like fractional or equilibrium crystallization, assimilation, and partial melting. The increase in DREE values with time observed in some runs of this work is not

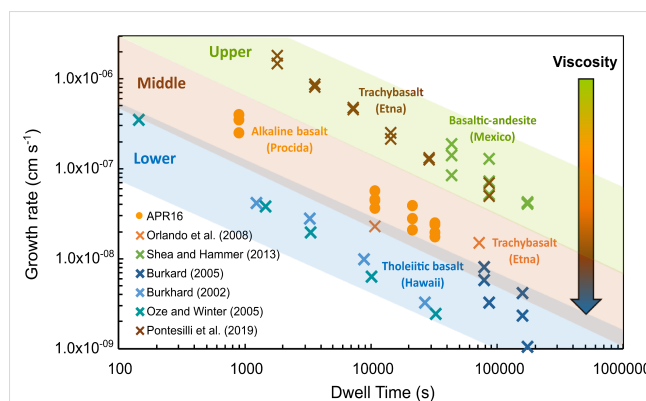


Fig. 4 - Relation between crystal growth rate and experimental duration for this and previous studies on clinopyroxenes. Literature experimental data are from Burkhard (2002; 2005), Oze & Winter (2005), Orlando *et al.* (2008), Shea & Hammer (2013) and Pontesilli *et al.* (2019). The coloured fields represent: the upper trend in green, the middle trend in dark orange and the lower trend in light blue. Coloured fields correspond to different viscosity values that tend to increase from the upper to the lower trend, as shown by the coloured arrow on the right. The runs of Pontesilli *et al.* (2019), which should fall in the middle trend based on viscosity, fall instead in the upper one due to the higher undercooling and cooling rate. After Bonechi *et al.* (2020a).

related to a change in time but rather to the different degrees of polymerization expressed as NBO/T ratio (Fig. 5). Indeed, since growth rates are fast at the beginning of the crystallization process and then decrease with increasing time, D_i values should decrease with increasing time. The low NBO/T ratio calculated in the run with longer duration (9 hours) is linked to its higher loss of Fe with respect to the other run at 3 and 6 hours, pointing out the strong influence of melt structure and thus of melt viscosity on the partitioning behaviour of trace elements between cpx and basaltic melt. Finally, the modelling of a fractional crystallization process of primitive parental K-basaltic magmas, performed by using the partition coefficients determined in this study, highlights that significant amounts of plagioclase crystallization (> 10 wt.%) do not fully mimic the composition of CFVD trachybasalts, which, on the other hand, results to be well reproduced by the fractionation of 15-26 wt.% of clinopyroxene +2-6 wt.% of olivine (Fig. 6).

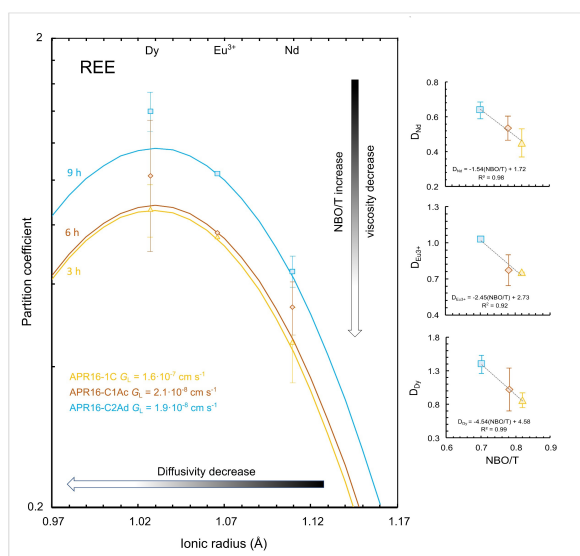


Fig. 5 - Plot of clinopyroxene-liquid partition coefficients for REEs vs. ionic radius (Å). The curves represent the fits of the lattice strain model to $C_{\text{cpx/L}}/D_i$ values while symbols represent measured $C_{\text{cpx/L}}/D_i$ values for Dy (HREE), Eu^{3+} (MREE) and Nd (LREE) in the APR16-C2Ad (1220 °C; in light blue), APR16-C1Ac (1250 °C; in orange) and APR16-1C (1225 °C; in yellow) runs. Horizontal arrow indicates the diffusivity decrease from LREEs to HREEs, while vertical arrow indicates NBO/T increase and viscosity decrease with decreasing time (from APR16-C2Ad to APR16-1C). On the right side of the figure are reported plots of partition coefficients for Dy, Eu^{3+} and Nd vs. NBO/T, in which it is possible to see the negative correlation between D values and NBO/T. After Bonechi *et al.* (2021).

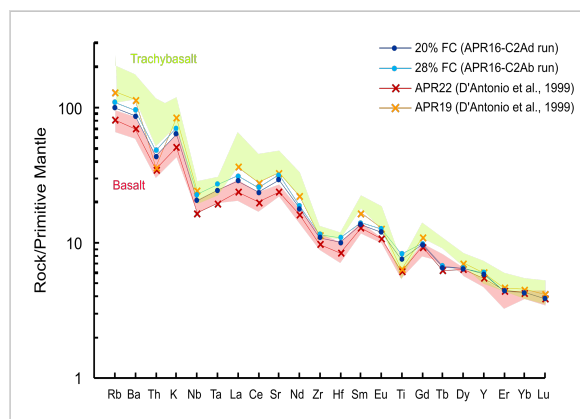


Fig. 6 - Primitive Mantle normalized (McDonough & Sun, 1995) trace elements patterns for primitive basaltic (APR22; D'Antonio *et al.*, 1999) and trachybasaltic (APR19; D'Antonio *et al.*, 1999) rocks, and the predicted composition of differentiated melts obtained after 20 and 28% of fractional crystallization of APR22 basalt assumed as primitive parental K-basaltic magma. The reported degrees of fractionation (FC) reflect the crystallized phase assemblage and proportions determined for runs APR16-C2Ad (Cpx(17)+Ol(3)) and AR16-C2Ab (Cpx(23)+Ol(4)+Plg(1)) that produced trachybasaltic residual glass. Normalized patterns for CFVD basalts and trachybasalts (D'Antonio *et al.*, 1999; Pappalardo *et al.*, 1999; De Astis *et al.*, 2004), indicated with red and green field, respectively, are shown for comparison. After Bonechi *et al.* (2021).

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