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Trace element partitioning between clinopyroxene and trachy-phonolitic melts: A case study from the Campanian Ignimbrite (Campi Flegrei, Italy)

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Abstract

The partitioning of trace elements between crystals and melts provides an important petrogenetic tool for understanding magmatic processes. We present trace element partition coefficients measured between clinopyroxene phenocrysts and trachy-phonolitic magmas at the Campi Flegrei (Italy), whose late Quaternary volcanism has been characterized by two major caldera-forming events (Campanian Ignimbrite at ~39 ka, and the Neapolitan Yellow Tuff at ~15 ka). Our data indicate that the increase of trivalent rare earth elements and yttrium into the crystal lattice M2 site is facilitated by the charge-balancing substitution of Si\(^{4+}\) with Al\(^{3+}\) on the tetrahedral site. Higher concentrations of tetravalent and pentavalent high field strength elements on the M1 site are also measured when the average charge on this site is increased by the substitution of divalent cations by Al\(^{vi}\). In contrast, due to these charge balance requirements, divalent transitional elements become less compatible within the crystal lattice. On the basis of the lattice strain theory, we document that the incorporation of rare earth elements and yttrium in clinopyroxene is influenced by both compositional and physical parameters. Data from this study allow to update existing partitioning equations for rare earth elements in order to construct a self-consistent model for trachy-phonolitic magmas based on the lattice strain theory. The application of this model to natural products from the Campanian Ignimbrite, the largest caldera-forming eruption at the Campi Flegrei, reveals that the complex rare earth element pattern recorded by the eruptive products can be successfully described by the stepwise fractional crystallization of clinopyroxene and feldspar where the clinopyroxene-melt partition coefficient changes progressively as a function of the physicochemical conditions of the system.

Keywords: clinopyroxene-melt trace element partitioning; lattice strain theory; trachy-phonolitic magmas; Campi Flegrei.
**Introduction**

Clinopyroxene is one of the most important constituents of igneous rocks and its crystallization behaviour impacts significantly the composition of magmas. The partitioning of trace elements between clinopyroxene and melt is frequently used in petrological and geochemical studies to better understand magma differentiation processes, such as fractional or equilibrium crystallization, assimilation, and partial melting. For simplicity, the clinopyroxene-melt partition coefficient \[ D_i = \frac{x_i(I)}{x_i(melt)} \] on a weight basis] is generally assumed to be constant for magma modelling. However, this simple approximation does not take into account for the effects of crystal and melt compositions, as well as the physical conditions of the system on trace element partitioning. Wood and Blundy (1997) showed for the first time that partition coefficients of rare earth elements (REE) can be modelled as a function of composition of the crystal \( X_{Mg}^{M1} \), Mg-number of the melt \( Mg^{melt} \), pressure \( P \) and temperature \( T \). Crystal chemistry influences both the dimensions of the M2 site, into which REE partition, and the molar fraction of the hypothetical REE end-member, such as REEMgAlSiO$_6$. Blundy et al. (1998) and Bennett et al. (2004) also argued that \( D_{\text{REE}} \) is dependent on \( X_{Na}^{M2} \) due to the higher incorporation of Na$^+$ in M2 with increasing \( P \), for example via the hypothetic end-member Na$_{0.5}$REE$_{0.5}$MgSi$_2$O$_6$. Furthermore, Hill et al. (2000), Wood and Trigila (2001) and Wood and Blundy (2001) documented a close relationship between REE partitioning and the concentration of tetrahedrally-coordinated aluminum in clinopyroxene, as required for charge balance. Sun and Liang (2012) derived a predictive model in which \( D_{\text{REE}} \) is positively correlated with \( X_{Al}^{iv} \) and \( X_{Mg}^{M2} \), and negatively correlated with \( T \) and H$_2$O dissolved in the melt. Gaetani et al. (2003) attributed the decrease of \( D_{\text{REE}} \) with increasing H$_2$O to the depolymerizing effect of water on the melt structure. Moreover, complementary studies of Gaetani (2004) and Huang et al. (2006) pointed out that the melt structure becomes dominantly important
below a threshold value of the number of non-bridging oxygens per tetrahedral cations ($NBO/T$) corresponding to 0.4. As a whole, results from previous works highlight that the partitioning of trace elements between clinopyroxene and melt is governed by complex mechanisms whose effects and magnitudes on $D_i$ depend on specific compositional and physical parameters that are still poorly understood for a significant number of natural cases.

In this study, we present a new set of apparent partition coefficients calculated for clinopyroxene phenocrysts in equilibrium with trachytic and phonolitic compositions from the Campi Flegrei (Italy). Despite the highly explosive nature of these magmas and their common involvement in hazardous volcanic settings, little attention has been given to the most important parameters that influence the partitioning of trace elements (however, see Pappalardo et al., 2008; Fedele et al., 2009). On the basis of the lattice strain theory derived by Blundy and Wood (1994), it has been determined to what extent the physicochemical conditions of the system may influence the partitioning of trace elements. Through an improved version of the predictive equations of Wood and Blundy (1997), we have also modelled the complex trace element compositions of several rock samples from the Campanian Ignimbrite, one of the largest late Quaternary volcanic eruptions in Europe.

**Geological background**

The Campi Flegrei, located within the Campanian Plain, belong to the potassic alkaline volcanic province of central Italy. Volcanism is still active, as demonstrated by fumarolic and seismic activity, and by recurrent episodes of unrest in the past 30 years (Orsi et al., 1999 and references therein). The highly explosive behaviour of magmas represents a continuous threat to more than one million people living in the city of Naples and its densely inhabited suburbs. This makes the Campi Flegrei one of the most dangerous volcanic systems in the world.
The caldera is a resurgent nested structure formed during two major collapses related to the eruptions of the Campanian Ignimbrite (CI) and the Neapolitan Yellow Tuff (NYT). Seismic reflections indicate the presence of a discontinuity at 7.5 km depth, where seismic velocities are consistent with values expected for a magma body set in a densely fractured volume of rock (Zollo et al., 2008). Petrological and melt inclusion studies suggest that differentiated alkaline melts formed dominantly through fractional crystallization from a more mafic parental magma, likely emplaced at depths between 4 and 8 km, with little assimilation of surrounding crust (Signorelli et al., 2001; Webster et al., 2003; Marianelli et al., 2006; Pabst et al., 2008; D’Antonio, 2011).

The Campanian Ignimbrite eruption (~39 ka; De Vivo et al., 2001) is regarded as the dominant event in the history of the Campi Flegrei with an initial areal distribution of ~30,000 km² (Rolandi et al., 2003). It consists of ~200 km³ of pyroclastic-fall and pyroclastic-flow deposits (Civetta et al., 1997). The composition of the erupted products changed from trachyte to phonolite during the eruption. Phase equilibria data, geothermometry, and fluid inclusion analysis, suggest an overall thermal path of the magma from 840 to 1,080 °C (Fulignati et al., 2004; Marianelli et al., 2006; Fowler et al., 2007; Fedele et al., 2009; Masotta et al., 2013). Melt inclusion measurements and hygrometric predictions indicate a melt-water concentration ranging from 3 to 6 wt.% (Signorelli et al., 2001; Webster et al., 2003; Marianelli et al., 2006; Mollo et al., 2014). On the basis of these heterogeneous petrological information, it has been proposed that the CI magma evolved in a thermally and chemically zoned magmatic reservoir (Pappalardo et al., 2008; Pappalardo and Mastrolorenzo, 2012).

The Neapolitan Yellow Tuff eruption (~15 ka; Deino et al., 2004) was the second more recent phreatoplinian event in the history of the Campi Flegrei. It erupted ~40 km³ of pyroclastic-fall and pyroclastic-flow deposits dispersed over an area of more than ~1,000 km² (Orsi et al. 1992). The erupted products are characterized by latitic to trachytic compositions. The vent for the NYT eruption was located inside the caldera formed during collapse of the CI eruption, resulting in a final caldera that covered an area of ~90 km² (Orsi et al., 2009).
**Analytical methods**

Field emission gun scanning electron microscope (FE-SEM) images and electron probe microanalyses (EPMA) of twelve clinopyroxenes were collected at the HPHT Laboratory of Experimental Volcanology and Geophysics of the Istituto Nazionale di Geofisica e Vulcanologia (INGV) in Rome, Italy. Images were obtained through the backscattered electron (BSE) mode of a JEOL 6500F FE-SEM equipped with an energy-dispersive spectrometer (EDS) detector. Microprobe analyses were performed with a JEOL-JXA8200 EPMA equipped with five spectrometers. The beam diameter was ~1 μm with a counting time of 20 and 10 s on peaks and background respectively. The following standards were used: jadeite (Si and Na), corundum (Al), forsterite (Mg), andradite (Fe), rutile (Ti), orthoclase (K), barite (Ba), apatite (P), spessartine (Mn) and chromite (Cr). Sodium and potassium were analyzed first to prevent alkali migration effects. The precision of the microprobe was measured through the analysis of well-characterized synthetic oxides and minerals. Data quality was ensured by analyzing standard materials as unknowns. Based on counting statistics, analytical precision was better than 5% for all cations.

Major and trace elements of whole-rocks, and trace elements of clinopyroxene phenocrysts were measured at the Institute of Geochemistry and Petrology of the ETH Zürich, Switzerland. For the whole-rock analyses 1.5 g of powdered sample was heated to 950 °C for 2 h in a chamber furnace and then weighed to determine the loss on ignition (LOI). The ignited material was charged in a Pt-Au crucible and fused with a 1:5 Lithium-Tetraborate mixture using a Claissé M4® fluxer. The fused disk was analysed for major elements using a wave-length dispersive X-ray fluorescence spectrometer (WD-XRF; Axios PANanalytical) equipped with five diffraction crystals. Calibration was based on thirty certified international standards of predominantly igneous and metamorphic rocks. Trace element analyses of both whole-rock disks and clinopyroxene phenocrysts were performed through a 193 nm excimer laser coupled with a second generation two-volume constant
geometry ablation cell (Resonetics:S-155LR) and a high-sensitivity, sector-field inductively-coupled plasma mass spectrometer (ICP-MS; Thermo:Element XR). Points with a spot size of 45 μm were set on chemically homogeneous portions of the material (i.e., clinopyroxene cores) previously analyzed by EPMA, and ablated with a pulse rate of 10 Hz and an energy density of 3.5 J/cm³ for 40 sec. The isotopes were analyzed relative to an internal standard of known composition (i.e., NIST612). A second standard (i.e., GSD-1G) was used as an unknown to check the quality of data during each analytical run. ⁴³Ca or ²⁹Si were used as internal standards for clinopyroxene and whole-rock analyses, respectively, in order to recover the concentrations of light and heavy rare earth elements (REE divided in LREE and HREE), high field strength elements (HFSE), large ion lithophile elements (LILE) and transition elements (TE). The precision of individual analyses varied depending upon a number of factors, e.g., the element and isotope analyzed as well as the homogeneity of the ablated material. However, the 1 sigma errors calculated from variations in replicate analyses of crystals and whole-rock disks were invariably several times larger than the fully integrated 1 sigma errors determined from counting statistics alone.

Sample description

Sampled rocks belong to twelve pyroclastic deposits at the Campi Flegrei characterized by variable proportions of juvenile material (i.e., pumices, scoriae, spatter clasts, fiamme and obsidians), variably porphyritic textures (10-25 vol.% of phenocrysts), and the ubiquitous occurrence of clinopyroxene, biotite, K-feldspar, plagioclase, opaques, and rare apatite. Samples were collected from different outcrops in order to fully characterize the compositions of clinopyroxene phenocrysts and host magmas of pre-CI, CI, post-CI, NYT, and post-NYT eruptions (see Table 1S for the locations). Major and trace element concentrations measured for crystals and melts are reported in Tables 1S and 2S, respectively. We present our data in comparison with those of Pappalardo et al. (2008) and Fedele et al. (2009) that provided a complete dataset comprising whole-rock analyses,
Clinopyroxene chemistries, apparent partition coefficients for REE, and lattice strain parameters (see below) of four additional rock samples from the Campanian Ignimbrite eruption.

Whole-rock analyses show increasing SiO$_2$ contents (57-62 wt.%) with decreasing CaO (1.8-5.3 wt.%) and $Mg^{#\text{melt}}$ (16-40). All compositions are also rich in alkali ($Na_2O+K_2O = 11-14$ wt.%). In the TAS (total alkali vs. silica; Le Bas et al., 1986) diagram, samples are classified as trachytes and phonolites, in agreement with most of the differentiated alkaline products at Campi Flegrei (Fig. 1a). Whole-rocks exhibit a variable degree of differentiation that, in terms of trace element concentrations, reproduces well the evolutionary behaviour of magmas (Fig. 1b). The increase of REE is commonly associated with a significant increase in Th, U, Nb, Ta, Zr and Hf, and decrease in Sr testifying to an increased plagioclase fractionation (Table 2S).

Clinopyroxenes occur as euhedral phenocrysts (longest size dimensions > 0.3 mm) with diopsidic compositions (Morimoto, 1988). $Al^{iv}$ (0.05-0.13 apfu) is positively correlated with $Ti^{+4}$ (0.01-0.04 apfu) and negatively correlated with $Mg^{#\text{px}}$ (0.73-0.84). The ratio of octahedrally-coordinated to tetrahedrally-coordinated aluminium cations is less than 1 in all phenocrysts, indicating preferential incorporation of $Al^{iv}$ at low pressure crystallization conditions (Muñoz and Sagredo, 1974; Putirka, 1996; Mollo et al., 2011b). The ratio of $Fe^{3+}/Fe^{2+}$ in clinopyroxenes, as calculated from stoichiometry, ranges between 0 and 0.5 with values identical to those experimentally-derived for magmas at Campi Flegrei equilibrated at NNO+1 and NNO+2 oxygen fugacity (Fabbrizio and Carroll, 2008; Masotta et al., 2013). Diopside vs. hedenbergite (Fig. 1c) and Ce vs. Y (Fig. 1d) diagrams suggest that major and trace elements of our clinopyroxenes capture most of the geochemical evolution of phenocrysts at Campi Flegrei.

Apparent trace element partition coefficients were measured for pre-CI, CI, post-CI, NYT, and post-NYT samples using clinopyroxene core and whole-rock analyses that were found to be in equilibrium (see below) and are reported in Table 3S. The most important changes of $D_i$ can be summarized as follows: (i) LREE (e.g., $D_{La} \leq 0.27$) are more incompatible than HREE (e.g., $D_{Dy} \leq 1.67$); (ii) TE are always compatible within clinopyroxene (e.g., $D_{Co} \leq 10.07$); (iii) pentavalent
HFSE cations are more incompatible ($D_{\text{Nb}}$ and $D_{\text{Ta}} \leq 0.05$) that tetravalent HFSE cations ($D_{\text{Zr}}$ and $D_{\text{Hf}} \leq 0.87$) and; (iv) LILE are generally incompatible (e.g., $D_{\text{Sr}} \leq 0.8$) with the exception of one sample ($D_{\text{Sr}} = 1.39$ for PM2).

Assessment of equilibrium crystallization conditions

Laboratory investigations of clinopyroxene-melt partition coefficients are generally designed to guarantee the achievement of equilibrium between crystals and melts. The initial rate of cooling and the time duration of experiments are set to ensure that the melt supplies nutrients at equilibrium proportions to the growing crystals. The experimental charges are then quenched at very fast cooling rates and the system is almost instantaneously “frozen-in” (e.g., quenching rate of 2,000 °C/min; Freda et al., 2008). Due to the use of rapid quenching conditions, disequilibrium processes may only operate at the nanometre scale, leading to the formation of a diffusive boundary layer with thickness orders of magnitude lower that the analytical spot size used for major and trace element measurements (e.g., Mollo et al., 2012). On the other hand, apparent partition coefficients obtained from natural samples measuring the compositional ratios between bulk phenocrysts and host lavas (i.e., whole-rock analyses) are potentially biased by contamination or disequilibrium processes. Even when single point analyses are carried out at the crystal-melt interface, the compositional zoning of minerals and surrounding glasses can make the accurate determination of $D_i$ extremely difficult. The entrapment of melt in rapidly growing crystals may increase the value of $D_i$ by up to 3 orders of magnitude (Kennedy et al., 1993). Additionally, rapid crystal growth conditions are not necessary accompanied by detectable melt entrapments or crystal discontinuities and, under such circumstances, disequilibrium values of $D_i$ can exhibit variations in the same order of magnitude of equilibrium data (Mollo et al., 2013a).

For the purpose of this study, we have accurately inspected each phenocryst and coexisting glass using SEM and EPMA, in order to make sure that the occurrence of melt inclusions, crystal
zoning and/or melt diffusion phenomena were kept to a minimum. Clinopyroxenes are generally euhebral with well-defined edges and without evident zoning patterns (Fig. 2a). However, microprobe compositional profiles reveal the occurrence of chemical heterogeneities at the crystal-melt interface (Fig. 2b and Table 5S). A diffusive boundary layer occurs into the glass next to clinopyroxene surface. This thin diffusive boundary layer is enriched in chemical species less compatible in clinopyroxene crystal lattice (e.g., Al and Na). Concentration–dependent partitioning produces crystal growth layers that respond to the chemical gradients in the melt, producing Al and Na enrichments in clinopyroxene that are identical to those experimentally documented by cooling rate studies (Lofgren et al., 2006; Mollo et al., 2013b). Compositional perturbations at the crystal rim also suggest that, at the closure temperature of the crystal growth (i.e., $T_{\text{final}} \ll T_{\text{liquidus}}$), the free energy difference between the crystal surface and the liquid was large enough that diffusion became the rate-controlling process (Watson and Muller, 2009). Due to the high explosivity of eruptions at Campi Flegrei, phenocrysts underwent typically high degrees of undercooling during magma ascent in the volcanic conduit and eruption to the surface (Pappalardo and Mastrolorenzo, 2012 and references therein). Mollo et al. (2013b) proposed an equilibrium model based on the difference ($\Delta$) between diopside+hedenbergite (DiHd) components predicted for clinopyroxene via regression analyses of clinopyroxene-liquid pairs in equilibrium conditions, with those measured in the analyzed phenocrysts. Mollo and Masotta (2014) successfully tested this model on trachytic and phonolitic compositions obtained at both equilibrium and disequilibrium conditions. Calculations performed using clinopyroxene rim and coexisting melt compositions yield values of 0.11-0.16 (Fig. 2b) that are considerably higher than those measured at near-equilibrium conditions ($\Delta$DiHd $\leq$ 0.02). This suggests that $D_i$ values measured at the crystal-melt interface results from disequilibrium partitioning due to the effect of rapid magma decompression and degassing at the time of eruption (e.g., Lanzafame et al., 2013; Mollo et al., 2015a). On the other hand, it is reasonable to infer that, over the timescale of magma chamber evolution and in absence of perturbation phenomena (e.g., magma mixing), early-formed clinopyroxene phenocrysts may have crystallized in equilibrium with
the host magma, despite the occasional occurrence of chemical heterogeneities or melt inclusions in crystal that tend to reduce the accuracy of $D_i$ calculations. In light of this, apparent trace element partition coefficients have been calculated by the analyses of bulk phenocrysts and whole-rock compositions (e.g., Schnetzler and Philpotts 1970; Nagasawa and Schnetzler 1971; Nagasawa 1973; Mahood and Hildreth 1983; Lemarchand et al. 1987; Villemant 1988).

Experiments and thermodynamic studies have clearly documented that clinopyroxene is the liquidus phase of trachytic and phonolitic melts (Fowler et al., 2007; Fabbrizio and Carroll, 2008; Masotta et al., 2013, Del Bello et al., 2014). Under such circumstances, near-liquidus crystals are represented by early-formed cores of large phenocrysts that likely equilibrated with the host magma (i.e., whole-rock analysis) in terms of major and trace element concentrations (see for example the studies of Armienti et al., 2007; Masotta et al., 2010; Mollo et al., 2011a; Lanzafame et al., 2013; Scarlato et al., 2014). In this respect, Fig. 2b shows the development of an almost homogeneous plateau composition at the clinopyroxene core that suggests near-equilibrium crystallization and excludes chemical perturbations in the original magma. Tests conducted with the model of Mollo et al. (2013b) yield $\Delta D_i$ values between 0 and 0.02 testifying to equilibrium or near-equilibrium conditions between phenocryst core and whole-rock data that were therefore used for our $D_i$ calculations (see also $\Delta D_i$ values reported in Table 1S).

As stated above, the differentiation of magmas mostly occurs at shallow crustal levels (100-300 MPa) where the effect of pressure on near-liquidus clinopyroxene-melt partition coefficients is expected to be minimal. Thermodynamic data derived by the lattice strain model indicate that the influence of $P$ on $D_i$ can be considered negligible at pressures lower than 500 MPa (Blundy and Wood, 2003). It could be argued that REE partitioning is also sensitive to sodium in clinopyroxene, which in turn varies with pressure (Blundy et al., 1995; Bennett et al., 2004). However, the control of $Na^+$ on $D_{REE}$ is dominant only at mantle pressures ($\geq 3$ GPa) where sodium concentration ($Na_2O = 2.2$-$13.5$ wt.%; data from Klemme et al., 2002; Bennett et al., 2004; Marks et al., 2004) is one to two order of magnitude higher than that measured in our phenocrysts ($Na_2O = 0.15$-$0.56$ wt.%);
Table 1S). Therefore, in terms of physical parameters, temperature is likely the most important variable that can influence $D_i$ at the crystallization conditions of magmas. To estimate the equilibration temperatures and pressures of clinopyroxene-melt pairs from this study (Table 1S), we have used the thermometers and barometers of Masotta et al. (2013) specifically calibrated for trachytic and phonolitic compositions. A melt-water content of 3 wt.% has been set in the model, in agreement with most of the water concentrations measured by melt inclusion studies on Campi Flegrei (Signorelli et al., 2001; Webster et al., 2003; Marianelli et al., 2006). We have established that a water change of ±2 wt.% produces temperature and pressures variations of only ±12 °C and ±15 MPa, which are well below the errors of estimate of the thermometer (±24 °C) and barometer (±114 MPa). Results from calculations indicate that our clinopyroxenes crystallized at temperatures and pressures of 840-1,020 °C and 85-309 MPa (Table 1S), in close correspondence with those (840-1,080 °C and 20-300 MPa) derived for trachy-phonolitic products belonging to the Campanian Ignimbrite eruption (Fedele et al., 2009; Masotta et al., 2013).

**Discussion**

Trace element partition coefficients

The dependence of trace element partition coefficient on tetrahedrally-coordinated aluminium has been the focus of many studies on clinopyroxene (Lindstrom 1976; Ray et al. 1983; Hart and Dunn 1993; Forsythe et al. 1994; Lundstrom et al. 1994, 1998; Skulski et al. 1994; Blundy et al. 1998; Hill et al. 2000; Wood and Trigila 2001; Sun and Liang, 2012; 2013; Mollo et al., 2013a; Yao et al., 2013; Scarlato et al., 2014). In Fig. 3, the close correspondence between $D_i$ and $\text{Al}^{IV}$ for representative HFSE, REE and TE, is confirmed and extended to trachytic and phonolitic magmas. Note that the gray fields in Fig. 3 indicate that our $D_i$ values are consistent with those previously calculated for magmas at Campi Flegrei (data from Pappalardo et al., 2008 and Fedele et al., 2009).
From a crystallochemical point of view, HFSE enter the smaller M1 octahedral site, and the
correlation between $D_{\text{HFSE}}$ and Al reflects the increasing charge on this site with increasing
CaAl$_2$SiO$_6$ and CaFeAlSiO$_6$ substitution, i.e., with increasing replacement of Mg$^{2+}$ by Fe$^{3+}$ and Al$^{3+}$
(Wood and Trigila, 2001). Thus, entry of +4 and +5 ions into M1 is enabled by the substitution of
Al$^{3+}$ for Si$^{4+}$ in the tetrahedral site (Hill et al., 2000; Mollo et al., 2013a). In the case of trivalent
trace elements, REE and Y enter the large M2 site that, apart from minor amounts of Na$^+$, is almost
exclusively occupied by Ca$^{2+}$, Mg$^{2+}$, and Fe$^{2+}$. Data plotted in Fig. 3 show a clear positive
correlation between $D_{\text{La}}$ and Al$^{iv}$ that has been extensively documented under both equilibrium and
disequilibrium crystal growth conditions (Gaetani and Grove, 1995; Blundy et al., 1998; Mollo et
al., 2013a; Scarlato et al., 2014). The dependence of REE partitioning on tetrahedral aluminium
reflects an increased ease of locally balancing the excess charge at M2 as the number of
surrounding Al$^{iv}$ atoms increases. For example, the concentration of La in our clinopyroxenes
progressively increases from 8 to 46 ppm as the molar Al/Si ratio decreases from 0.11 to 0.05
(Tables 1S and 2S). This matches with the consideration that clinopyroxenes can accommodate
REE simply by adjusting their Al/Si ratios, without producing an energetically unfavourable
vacancy (Hill et al., 2000; Wood and Trigila, 2001). The importance of site charge for achieving
local charge balance is provided by the different behaviour of Sr and Co as divalent cations entering
M2 and M1 sites, respectively. Since charge on the M2 site is the same in both CaMgSiO$_2$ and
CaAl$_2$SiO$_6$, no correlation is found between $D_{\text{Sr}}$ and tetrahedrally-coordinated aluminum (cf. Hill et
al., 2000). In contrast, the M1 site requires an increased net charge (2+ to 3+) to balance the
increase in Al substitution for Si (cf. Mollo et al., 2013a), such that Co becomes less compatible as
CaAl$_2$SiO$_6$ content increases (Fig. 3).

The lattice strain model
Fig. 4 shows that our apparent partition coefficients for REE and Y lie on parabola-like curves of Onuma diagrams (Onuma et al., 1968), resembling the regular trajectories found by Pappalardo et al. (2008) and Fedele et al. (2009) for magmas at Campi Flegrei. The height of the parabola depends on the crystal composition (Matsui et al., 1977; Blundy and Wood, 1994; 2003) and the physical conditions of the system (Blundy and Wood, 2001; Sun and Liang, 2012). Blundy and Wood (1994) provided a quantitative model for the parabolic trend of an isovalent series of cations with radius, $r_i$, entering crystal lattice site M, where the partition coefficient, $D_i$, can be described in terms of (i) the radius of the site, $r_0$, (ii) the elastic response of that site, $E$ (as measured by Young’s Modulus), to lattice strain caused by cations that are larger or smaller than $r_0$, and (iii) the strain-free partition coefficient, $D_0$, for a (fictive) cation with radius $r_0$:

$$D_i = D_0 \exp \left( \frac{-4\pi EN_A \left( \frac{r_0}{2} (r_i - r_0)^2 + \frac{1}{3} (r_i - r_0)^3 \right)}{RT} \right)$$

(1)

In Eqn. (1), $N_A$ is Avogadro’s number ($6.022 \times 10^{23}$ mol$^{-1}$), $R$ is the universal gas constant (8.3145 J mol$^{-1}$ K$^{-1}$), and $T$ is the temperature (in Kelvin). The effective use of the lattice strain model requires partition coefficients for a large range of isovalent cations of appropriate ionic radii for substitution into the M site. Therefore, to obtain reliable estimates and minimize the standard error, we focused on $r_0$, $D_0$, and $E$ for the partitioning of trivalent REE and Y cations (Table 3S), as they form the largest group of isovalent elements in our analytical dataset. Except for one sample with $D_0^{3+} \approx 1$, we observe that, as a general rule, the peak position of our partitioning parabolas corresponds to $D_0^{3+} \geq 1$ when $\text{Al}^{iv} \geq 0.09$ apfu and $T \leq 950 \,^\circ C$ (Tables 1S and 3S and Fig. 4). Otherwise, the peak position can be alternatively higher or lower than 1 as a function of $\text{Al}^{iv}$ and $T$, in agreement with the observation that these parameters have opposing effects on trace element partitioning (cf. Sun and Liang, 2012). Fitting of the parabolic trends indicates a good agreement between modelled and
measured values of $D_0^{3+}$ (Table 4S and Fig. 4), suggesting the attainment of a thermodynamic
equilibrium between phenocrysts and host magmas.

At first, $D_0^{3+}$ and $D_{REE}$ were taken to be independent of the Al$^{iv}$ content in clinopyroxene
due to assumed complete short-range order between REE on M2 site and Al in T site in the
molecule REEMgAlSiO$_6$ (e.g., Wood and Blundy, 1997). Subsequently, this assumption has since
been found to be an oversimplification (Wood and Trigila, 2001; Hill et al., 2000; Tuff and Gibson,
2007, Mollo et al., 2013a; Scarlato et al., 2014), probably due to more complex charge-balance
mechanisms than simple short-range order (Wood & Blundy, 2001). In Fig. 5, lattice strain-free
partition coefficients for clinopyroxenes in trachy-phonolitic melts are compared with those
obtained by previous studies on ultramafic, mafic and silicic compositions. $D_0^{3+}$ increases
significantly with increasing tetrahedral aluminium, providing clear evidence of the effect of crystal
composition on REE and Y partitioning. Importantly, three different trends are depicted in Fig. 5 for
different bulk melt chemistries. The value of $D_0^{3+}$ and the slope of each single trend increase as a
function of the melt composition (i.e., SiO$_2$), suggesting that the control of Al$^{iv}$ on $D_0^{3+}$ is mediated
by the increasing silicic character of the bulk melt (Fig. 5). Gaetani (2004) observed that the
magnitude of the partition coefficient correlates with the degree of melt polymerization due to a
melt structural influence on trace element partitioning. The complementary results from Gaetani
(2004) and Huang et al. (2006) noted that melt structure affects the trace element compatibility only
if $[NBO/T]^{melt} < 0.4$. This is confirmed by our data showing a somewhat higher $D_0^{3+}$ for a lower
$[NBO/T]^{melt}$ (Fig. 6a), although this parameter may not provide a comprehensive description of melt
structure at a level relevant to trace element partitioning (e.g., Bennett et al., 2004). On this basis,
Huang et al. (2006) found that $D_0^{3+}$ is better correlated with the ratio of molar $[Ca^{2+}/(M^+M^{2+})]^{melt}$,
where $M^+$ and $M^{2+}$ are, respectively, Na$^+$ and K$^+$, and Fe$^{2+}$, Ca$^{2+}$ and Mg$^{2+}$ of the melt given as
percentages. Because of the similarity in ionic radius (and charge), REE$^{3+}$ are more likely to
substitute for Ca$^{2+}$ in the melt than Mg$^{2+}$, Fe$^{2+}$, or alkalis, so that the value of $D_{REE}$ decreases
according to the following exchange reaction (Huang et al., 2006):
Our data show that, for higher values of \( \frac{[Ca^{2+}/(M^{+}+M^{2+})]}{\text{melt}} \), there is an effective increase in the number of large structural sites critically important to accommodating large trace element cations in the melt, serving to reduce the partition coefficient (Fig. 6b). However, due to simultaneous effects of crystal and melt compositions on REE and Y partitioning, data in Fig. 6b do not align on a single linear fit for the substitution reaction described by Eqn. (2). To eliminate such an effect, some experiments should be designed for the comparison between clinopyroxenes with similar crystal-chemical formulas and compositionally distinct host melts (cf. Huang et al. 2006).

Testing the model of Wood and Blundy (1997)

Most of the mathematical expressions used to model the evolutionary behaviour of magma assume that the value of \( D_i \) remains constant throughout the entire differentiation process. This raises issues for petrological and geochemical modelling to (i) adopt the best possible partition coefficients, (ii) evaluate the extent to which these partition coefficients vary in the course of magma differentiation, (iii) find the physicochemical parameters that closely describe the variance of \( D_i \), and (iv) derive a good predictive model that is easy and rapid to use (e.g., based on microprobe analyses). In order to address all these issues, an increasing number of predictive equations for \( D_i \) have been derived in the last decades on the basis of thermodynamic approaches (e.g., Wood and Blundy, 1997, 2011; Hill et al., 2011), linear least squares regression analyses (e.g., Forsythe et al., 1994; Skulski et al., 1994; Gaetani and Grove, 1995) and multivariable nonlinear least squares analyses (Yao et al., 2012; Sun and Liang, 2012, 2013; Dygert et al., 2014). Among the number of equations found in literature, we have primary used the whole dataset for partition coefficients of Campi Flegrei (i.e., \( D_{\text{REE}} \) from this study, Pappalardo et al., 2008, and Fedele et al., 2009) to test the early predictive
model of Wood and Blundy (1997). The authors modelled the clinopyroxene–melt REE partitioning using the theoretical strain-free partition coefficient for 3+ cations in M2, which they then parameterised as a function of $P$ and $T$. By fitting experimental data to the temperature ($T$ in Kelvin) and pressure ($P$ in GPa) derivatives of the bulk and shear moduli of diopside, Wood and Blundy (1997) found a simple equation for calculating the Young’s Modulus for the trace elements of +3 charge in the M2 site of clinopyroxene:

$$E_{M2}^{3+} = 318.6 + 6.9P - 0.036T$$  \hspace{1cm} (3)$$

Given the expression (3) for $E_{M2}^{3+}$, the change of $r_0$ was also modelled through stepwise linear regression of the values of $r_0$ derived from literature data against all major compositional parameters, pressure and temperature. It emerged that only $X_{Al}^{iv}$ and $X_{Ca}^{M2}$ were important controlling factors for $r_0$:

$$r_0 = 0.974 + 0.067X_{Ca}^{M2} - 0.051X_{Al}^{M1}$$  \hspace{1cm} (4)$$

To calculate $D_0^{3+}$, a simple ionic equilibrium involving melt and clinopyroxene was considered:

$$\text{REE}_\text{melt} MgAlSiO_6 = \text{REE}_\text{cpx} MgAlSiO_6$$  \hspace{1cm} (5)$$

The equilibrium constant of the exchange reaction (5) is:

$$K_{ex}^{3+} = \frac{X_{REE}^{M2} X_{Mg}^{M1} X_{Al}^{T} X_{Si}^{T}}{X_{REE}^{melt} X_{Mg}^{melt} X_{Al}^{melt} X_{Si}^{melt}}$$  \hspace{1cm} (6)$$
In a thermodynamic approach based on the lattice strain theory, \( X_{Mg}^{M1} \) and \( Mg^{#}^{melt} \) are the expression of the activity compositions of clinopyroxene (\( a_{REEMgAISiO}^{Ox} = X_{REE}^{M2}X_{Mg}^{M1} \)) and melt (\( a_{REEMgAISiO}^{melt} = X_{REE}^{melt}Mg^{#}^{melt} \)), and \( D_0^{3+} \) is the ratio of \( X_{REE}^{M2} \) to \( X_{REE}^{melt} \). Using these parameters, the equilibrium constant (6) was rearranged as:

\[
K_{ex}^{3+} = \frac{D_0^{3+} X_{Mg}^{M1}}{Mg^{#}^{melt}}
\]

(7)

If \( \Delta H^0, \Delta S^0, \) and \( \Delta V \) refer to the differences in thermodynamic properties between pure melt and pure crystal, it was found that:

\[
\Delta H^0_T - T\Delta S^0_T + P\Delta V = \frac{1}{2} \left( \frac{\partial \Delta V}{\partial P} \right) P^2 = RT \ln \left( \frac{D_0^{3+} X_{Mg}^{M1}}{Mg^{#}^{melt}} \right)
\]

(8)

The regression analysis of REE data from literature provided the best fit of the thermodynamic parameters on the left side of the reaction (8):

\[
RT \ln \left( \frac{D_0^{3+} X_{Mg}^{M1}}{Mg^{#}^{melt}} \right) - 7,050P + 770P^2 = 88,750 - 65.644T
\]

(9)

When the dataset from the Campi Flegrei is used to test the equation (9), all the strain-free partition coefficients are successfully predicted (Fig. 7), and the regression analysis of measured vs. predicted values of \( D_0^{3+} \) yields a very high correlation coefficient (\( R^2 = 0.997 \)) and low standard error of estimate (\( \text{SEE} = 0.048 \)). To account for the dependence of \( D_i \) (Fig. 3) and \( D_0^{3+} \) (Fig. 5) on the amount of aluminium in the tetrahedral site of clinopyroxene, Wood and Trigila (2001) re-fitted
the original calibration dataset of $D_0^{3+}$ by adding $\text{Al}^{4+}$ as predictor to the $P$ and $T$ parameters previously employed. It was found, however, that the tetrahedral aluminium is not statistically significant for the predictive equation (9) and that $D_0^{3+}$ is adequately described in terms of pressure and temperature only. Moreover, when the value of $D_0^{3+}$ is modelled after Wood and Blundy (2001) assuming local charge balance between REE in the M2 site and adjacent $\text{Al}^{4+}$ within clinopyroxene (i.e., $[\text{REE}]^{\text{ps}}/[X^{3+}]$, where $[X^{3+}]$ is the proportion of M2 sites charge-balanced by a 3+ cation), we found that the ability prediction of equation (9) does not substantially change ($R^2 = 0.997$ and $\text{SEE} = 0.046$; Fig. 7). On the other hand, Wood & Blundy (1997) assumed for simplicity that the activity of REE in the melt is equal to its concentration, thus ignoring that the melt structure may potentially control $D_0^{3+}$. Indeed, data plotted on Fig. 6a seems to suggest that $X_{\text{REE}}^{\text{melt}}$ is better described by $[\text{REE}]^{\text{melt}}/[\text{Ca}^{2+}/(M^{2+}+M^{2+})]^{\text{melt}}$ rather than the simple concentrations of REE in the melt. Therefore, we have incorporated the melt structure parameter into the predictive equation (9) but the regression analysis of measured vs. predicted values did not provide any improvement for the prediction of $D_0^{3+}$ ($R^2 = 0.994$ and $\text{SEE} = 0.063$; Fig. 7). The same conclusion was reached in recent studies for the partitioning of REE and Y between clinopyroxene/orthopyroxene and picritic/basaltic melts (Yao et al., 2012; Sun and Liang, 2012, 2013). This finding is apparently in contrast with the effects of $[\text{NBO}/T]^{\text{melt}}$ and $[\text{Ca}^{2+}/(M^{2+}+M^{2+})]^{\text{melt}}$ on the lattice-free partition coefficient (Fig. 6). One possible explanation is that, for moderately to highly depolymerized magmas, $[\text{NBO}/T]^{\text{melt}}$ is constantly higher than the threshold value of 0.4 (cf. Sun and Liang, 2012), whereas its value is persistently lower than 0.2 for polymerized magmas (Fig. 6a). On the other hand, due to the strong rival effects of $X_{\text{Al}}^{\text{iv}}$, $P$, and $T$, no obvious correlations are found between $[\text{Ca}^{2+}/(M^{2+}+M^{2+})]^{\text{melt}}$ and $D_0^{3+}$ when pressure, temperature, and clinopyroxene components change at the same time (cf. Huang et al., 2006). As these parameters are to some extent interdependent, it is not easy to differentiate between their relative influences over a broad range of crystallization conditions and compositions (crystal and melt). It can be concluded that the role of melt chemistry is to reduce the number of melt sites onto which REE can be accommodated. Thus, the melt structure can
potentially control the partitioning of trace elements over a wide spectrum of melt compositions (Fig. 6). However, for an isolated bulk melt composition, the final value of the REE partition coefficient is also determined by the relative (rival) effects of pressure, temperature and mineral chemistry.

Using a calibration dataset specific to basaltic compositions, Wood and Blundy (1997) found that $P$ and $T$ closely describe the variance of $E$ according to the regression equation (3), whereas $X_{Al}^{M1}$ and $X_{Ca}^{M2}$ are the best predictors for $r_0$, as provided by the best fitting equation (4). Further nonlinear regression calculations performed by Sun and Liang, (2012) and Yao et al. (2012) on a more recent basaltic dataset provided that $X_{Mg}^{M2}$ and $X_{Al}^{M1}$ can also be suitable predictors for $r_0$. Due to the strong relationship between $E$ and $r_0$, Wood and Blundy (1997) preferred to estimate the value of Young’s modulus using only $P$ and $T$. Conversely, an intrinsic trade-off between $E$ and $r_0$ was also found by Sun and Liang, (2012) that favoured calculating $E$ as a linear function of $r_0$. The authors demonstrated that the dependence of $E$ and $r_0$ on the same clinopyroxene components does not weaken the predictive power of the lattice strain model. However, in multiple linear regression analyses some variables may closely describe the variance of the dataset, whereas some others may generate a set of predictions with low degrees of freedom that lead to strong data overfitting. Therefore, variables that do not improve the fit must be identified and removed from a model.

Through an algorithm based on the Mallows’ $C_p$ statistic, we have performed systematic permutations of a number of independent variables to derive the best predictive models for $r_0$, and $E$. Mallows’ $C_p$ is expressed as (Hair et al., 1995):

$$C_p = \frac{RSS_k}{RSS_p} - n + 2p$$ (10)

$RSS_k$ is the ratio of the residual sum of squares of all predictors $k$, $RSS_p$ is the residual sum of squares of only $p$ of the $k$ predictors, and $n$ is the number of observations. Mallows’ $C_p$ is a measure
of the bias in a model: if the type and number of selected predictors \( p \) (including the constant term in linear regression) are sufficient to provide a good description of the data, then \( Cp \) has values as close as possible to \( p \). The independent variables used for permutations were \( X_{Al}^M \), \( X_{Al}^{M1} \), \( X_{Co}^{M2} \), \( X_{Na}^{M2} \), \( X_{Mg}^{M1} \), \( X_{Mg}^{M2} \), \( \left[ \frac{Ca^{2+}/(M^{2+}+Mg^{2+})}{\text{melt}} \right] \), \( \left[ \text{NBO/T} \right] \), \( P \) and \( T \). Results are reported in Table 6S together with the mean squared error (MSE), \( R^2 \), \( p \), and \( Cp \). The Mallows’ \( Cp \) statistic indicates that \( E \) and \( r_0 \) are both primary influenced by the same variables (i.e., \( X_{Ca}^{M2} \) and \( X_{Mg}^{M2} \)), corroborating the observation of Sun and Liang (2012) that \( E \) is indeed linearly correlated to \( r_0 \) (\( R^2 = 0.968 \)). In contrast, the temperature, pressure and melt composition have minor effects on these parameters, as would be expected given (a) these are crystal-chemical parameters and (b) that the thermal expansivity of the M2 site is relatively small for the temperature range considered here (Nimis, 1999). Therefore, using \( X_{Ca}^{M2} \) and \( X_{Mg}^{M2} \) as independent variables, we have performed a multiple linear regression analysis of the data from the Campi Flegrei to derive an improved predictive model for \( E \) (Fig. 8a):

\[
E = -82.35 + 636.56 X_{Ca}^{M2} - 253.29 X_{Mg}^{M2} \tag{11}
\]

The statistics (\( R^2 = 0.967 \) and SEE = 4.72) of the equation (11) are much better than those observed for the original equation (3) when \( T \) and \( P \) of trachyphonolitic magmas are used as input data (\( R^2 = 0.495 \) and SEE = 17.78). Through the same approach, we have also derived a predictive model for \( r_0 \) (Fig. 8b):

\[
r_0 = 1.0231 + 0.0278 X_{Ca}^{M2} - 0.0101 X_{Mg}^{M2} \tag{12}
\]

The equation (12) produces an improved fit to the data of the Campi Flegrei (\( R^2 = 0.954 \) and SEE = 0.002). Conversely, clinopyroxene compositions from trachytes and phonolites provide low
It is apparent that the uncertainty measured for the recalibrated equations (11) and (12) is reasonably low due to the restricted bounds of the calibration dataset that, in turn, closely describe the crystallization conditions and compositions of magmas at Campi Flegrei (Fig. 1 and Table 1S). On the other hand, the original equations (3) and (4) of Wood and Blundy (1997) were calibrated using primitive compositions obtained prevalently at high-temperatures that, in turn, do not reproduce the variability internal to the trachy-phonolitic dataset. For example, the percentage error of \( E \) predicted by the equation (3) increases as the temperature decreases (Fig. 9a) due to the fact that thermal conditions below 1,100 °C are not adequately represented into the calibration dataset of Wood and Blundy (1997). Fig. 9a shows that this is valid either to natural alkaline differentiated magmas from this study or to experimental basaltic compositions equilibrated at relatively low temperatures (data from experiments of Green et al., 2000 and Adam and Green, 2006). Conversely, Fig. 9b shows that the equation (11) has a very low percentage error of \( E \) at temperatures below 1,050 °C, but the error progressively increases with temperature, although \( T > 1,100 \) °C are rarely recorded by alkaline differentiated products. This simple test clearly makes the recalibrated equations (11) and (12) not suitable for high-temperature primitive magmas. We also observe that values of \( E \) and \( r_0 \) from basaltic and more differentiated compositions are scattered through the literature, consequently, the global regression analysis of these data did not provide statistically significant parameters applicable over a wide range of temperatures, pressures, and compositions.

In the online supplementary material, we provide an Excel spreadsheet in which equations (9), (11), and (12) are incorporated, and that can be used to predict \( D_{\text{REE}} \) and \( D_Y \) through major element analyses of clinopyroxene in equilibrium with trachy-phonolitic magmas. In Fig. 10a we have compared the standard error of estimate of each partition coefficient predicted by (i) the original model of Wood and Blundy (1997), (ii) the Excel spreadsheet from this study, and (iii) the parameterized model of Sun and Liang (2012). It is worth noting that this latter model was...
calibrated specifically to basaltic systems. With respect to the original model of Wood and Blundy (1997), our recalibrated model offers little improvements in the prediction of $D_{\text{LREE}}$, whereas its accuracy is remarkably high for most of the $D_{\text{HREE}}$ values. Conversely, the model of Sun and Liang (2012) is affected by a systematic uncertainty in the prediction of $D_{\text{LREE}}$. This is not surprising if we consider that the model was parameterized over crystallization conditions and compositions rather different to those presented in this study. However, in the case of $D_{\text{Yb}}$, $D_{\text{Lu}}$, and $D_{\text{Eu}}$, the standard error of estimate is found to be lower than that of other models. This is due to the fact that the model of Sun and Liang (2012) tends to overestimate the value of $E$ that, in turn, reduces the width of the partitioning parabola with minor effects on trace elements having low ionic radii. For example, measured vs. predicted values for $D_{\text{Ce}}$ (Fig. 10b) and $D_{\text{Yb}}$ (Fig. 10c) show that partition coefficients for larger LREE cations predicted by the model of Sun and Liang (2012) deviate significantly from the one-to-one line, whereas partition coefficients for smaller HFSE cations approach to the one-to-one line much better than those predicted by other models (see also Table 7S for the whole dataset).

Applications to the Campanian Ignimbrite

As anticipated from the preceding discussion, the dependence of trace element partitioning on $P$, $T$, and composition (crystal and melt) results in a variety of $D_i$ values. However, most of the petrological models from literature assume for simplicity that $D_i$ is independent on the physicochemical conditions of system, despite such an assumption is unlikely during crystallization of natural magmas. In order to clearly demonstrate the importance of considering the change of $D_i$ for a better understanding of magmatic differentiation, we have selected four natural clinopyroxene-melt pairs representative of the internal compositional variability of the Campanian Ignimbrite eruption (data from Civetta et al., 1997 and Arienzo et al., 2009). These data yield $\Delta D_{\text{Hd}}$ between 0.01 and 0.12 suggestive of near-equilibrium crystallization conditions (Mollo et al., 2013a), but are
also characterized by distinct features in terms of $P$, $T$, and composition (Table 8S). In particular, thermometers and barometers of Masotta et al. (2013) suggest that the natural clinopyroxene-melt pairs equilibrated at 100-300 MPa and 914-982 °C, in agreement with previous estimates from petrological (e.g., Fulignati et al., 2004; Marianelli et al., 2006; Fowler et al., 2007) and geophysical (e.g., Zollo et al., 2008) studies. As discussed above, the effect of pressure on trace element partitioning between clinopyroxene and melt can be considered negligible at shallow crustal depths.

On the other hand, there is a well-documented inverse correlation between the concentration of water dissolved in the melt and $D_{\text{REE}}$ (cf. Blundy et al., 2002; Gaetani, 2004; Sun and Liang, 2012). For trachytic and phonolitic compositions, it is not clear to what extent $H_2O$ can influence $D_0^{3+}$ during magma differentiation. Undoubtedly, the macroscopic effect of increasing water is to depress the liquidus temperature of the melt (Putirka, 2008). However, we have already tested that a water change of ±2 wt.% in trachytic and phonolitic magmas corresponds to a negligible temperature variation of ±12 °C. According to Mollo and Masotta (2014), low $\Delta D_{\text{Hd}}$ values allow to (1) minimize significantly the uncertainty of barometers and thermometers, and (2) find a good correspondence between the crystallization temperature of magma and the geochemical evolution of clinopyroxene. This latter point is better explained in Fig. 11a where $Mg#^{\text{px}}$ correlates positively with $T$, evidencing the relative effects of temperature and clinopyroxene composition on trace element partitioning. Only when magnitudes of these two opposing effects are reciprocally compensated, a set of nearly constant partition coefficients can be expected. Otherwise, temperature and clinopyroxene composition dominate over the final value of $D_n$, hence controlling the partitioning of trace elements during magma crystallization (e.g., Sun and Liang, 2012). Each symbol plotted on Fig. 11a refers to the value of $D_0^{3+}$ predicted using the Excel spreadsheet from this study. $D_0^{3+}$ increases from 0.67 to 0.91 with decreasing both $T$ and $Mg#^{\text{px}}$. In this view, the whole range of values calculated for $D_{\text{REE}}$ and $D_Y$ has been used as input data for the Rayleigh fractional crystallization equation (FC):
\[ C_l^{FC} = C_0 F^{(Di-1)} \]  

(13)

Where \( C_l^{FC} \) is the concentration of an element in remaining melt during fractional crystallization, \( C_0 \) is the concentration of the trace element in parental liquid (starting composition), \( D_i \) is the partition coefficient of the trace element of interest whose value changes as a function of the physicochemical conditions of the system (see below), \( F \) is the fraction of melt remaining during crystallization. At the beginning of the modelling, low degrees of clinopyroxene fractionation (i.e., 3%, 5%, 7%, and 9%) have been considered to constrain its early effect as liquidus phase on the geochemical signature of magma. Stepwise calculations were performed changing the clinopyroxene composition and temperature at each step of fractionation (Fig. 11a), in order to derive a set of four different partition coefficients rather than one single value. In Fig. 11b, modelled Ce and Y concentrations are compared with those of rock samples from the Campanian Ignimbrite. Notably, the ratio of Ce/Y for the Campanian Ignimbrite eruption changes significantly from 0.21 to 0.33, in contrast to what would be expected for igneous products sharing a common parental magma. This discrepancy is reconciled by the nonlinear trajectory of the \( ^{cpx} FC \) vector that is controlled by the variation of the partition coefficient. Thus, at the early stage of clinopyroxene crystallization, the incorporation of variable proportions of Ce and Y into the crystal lattice provides explanation for the strong variability of the natural dataset. According to Civetta et al. (1997), the internal differentiation of the Campanian Ignimbrite can be addressed to the fractionation of <10% and ~50% of clinopyroxene and feldspar, respectively. Considering that Ce and Y are highly incompatible in feldspar (\( D_{Ce} = 0.039 \) and \( D_Y = 0.017 \); Larsen, 1979), further fractional crystallization steps have been developed accounting for the segregation of 50% of feldspars from the solidifying magma. Notably, due to the highly incompatible behaviour of Ce and Y, feldspar fractionation may only increase the REE content in magma but cannot control the internal REE variability of the Campanian Ignimbrite eruption. Modelling results are aligned along four different FC trajectories (i.e., from \( ^{kfs} FC1 \) to \( ^{kfs} FC4 \)) that faithfully reproduce the entire differentiation path of
the Campanian Ignimbrite, from lowest to highest Ce/Y ratios (Fig. 11a). Clearly, the constancy of the clinopyroxene-melt partition coefficient would yield only one single FC trend that, in turn, is inadequate to reproduce in full the complex trace element pattern of natural products. Therefore, the process responsible for the heterogeneous REE concentrations of the Campanian Ignimbrite products is twofold: (1) the early fractionation of clinopyroxene at relative high temperature and (2) the subsequent fractionation of feldspars during the final stage of magma cooling (cf. Fowler et al., 2007). Additional complexities, including crystallization of other phases (oxides, biotite, apatite) and partial cumulate mush remelting (e.g., Wolff et al., 2015) can further explain some of the trace element variations observed in the Campanian Ignimbrite.

Conclusions

Coherently with previous natural and experimental studies, we documented that the partitioning of trace elements between clinopyroxene and trachy-phonolitic melts can be addressed to (1) the entry of REE+Y and HFSE in the M2 and M1 sites, respectively, due to substitution of Si\(^{4+}\) with Al\(^{iv}\), (2) the increased net charge on the M1 site that causes divalent TE to become less compatible within clinopyroxene crystal lattice, (3) a charge-balanced cation substitution reaction reflecting an increased ease of locally balancing the excess charge as the number of surrounding tetrahedrally-coordinated aluminium atoms increases, and (4) the effect of changes in melt structure that increase the number of large sites critically important to accommodating large REE cations. On the other hand, we tested that the incorporation of additional crystallochemical parameters (assuming local charge balance between REE in the M2 site and adjacent Al\(^{iv}\)) and melt structure parameters (given as the ratio of non-bridging oxygens to tetrahedral cations and/or the ratio of molar calcium to the sum of monovalent and divalent cations) into the lattice strain model of Wood & Blundy (1997) did not provide any improvement for its ability prediction. This is due to the strong rival effects of pressure, temperature, and crystal/melt parameters. Therefore, over a broad range of crystallization
conditions and crystal/melt compositions, it is not possible to differentiate between the relative influence of each single parameter on REE+Y partitioning. As a consequence, no obvious correlations are found when the physicochemical conditions of the system change at the same time. According to the lattice strain theory, we observe that, $D_0^{3+}$, $r_0$ and $E$ can be successfully predicted once $T$, $P$, $X_{Cu}^{M^2}$ and $X_{Mg}^{M^2}$ are knows for trachy-phonolitic compositions. On this basis, we updated the existing partitioning equations to derive a self-consistent model for trachy-phonolitic magmas. The application of this model to natural products from the Campanian Ignimbrite, the largest caldera-forming eruption at the Campi Flegrei, reveals that the complex REE pattern of magma can be successfully described by the stepwise fractional crystallization of clinopyroxene and feldspar where the clinopyroxene-melt partition coefficient changes progressively as a function of the physicochemical conditions of the system.

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**Figure captions**

Fig. 1. The compositions of host melts and clinopyroxene phenocryst cores from this study are compared with those of natural products at Campi Flegrei in terms of total alkali vs. silica of the melt (a), $\Sigma$HREE vs. $\Sigma$LREE of the melt (b), Di vs. Hd of clinopyroxene, and (c) $\Sigma$HREE vs. $\Sigma$LREE of clinopyroxene. Natural data from Villemant (1988), Civetta et al. (1997), Fulignati et al. (2004), Marianelli et al. (2006), Fedele et al. (2007), Pappalardo et al. (2002; 2008), and Arienzo et al. (2009).

Fig. 2. Example of the textural features of clinopyroxene phenocrysts from this study. (a) Backscattered electron images show that crystals are euhedral and complex zoning patterns are absent. Microprobe compositional profiles reveal the occurrence of some chemical heterogeneities.
at the crystal-melt interface. (b) Diffusive boundary layer occurs into the glass next to clinopyroxene rims showing Al and Na enrichments (see also data in Table 5S).

Fig. 3. Plots of partition coefficients for HFSE (Ti, Zr, Nb, Ta), REE (La) and TE (Co) vs. Al$^{iv}$. Data from this study have been compared with those from literature to highlight the dependence of $D_i$ on Al$^{iv}$.

Fig. 4. Plots of partition coefficients for REE and Y vs. ionic radii (data from Shannon 1976) for the samples object of this study. The near parabolic dependence found by Onuma et al. (1968) dictates the distribution of the data. The lines show fits to the lattice strain model of Blundy and Wood (1994). Fit parameters are listed in Table 4S. The agreement of our data with the model emphasizes the importance of lattice strain in controlling REE and Y partitioning at equilibrium crystallization conditions.

Fig. 5. Plots of $D_{0}^{3+}$ for clinopyroxene-melt partitioning of REE vs. Al$^{iv}$ content in clinopyroxenes from this study and previous works. $D_{0}^{3+}$ is calculated through the lattice strain model of Blundy and Wood (1994).

Fig. 6. Plot of $D_{0}^{3+}$ for clinopyroxene-melt partitioning of REE vs. $NBO/T$ of the melt. (a) Our data for trachy-phonolitic melts are compared with those from literature obtained for highly polymerized silicic melts, and moderately-to-poorly polymerized silicic melts. According to Gaetani (2004) and Huang et al. (2006) the melt structure have a significant influence on partition coefficients for $[NBO/T]^{melt}$ values higher than 0.4. (b) Plot of $D_{0}^{3+}$ for clinopyroxene–melt partitioning of REE vs. $[Ca^{2+}/(M^{+}+M^{2+})]^{melt}$, where $M^{+}$ and $M^{2+}$ are Na$^{+}$+K$^{+}$ and Fe$^{2+}$+Ca$^{2+}$+Mg$^{2+}$, respectively. The negative correlation between $D_{0}^{3+}$ and $[Ca^{2+}/(M^{+}+M^{2+})]^{melt}$ confirms the reliability of Eqn. (2)
favouring large structural sites critically important to accommodating large trace element cations in
the melt.

Fig. 7. Clinopyroxene-melt pairs from this study, Pappalardo et al. (2008) and Fedele et al. (2009)
have been used as input data for the original equation for $D_0^{3+}$ derived by Wood and Blundy (1997).
New predictors have been also introduced in this equation, i.e., \([REE]^{ps}/[X^{3+}]\) (after Wood and
Blundy, 2001) and \([REE]^{melt}/[Ca^{2+}/(M^++M^{2+})]^{melt}\). The analysis of predicted vs. measured values
indicates that these new predictors do not offer improvements for the ability prediction of the
original equation of Wood and Blundy (1997).

Fig. 8. Clinopyroxene-melt pairs from this study, Pappalardo et al. (2008) and Fedele et al. (2009)
have been used as input data for the original equations for (a) $E$ and (b) $r_0$ derived by Wood and
Blundy (1997). The analysis of predicted vs. measured values indicates that these equations are
affected by a high uncertainty. The best fitting equations have been derived through the regression
analysis of trachy-phonolitic data using $X_{Ca}^{M^2}$ and $X_{Mg}^{M^2}$ as predictors.

Fig. 9. The predictive equations for $E$ from (a) Wood and Blundy (1997) and (b) this study have
been tested using trachy-phonolitic (this study, Pappalardo et al., 2008 and Fedele et al., 2009) and
basaltic (Green et al., 2000 and Adam and Green, 2006) data. For the original equation of Wood
and Blundy (1997), the percentage error of E increases with decreasing temperature. The opposite
occurs for the equation from this study showing low ability prediction for high-temperature basaltic
magmas.

Fig. 10. $D_{REE}$ and Dy “measured” in this study are compared with those “predicted” by the original
model of Wood and Blundy (1997), the parameterized model of Sun and Liang (2012) for basaltic
compositions, and the recalibrated model from this study for trachy-phonolitic compositions. (a)
Comparison of the standard error of estimate. (b) Comparison of $D_{\text{Ce}}$ values as representative of partitioning of larger LREE cations. (c) Comparison of $D_{\text{Yb}}$ values as representative of partitioning of smaller LREE cations.

Fig. 11. Natural clinopyroxene-melt pairs from the Campanian Ignimbrite have been used as input data for the thermobarometer of Masotta et al. (2013) and the trace element model presented in this study. (a) Temperature vs. $Mg^{\#}_{\text{cpx}}$ diagram shows that the geochemical evolution of clinopyroxene parallels the decreasing temperature of magma. Each symbol plotted on the diagram refers to the value of $D_0^{3+}$ predicted using the Excel spreadsheet from this study. $D_0^{3+}$ is found to increase from 0.60 to 0.85 with decreasing both $T$ and $Mg^{\#}_{\text{cpx}}$. (b) Ce vs. Y diagram showing the geochemical evolution of the Campanian Ignimbrite modelled through the Rayleigh fractional crystallization equation. At the beginning of the modelling, low degrees of clinopyroxene fractionation (i.e., 3%, 5%, 7%, and 9%) have been considered. Stepwise calculations were performed changing the clinopyroxene composition and temperature at each step of fractionation. Modelled Ce and Y concentrations were used to draw the $cpx$FC vector. Fractional crystallization calculations were further developed accounting for the segregation of ~50% of K-feldspar from the solidifying magma. Modelling results are aligned along four different FC trajectories (i.e., from $kfsFC1$ to $kfsFC4$).
Trace element partitioning between clinopyroxene and trachy-phonolitic melts: A case study from the Campanian Ignimbrite (Campi Flegrei, Italy)

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Abstract

The partitioning of trace elements between crystals and melts provides an important petrogenetic tool for understanding magmatic processes. We present trace element partition coefficients measured between clinopyroxene phenocrysts and trachy-phonolitic magmas at the Campi Flegrei (Italy), whose late Quaternary volcanism has been characterized by two major caldera-forming events (Campanian Ignimbrite at ~39 ka, and the Neapolitan Yellow Tuff at ~15 ka). Our data indicate that the increase of trivalent rare earth elements and yttrium into the crystal lattice M2 site is facilitated by the charge-balancing substitution of Si$^{4+}$ with Al$^{3+}$ on the tetrahedral site. Higher concentrations of tetravalent and pentavalent high field strength elements on the M1 site are also measured when the average charge on this site is increased by the substitution of divalent cations by Al$^{6+}$. In contrast, due to these charge balance requirements, divalent transitional elements become less compatible within the crystal lattice. On the basis of the lattice strain theory, we document that the incorporation of rare earth elements and yttrium in clinopyroxene is influenced by both compositional and physical parameters. Data from this study allow to update existing partitioning equations for rare earth elements in order to construct a self-consistent model for trachy-phonolitic magmas based on the lattice strain theory. The application of this model to natural products from the Campanian Ignimbrite, the largest caldera-forming eruption at the Campi Flegrei, reveals that the complex rare earth element pattern recorded by the eruptive products can be successfully described by the stepwise fractional crystallization of clinopyroxene and feldspar where the clinopyroxene-melt partition coefficient changes progressively as a function of the physicochemical conditions of the system.

Keywords: clinopyroxene-melt trace element partitioning; lattice strain theory; trachy-phonolitic magmas; Campi Flegrei.
Clinopyroxene is one of the most important constituents of igneous rocks and its crystallization behaviour impacts significantly the composition of magmas. The partitioning of trace elements between clinopyroxene and melt is frequently used in petrological and geochemical studies to better understand magma differentiation processes, such as fractional or equilibrium crystallization, assimilation, and partial melting. For simplicity, the clinopyroxene-melt partition coefficient \[ D_i = \frac{x_i(I)}{x_i(melt)} \] on a weight basis is generally assumed to be constant for magma modelling. However, this simple approximation does not take into account for the effects of crystal and melt compositions, as well as the physical conditions of the system on trace element partitioning. Wood and Blundy (1997) showed for the first time that partition coefficients of rare earth elements (REE) can be modelled as a function of composition of the crystal \( X_{Mg}^{M1} \), Mg-number of the melt \( Mg^{#melt} \), pressure \( P \) and temperature \( T \). Crystal chemistry influences both the dimensions of the M2 site, into which REE partition, and the molar fraction of the hypothetical REE end-member, such as REEMgAlSiO\(_6\). Blundy et al. (1998) and Bennett et al. (2004) also argued that \( D_{REE} \) is dependent on \( X_{Na}^{M2} \) due to the higher incorporation of Na\(^+\) in M2 with increasing \( P \), for example via the hypothetic end-member Na\(_{0.5}\)REE\(_{0.5}\)MgSi\(_2\)O\(_6\). Furthermore, Hill et al. (2000), Wood and Trigila (2001) and Wood and Blundy (2001) documented a close relationship between REE partitioning and the concentration of tetrahedrally-coordinated aluminum in clinopyroxene, as required for charge balance. Sun and Liang (2012) derived a predictive model in which \( D_{REE} \) is positively correlated with \( X_{Al}^{iv} \) and \( X_{Mg}^{M2} \), and negatively correlated with \( T \) and H\(_2\)O dissolved in the melt. Gaetani et al. (2003) attributed the decrease of \( D_{REE} \) with increasing H\(_2\)O to the depolymerizing effect of water on the melt structure. Moreover, complementary studies of Gaetani (2004) and Huang et al. (2006) pointed out that the melt structure becomes dominantly important
below a threshold value of the number of non-bridging oxygens per tetrahedral cations ($NBO/T$) corresponding to 0.4. As a whole, results from previous works highlight that the partitioning of trace elements between clinopyroxene and melt is governed by complex mechanisms whose effects and magnitudes on $D_i$ depend on specific compositional and physical parameters that are still poorly understood for a significant number of natural cases.

In this study, we present a new set of apparent partition coefficients calculated for clinopyroxene phenocrysts in equilibrium with trachytic and phonolitic compositions from the Campi Flegrei (Italy). Despite the highly explosive nature of these magmas and their common involvement in hazardous volcanic settings, little attention has been given to the most important parameters that influence the partitioning of trace elements (however, see Pappalardo et al., 2008; Fedele et al., 2009). On the basis of the lattice strain theory derived by Blundy and Wood (1994), it has been determined to what extent the physicochemical conditions of the system may influence the partitioning of trace elements. Through an improved version of the predictive equations of Wood and Blundy (1997), we have also modelled the complex trace element compositions of several rock samples from the Campanian Ignimbrite, one of the largest late Quaternary volcanic eruptions in Europe.

**Geological background**

The Campi Flegrei, located within the Campanian Plain, belong to the potassic alkaline volcanic province of central Italy. Volcanism is still active, as demonstrated by fumarolic and seismic activity, and by recurrent episodes of unrest in the past 30 years (Orsi et al., 1999 and references therein). The highly explosive behaviour of magmas represents a continuous threat to more than one million people living in the city of Naples and its densely inhabited suburbs. This makes the Campi Flegrei one of the most dangerous volcanic systems in the world.
The caldera is a resurgent nested structure formed during two major collapses related to the eruptions of the Campanian Ignimbrite (CI) and the Neapolitan Yellow Tuff (NYT). Seismic reflections indicate the presence of a discontinuity at 7.5 km depth, where seismic velocities are consistent with values expected for a magma body set in a densely fractured volume of rock (Zollo et al., 2008). Petrological and melt inclusion studies suggest that differentiated alkaline melts formed dominantly through fractional crystallization from a more mafic parental magma, likely emplaced at depths between 4 and 8 km, with little assimilation of surrounding crust (Signorelli et al., 2001; Webster et al., 2003; Marianelli et al., 2006; Pabst et al., 2008; D’Antonio, 2011).

The Campanian Ignimbrite eruption (~39 ka; De Vivo et al., 2001) is regarded as the dominant event in the history of the Campi Flegrei with an initial areal distribution of ~30,000 km² (Rolandi et al., 2003). It consists of ~200 km³ of pyroclastic-fall and pyroclastic-flow deposits (Civetta et al., 1997). The composition of the erupted products changed from trachyte to phonolite during the eruption. Phase equilibria data, geothermometry, and fluid inclusion analysis, suggest an overall thermal path of the magma from 840 to 1,080 °C (Fulignati et al., 2004; Marianelli et al., 2006; Fowler et al., 2007; Fedele et al., 2009; Masotta et al., 2013). Melt inclusion measurements and hygrometric predictions indicate a melt-water concentration ranging from 3 to 6 wt.% (Signorelli et al., 2001; Webster et al., 2003; Marianelli et al., 2006; Mollo et al., 2014). On the basis of these heterogeneous petrological information, it has been proposed that the CI magma evolved in a thermally and chemically zoned magmatic reservoir (Pappalardo et al., 2008; Pappalardo and Mastrolorenzo, 2012).

The Neapolitan Yellow Tuff eruption (~15 ka; Deino et al., 2004) was the second more recent phreatoplinian event in the history of the Campi Flegrei. It erupted ~40 km³ of pyroclastic-fall and pyroclastic-flow deposits dispersed over an area of more than ~1,000 km² (Orsi et al. 1992). The erupted products are characterized by latitic to trachytic compositions. The vent for the NYT eruption was located inside the caldera formed during collapse of the CI eruption, resulting in a final caldera that covered an area of ~90 km² (Orsi et al., 2009).
Analytical methods

Field emission gun scanning electron microscope (FE-SEM) images and electron probe microanalyses (EPMA) of twelve clinopyroxenes were collected at the HPHT Laboratory of Experimental Volcanology and Geophysics of the Istituto Nazionale di Geofisica e Vulcanologia (INGV) in Rome, Italy. Images were obtained through the backscattered electron (BSE) mode of a JEOL 6500F FE-SEM equipped with an energy-dispersive spectrometer (EDS) detector. Microprobe analyses were performed with a JEOL-JXA8200 EPMA equipped with five spectrometers. The beam diameter was ~1 μm with a counting time of 20 and 10 s on peaks and background respectively. The following standards were used: jadeite (Si and Na), corundum (Al), forsterite (Mg), andradite (Fe), rutile (Ti), orthoclase (K), barite (Ba), apatite (P), spessartine (Mn) and chromite (Cr). Sodium and potassium were analyzed first to prevent alkali migration effects. The precision of the microprobe was measured through the analysis of well-characterized synthetic oxides and minerals. Data quality was ensured by analyzing standard materials as unknowns. Based on counting statistics, analytical precision was better than 5% for all cations.

Major and trace elements of whole-rocks, and trace elements of clinopyroxene phenocrysts were measured at the Institute of Geochemistry and Petrology of the ETH Zürich, Switzerland. For the whole-rock analyses 1.5 g of powdered sample was heated to 950 °C for 2 h in a chamber furnace and then weighed to determine the loss on ignition (LOI). The ignited material was charged in a Pt-Au crucible and fused with a 1:5 Lithium-Tetraborate mixture using a Claisse M4® fluxer. The fused disk was analysed for major elements using a wave-length dispersive X-ray fluorescence spectrometer (WD-XRF; Axios PANanalytical) equipped with five diffraction crystals. Calibration was based on thirty certified international standards of predominantly igneous and metamorphic rocks. Trace element analyses of both whole-rock disks and clinopyroxene phenocrysts were performed through a 193 nm excimer laser coupled with a second generation two-volume constant
geometry ablation cell (Resonetics:S-155LR) and a high-sensitivity, sector-field inductively-coupled plasma mass spectrometer (ICP-MS; Thermo:Element XR). Points with a spot size of 45 μm were set on chemically homogeneous portions of the material (i.e., clinopyroxene cores) previously analyzed by EPMA, and ablated with a pulse rate of 10 Hz and an energy density of 3.5 J/cm³ for 40 sec. The isotopes were analyzed relative to an internal standard of known composition (i.e., NIST612). A second standard (i.e., GSD-1G) was used as an unknown to check the quality of data during each analytical run. ⁴³Ca or ²⁹Si were used as internal standards for clinopyroxene and whole-rock analyses, respectively, in order to recover the concentrations of light and heavy rare earth elements (REE divided in LREE and HREE), high field strength elements (HFSE), large ion lithophile elements (LILE) and transition elements (TE). The precision of individual analyses varied depending upon a number of factors, e.g., the element and isotope analyzed as well as the homogeneity of the ablated material. However, the 1 sigma errors calculated from variations in replicate analyses of crystals and whole-rock disks were invariably several times larger than the fully integrated 1 sigma errors determined from counting statistics alone.

**Sample description**

Sampled rocks belong to twelve pyroclastic deposits at the Campi Flegrei characterized by variable proportions of juvenile material (i.e., pumices, scoriae, spatter clasts, fiamme and obsidians), variably porphyritic textures (10-25 vol.% of phenocrysts), and the ubiquitous occurrence of clinopyroxene, biotite, K-feldspar, plagioclase, opaques, and rare apatite. Samples were collected from different outcrops in order to fully characterize the compositions of clinopyroxene phenocrysts and host magmas of pre-CI, CI, post-CI, NYT, and post-NYT eruptions (see Table 1S for the locations). Major and trace element concentrations measured for crystals and melts are reported in Tables 1S and 2S, respectively. We present our data in comparison with those of Pappalardo et al. (2008) and Fedele et al. (2009) that provided a complete dataset comprising whole-rock analyses,
clinopyroxene chemistries, apparent partition coefficients for REE, and lattice strain parameters (see below) of four additional rock samples from the Campanian Ignimbrite eruption.

Whole-rock analyses show increasing SiO$_2$ contents (57-62 wt.%) with decreasing CaO (1.8-5.3 wt.%) and $Mg^{\#}_{\text{melt}}$ (16-40). All compositions are also rich in alkali (Na$_2$O+K$_2$O = 11-14 wt.%). In the TAS (total alkali vs. silica; Le Bas et al., 1986) diagram, samples are classified as trachytes and phonolites, in agreement with most of the differentiated alkaline products at Campi Flegrei (Fig. 1a). Whole-rocks exhibit a variable degree of differentiation that, in terms of trace element concentrations, reproduces well the evolutionary behaviour of magmas (Fig. 1b). The increase of REE is commonly associated with a significant increase in Th, U, Nb, Ta, Zr and Hf, and decrease in Sr testifying to an increased plagioclase fractionation (Table 2S).

Clinopyroxenes occur as euhedral phenocrysts (longest size dimensions > 0.3 mm) with diopsidic compositions (Morimoto, 1988). Al$^{\text{iv}}$ (0.05-0.13 apfu) is positively correlated with Ti$^{+4}$ (0.01-0.04 apfu) and negatively correlated with $Mg^{\#}_{\text{cpx}}$ (0.73-0.84). The ratio of octahedrally-coordinated to tetrahedrally-coordinated aluminium cations is less than 1 in all phenocrysts, indicating preferential incorporation of Al$^{\text{iv}}$ at low pressure crystallization conditions (Muñoz and Sagredo, 1974; Putirka, 1996; Mollo et al., 2011b). The ratio of Fe$^{3+}$/Fe$^{2+}$ in clinopyroxenes, as calculated from stoichiometry, ranges between 0 and 0.5 with values identical to those experimentally-derived for magmas at Campi Flegrei equilibrated at NNO+1 and NNO+2 oxygen fugacity (Fabbrizio and Carroll, 2008; Masotta et al., 2013). Diopside vs. hedenbergite (Fig. 1c) and Ce vs. Y (Fig. 1d) diagrams suggest that major and trace elements of our clinopyroxenes capture most of the geochemical evolution of phenocrysts at Campi Flegrei.

Apparent trace element partition coefficients were measured for pre-CI, CI, post-CI, NYT, and post-NYT samples using clinopyroxene core and whole-rock analyses that were found to be in equilibrium (see below) and are reported in Table 3S. The most important changes of $D_i$ can be summarized as follows: (i) LREE (e.g., $D_{\text{La}} \leq 0.27$) are more incompatible than HREE (e.g., $D_{\text{Dy}} \leq 1.67$); (ii) TE are always compatible within clinopyroxene (e.g., $D_{\text{Co}} \leq 10.07$); (iii) pentavalent
HFSE cations are more incompatible ($D_{\text{Nb}}$ and $D_{\text{Ta}} \leq 0.05$) that tetravalent HFSE cations ($D_{\text{Zr}}$ and $D_{\text{Hf}} \leq 0.87$) and; (iv) LILE are generally incompatible (e.g., $D_{\text{Sr}} \leq 0.8$) with the exception of one sample ($D_{\text{Sr}} = 1.39$ for PM2).

Assessment of equilibrium crystallization conditions

Laboratory investigations of clinopyroxene-melt partition coefficients are generally designed to guarantee the achievement of equilibrium between crystals and melts. The initial rate of cooling and the time duration of experiments are set to ensure that the melt supplies nutrients at equilibrium proportions to the growing crystals. The experimental charges are then quenched at very fast cooling rates and the system is almost instantaneously “frozen-in” (e.g., quenching rate of 2,000 °C/min; Freda et al., 2008). Due to the use of rapid quenching conditions, disequilibrium processes may only operate at the nanometre scale, leading to the formation of a diffusive boundary layer with thickness orders of magnitude lower that the analytical spot size used for major and trace element measurements (e.g., Mollo et al., 2012). On the other hand, apparent partition coefficients obtained from natural samples measuring the compositional ratios between bulk phenocrysts and host lavas (i.e., whole-rock analyses) are potentially biased by contamination or disequilibrium processes. Even when single point analyses are carried out at the crystal-melt interface, the compositional zoning of minerals and surrounding glasses can make the accurate determination of $D_i$ extremely difficult. The entrapment of melt in rapidly growing crystals may increase the value of $D_i$ by up to 3 orders of magnitude (Kennedy et al., 1993). Additionally, rapid crystal growth conditions are not necessary accompanied by detectable melt entrapments or crystal discontinuities and, under such circumstances, disequilibrium values of $D_i$ can exhibit variations in the same order of magnitude of equilibrium data (Mollo et al., 2013a).

For the purpose of this study, we have accurately inspected each phenocryst and coexisting glass using SEM and EPMA, in order to make sure that the occurrence of melt inclusions, crystal
zoning and/or melt diffusion phenomena were kept to a minimum. Clinopyroxenes are generally euhedral with well-defined edges and without evident zoning patterns (Fig. 2a). However, microprobe compositional profiles reveal the occurrence of chemical heterogeneities at the crystal-melt interface (Fig. 2b and Table 5S). A diffusive boundary layer occurs into the glass next to clinopyroxene surface. This thin diffusive boundary layer is enriched in chemical species less compatible in clinopyroxene crystal lattice (e.g., Al and Na). Concentration–dependent partitioning produces crystal growth layers that respond to the chemical gradients in the melt, producing Al and Na enrichments in clinopyroxene that are identical to those experimentally documented by cooling rate studies (Lofgren et al., 2006; Mollo et al., 2013b). Compositional perturbations at the crystal rim also suggest that, at the closure temperature of the crystal growth (i.e., $T_{\text{final}} \ll T_{\text{liquidus}}$), the free energy difference between the crystal surface and the liquid was large enough that diffusion became the rate-controlling process (Watson and Muller, 2009). Due to the high explosivity of eruptions at Campi Flegrei, phenocrysts underwent typically high degrees of undercooling during magma ascent in the volcanic conduit and eruption to the surface (Pappalardo and Mastrolorenzo, 2012 and references therein). Mollo et al. (2013b) proposed an equilibrium model based on the difference ($\Delta$) between diopside+hedenbergite (DiHd) components predicted for clinopyroxene via regression analyses of clinopyroxene-liquid pairs in equilibrium conditions, with those measured in the analyzed phenocrysts. Mollo and Masotta (2014) successfully tested this model on trachytic and phonolitic compositions obtained at both equilibrium and disequilibrium conditions. Calculations performed using clinopyroxene rim and coexisting melt compositions yield values of 0.11-0.16 (Fig. 2b) that are considerably higher than those measured at near-equilibrium conditions ($\Delta\text{DiHd} \leq 0.02$). This suggests that $D_i$ values measured at the crystal-melt interface results from disequilibrium partitioning due to the effect of rapid magma decompression and degassing at the time of eruption (e.g., Lanzafame et al., 2013; Mollo et al., 2015a). On the other hand, it is reasonable to infer that, over the timescale of magma chamber evolution and in absence of perturbation phenomena (e.g., magma mixing), early-formed clinopyroxene phenocrysts may have crystallized in equilibrium with
the host magma, despite the occasional occurrence of chemical heterogeneities or melt inclusions in
crystal that tend to reduce the accuracy of $D_i$ calculations. In light of this, apparent trace element
partition coefficients have been calculated by the analyses of bulk phenocrysts and whole-rock
compositions (e.g., Schnetzler and Philpotts 1970; Nagasawa and Schnetzler 1971; Nagasawa 1973; Mahood and Hildreth 1983; Lemarchand et al. 1987; Villemant 1988).

Experiments and thermodynamic studies have clearly documented that clinopyroxene is the
liquidus phase of trachytic and phonolitic melts (Fowler et al., 2007; Fabbrizio and Carroll, 2008;
Masotta et al., 2013, Del Bello et al., 2014). Under such circumstances, near-liquidus crystals are
represented by early-formed cores of large phenocrysts that likely equilibrated with the host magma
(i.e., whole-rock analysis) in terms of major and trace element concentrations (see for example the
studies of Armienti et al., 2007; Masotta et al., 2010; Mollo et al., 2011a; Lanzafame et al., 2013;
Scarlatò et al., 2014). In this respect, Fig. 2b shows the development of an almost homogeneous
plateau composition at the clinopyroxene core that suggests near-equilibrium crystallization and
excludes chemical perturbations in the original magma. Tests conducted with the model of Mollo et
al. (2013b) yield $\Delta D_{i\text{Hd}}$ values between 0 and 0.02 testifying to equilibrium or near-equilibrium
conditions between phenocryst core and whole-rock data that were therefore used for our $D_i$
calculations (see also $\Delta D_{i\text{Hd}}$ values reported in Table 1S).

As stated above, the differentiation of magmas mostly occurs at shallow crustal levels (100-300 MPa) where the effect of pressure on near-liquidus clinopyroxene-melt partition coefficients is
expected to be minimal. Thermodynamic data derived by the lattice strain model indicate that the
influence of $P$ on $D_i$ can be considered negligible at pressures lower than 500 MPa (Blundy and
Wood, 2003). It could be argued that REE partitioning is also sensitive to sodium in clinopyroxene,
which in turn varies with pressure (Blundy et al., 1995; Bennett et al., 2004). However, the control
of Na$^+$ on $D_{\text{REE}}$ is dominant only at mantle pressures ($\geq$ 3 GPa) where sodium concentration ($\text{Na}_2\text{O}
= 2.2-13.5$ wt.%; data from Klemme et al., 2002; Bennett et al., 2004; Marks et al., 2004) is one to
two order of magnitude higher than that measured in our phenocrysts ($\text{Na}_2\text{O} = 0.15-0.56$ wt.%;
Table 1S). Therefore, in terms of physical parameters, temperature is likely the most important variable that can influence $D_i$ at the crystallization conditions of magmas. To estimate the equilibration temperatures and pressures of clinopyroxene-melt pairs from this study (Table 1S), we have used the thermometers and barometers of Masotta et al. (2013) specifically calibrated for trachytic and phonolitic compositions. A melt-water content of 3 wt.% has been set in the model, in agreement with most of the water concentrations measured by melt inclusion studies on Campi Flegrei (Signorelli et al., 2001; Webster et al., 2003; Marianelli et al., 2006). We have established that a water change of ±2 wt.% produces temperature and pressures variations of only ±12 °C and ±15 MPa, which are well below the errors of estimate of the thermometer (±24 °C) and barometer (±114 MPa). Results from calculations indicate that our clinopyroxenes crystallized at temperatures and pressures of 840-1,020 °C and 85-309 MPa (Table 1S), in close correspondence with those (840-1,080 °C and 20-300 MPa) derived for trachy-phonolitic products belonging to the Campanian Ignimbrite eruption (Fedele et al., 2009; Masotta et al., 2013).

**Discussion**

Trace element partition coefficients

The dependence of trace element partition coefficient on tetrahedrally-coordinated aluminium has been the focus of many studies on clinopyroxene (Lindstrom 1976; Ray et al. 1983; Hart and Dunn 1993; Forsythe et al. 1994; Lundstrom et al. 1994, 1998; Skulski et al. 1994; Blundy et al. 1998; Hill et al. 2000; Wood and Trigila 2001; Sun and Liang, 2012; 2013; Mollo et al., 2013a; Yao et al., 2013; Scarlato et al., 2014). In Fig. 3, the close correspondence between $D_i$ and Al$^{iv}$ for representative HFSE, REE and TE, is confirmed and extended to trachytic and phonolitic magmas. Note that the gray fields in Fig. 3 indicate that our $D_i$ values are consistent with those previously calculated for magmas at Campi Flegrei (data from Pappalardo et al., 2008 and Fedele et al., 2009).
From a crystallochemical point of view, HFSE enter the smaller M1 octahedral site, and the correlation between $D_{\text{HFSE}}$ and Al reflects the increasing charge on this site with increasing CaAl$_2$SiO$_6$ and CaFeAlSiO$_6$ substitution, i.e., with increasing replacement of Mg$^{2+}$ by Fe$^{3+}$ and Al$^{3+}$ (Wood and Trigila, 2001). Thus, entry of +4 and +5 ions into M1 is enabled by the substitution of Al$^{3+}$ for Si$^{4+}$ in the tetrahedral site (Hill et al., 2000; Mollo et al., 2013a). In the case of trivalent trace elements, REE and Y enter the large M2 site that, apart from minor amounts of Na$^+$, is almost exclusively occupied by Ca$^{2+}$, Mg$^{2+}$, and Fe$^{2+}$. Data plotted in Fig. 3 show a clear positive correlation between $D_{\text{La}}$ and Al$^{\text{iv}}$ that has been extensively documented under both equilibrium and disequilibrium crystal growth conditions (Gaetani and Grove, 1995; Blundy et al., 1998; Mollo et al., 2013a; Scarlato et al., 2014). The dependence of REE partitioning on tetrahedral aluminium reflects an increased ease of locally balancing the excess charge at M2 as the number of surrounding Al$^{\text{iv}}$ atoms increases. For example, the concentration of La in our clinopyroxenes progressively increases from 8 to 46 ppm as the molar Al/Si ratio decreases from 0.11 to 0.05 (Tables 1S and 2S). This matches with the consideration that clinopyroxenes can accommodate REE simply by adjusting their Al/Si ratios, without producing an energetically unfavourable vacancy (Hill et al., 2000; Wood and Trigila, 2001). The importance of site charge for achieving local charge balance is provided by the different behaviour of Sr and Co as divalent cations entering M2 and M1 sites, respectively. Since charge on the M2 site is the same in both CaMgSiO$_2$ and CaAl$_2$SiO$_6$, no correlation is found between $D_{\text{Sr}}$ and tetrahedrally-coordinated aluminum (cf. Hill et al., 2000). In contrast, the M1 site requires an increased net charge (2+ to 3+) to balance the increase in Al substitution for Si (cf. Mollo et al., 2013a), such that Co becomes less compatible as CaAl$_2$SiO$_6$ content increases (Fig. 3).

The lattice strain model
Fig. 4 shows that our apparent partition coefficients for REE and Y lie on parabola-like curves of Onuma diagrams (Onuma et al., 1968), resembling the regular trajectories found by Pappalardo et al. (2008) and Fedele et al. (2009) for magmas at Campi Flegrei. The height of the parabola depends on the crystal composition (Matsui et al., 1977; Blundy and Wood, 1994; 2003) and the physical conditions of the system (Blundy and Wood, 2001; Sun and Liang, 2012). Blundy and Wood (1994) provided a quantitative model for the parabolic trend of an isovalent series of cations with radius, \( r_i \), entering crystal lattice site M, where the partition coefficient, \( D_i \), can be described in terms of (i) the radius of the site, \( r_0 \), (ii) the elastic response of that site, \( E \) (as measured by Young’s Modulus), to lattice strain caused by cations that are larger or smaller than \( r_0 \), and (iii) the strain-free partition coefficient, \( D_0 \), for a (fictive) cation with radius \( r_0 \):

\[
D_i = D_0 \exp \left( \frac{-4 \pi EN_A \left( \frac{r_0}{2} (r_i - r_0)^2 + \frac{1}{3} (r_i - r_0)^3 \right)}{RT} \right)
\]

In Eqn. (1), \( N_A \) is Avogadro’s number \((6.022 \times 10^{23} \text{ mol}^{-1})\), \( R \) is the universal gas constant \((8.3145 \text{ J mol}^{-1} \text{ K}^{-1})\), and \( T \) is the temperature (in Kelvin). The effective use of the lattice strain model requires partition coefficients for a large range of isovalent cations of appropriate ionic radii for substitution into the M site. Therefore, to obtain reliable estimates and minimize the standard error, we focused on \( r_0 \), \( D_0 \), and \( E \) for the partitioning of trivalent REE and Y cations (Table 3S), as they form the largest group of isovalent elements in our analytical dataset. Except for one sample with \( D_0 ^{3+} \approx 1 \), we observe that, as a general rule, the peak position of our partitioning parabolas corresponds to \( D_0 ^{3+} \geq 1 \) when \( Al^{iv} \geq 0.09 \text{ apfu} \) and \( T \leq 950 \degree C \) (Tables 1S and 3S and Fig. 4). Otherwise, the peak position can be alternatively higher or lower than 1 as a function of \( Al^{iv} \) and \( T \), in agreement with the observation that these parameters have opposing effects on trace element partitioning (cf. Sun and Liang, 2012). Fitting of the parabolic trends indicates a good agreement between modelled and...
measured values of $D_0^{3+}$ (Table 4S and Fig. 4), suggesting the attainment of a thermodynamic equilibrium between phenocrysts and host magmas.

At first, $D_0^{3+}$ and $D_{\text{REE}}$ were taken to be independent of the Al$^{\text{IV}}$ content in clinopyroxene due to assumed complete short-range order between REE on M2 site and Al in T site in the molecule REEMgAlSiO$_6$ (e.g., Wood and Blundy, 1997). Subsequently, this assumption has since been found to be an oversimplification (Wood and Trigila, 2001; Hill et al., 2000; Tuff and Gibson, 2007, Mollo et al., 2013a; Scarlato et al., 2014), probably due to more complex charge-balance mechanisms than simple short-range order (Wood & Blundy, 2001). In Fig. 5, lattice strain-free partition coefficients for clinopyroxenes in trachy-phonolitic melts are compared with those obtained by previous studies on ultramafic, mafic and silicic compositions. $D_0^{3+}$ increases significantly with increasing tetrahedral aluminium, providing clear evidence of the effect of crystal composition on REE and Y partitioning. Importantly, three different trends are depicted in Fig. 5 for different bulk melt chemistries. The value of $D_0^{3+}$ and the slope of each single trend increase as a function of the melt composition (i.e., SiO$_2$), suggesting that the control of Al$^{\text{IV}}$ on $D_0^{3+}$ is mediated by the increasing silicic character of the bulk melt (Fig. 5). Gaetani (2004) observed that the magnitude of the partition coefficient correlates with the degree of melt polymerization due to a melt structural influence on trace element partitioning. The complementary results from Gaetani (2004) and Huang et al. (2006) noted that melt structure affects the trace element compatibility only if $\left[\text{NBO}/\text{T}\right]^{\text{melt}} < 0.4$. This is confirmed by our data showing a somewhat higher $D_0^{3+}$ for a lower $\left[\text{NBO}/\text{T}\right]^{\text{melt}}$ (Fig. 6a), although this parameter may not provide a comprehensive description of melt structure at a level relevant to trace element partitioning (e.g., Bennett et al., 2004). On this basis, Huang et al. (2006) found that $D_0^{3+}$ is better correlated with the ratio of molar $\left[\text{Ca}^{2+}/(\text{M}^{+}+\text{M}^{2+})\right]^{\text{melt}}$, where $\text{M}^{+}$ and $\text{M}^{2+}$ are, respectively, Na$^+$ and K$^+$, and Fe$^{2+}$, Ca$^{2+}$ and Mg$^{2+}$ of the melt given as percentages. Because of the similarity in ionic radius (and charge), REE$^{3+}$ are more likely to substitute for Ca$^{2+}$ in the melt than Mg$^{2+}$, Fe$^{2+}$, or alkalis, so that the value of $D_{\text{REE}}$ decreases according to the following exchange reaction (Huang et al., 2006):
\[ [\text{REE}_{2/3}\text{MgSi}_2\text{O}_6]^{\text{cpx}} + [\text{Ca-NBO}]^{\text{melt}} \leftrightarrow [\text{CaMgSi}_2\text{O}_6]^{\text{cpx}} + [\text{REE}_{2/3-\text{NBO}}]^{\text{melt}} \] (2)

Our data show that, for higher values of \([\text{Ca}^{2+}/(\text{M}^+ + \text{M}^{2+})]^{\text{melt}}\), there is an effective increase in the number of large structural sites critically important to accommodating large trace element cations in the melt, serving to reduce the partition coefficient (Fig. 6b). However, due to simultaneous effects of crystal and melt compositions on REE and Y partitioning, data in Fig. 6b do not align on a single linear fit for the substitution reaction described by Eqn. (2). To eliminate such an effect, some experiments should be designed for the comparison between clinopyroxenes with similar crystal-chemical formulas and compositionally distinct host melts (cf. Huang et al. 2006).

Testing the model of Wood and Blundy (1997)

Most of the mathematical expressions used to model the evolutionary behaviour of magma assume that the value of \(D_i\) remains constant throughout the entire differentiation process. This raises issues for petrological and geochemical modelling to (i) adopt the best possible partition coefficients, (ii) evaluate the extent to which these partition coefficients vary in the course of magma differentiation, (iii) find the physicochemical parameters that closely describe the variance of \(D_i\), and (iv) derive a good predictive model that is easy and rapid to use (e.g., based on microprobe analyses). In order to address all these issues, an increasing number of predictive equations for \(D_i\) have been derived in the last decades on the basis of thermodynamic approaches (e.g., Wood and Blundy, 1997, 2011; Hill et al., 2011), linear least squares regression analyses (e.g., Forsythe et al., 1994; Skulski et al., 1994; Gaetani and Grove, 1995) and multivariable nonlinear least squares analyses (Yao et al., 2012; Sun and Liang, 2012, 2013; Dygert et al., 2014). Among the number of equations found in literature, we have primary used the whole dataset for partition coefficients of Campi Flegrei (i.e., \(D_{\text{REE}}\) from this study, Pappalardo et al., 2008, and Fedele et al., 2009) to test the early predictive
model of Wood and Blundy (1997). The authors modelled the clinopyroxene–melt REE partitioning using the theoretical strain-free partition coefficient for 3+ cations in M2, which they then parameterised as a function of $P$ and $T$. By fitting experimental data to the temperature ($T$ in Kelvin) and pressure ($P$ in GPa) derivatives of the bulk and shear moduli of diopside, Wood and Blundy (1997) found a simple equation for calculating the Young’s Modulus for the trace elements of +3 charge in the M2 site of clinopyroxene:

$$E_{M2}^{3+} = 318.6 + 6.9P - 0.036T$$  \hspace{1cm} (3)

Given the expression (3) for $E_{M2}^{3+}$, the change of $r_0$ was also modelled through stepwise linear regression of the values of $r_0$ derived from literature data against all major compositional parameters, pressure and temperature. It emerged that only $X_{Al}^iv$ and $X_{Ca}^M$ were important controlling factors for $r_0$:

$$r_0 = 0.974 + 0.067X_{Ca}^M - 0.051X_{Al}^iv$$  \hspace{1cm} (4)

To calculate $D_0^{3+}$, a simple ionic equilibrium involving melt and clinopyroxene was considered:

$$\text{REE}_{\text{Melt}}\text{MgAlSiO}_6 = \text{REE}_{\text{Cpx}}\text{MgAlSiO}_6$$  \hspace{1cm} (5)

The equilibrium constant of the exchange reaction (5) is:

$$K_{ex}^{3+} = \frac{X_{REE}^M X_{Mg}^M X_{Al}^T X_{Si}^T}{X_{REE}^{\text{melt}} X_{Mg}^{\text{melt}} X_{Al}^{\text{melt}} X_{Si}^{\text{melt}}}$$  \hspace{1cm} (6)
In a thermodynamic approach based on the lattice strain theory, $X^{M_1}_{Mg}$ and $Mg\#^{melt}$ are the expression of the activity compositions of clinopyroxene ($a^{QX}_{REEMgAlSiO6} = X^{M_2}_{REE}X^{M_1}_{Mg}$) and melt ($a^{melt}_{REEMgAlSiO6} = X^{melt}_{REE}Mg\#^{melt}$), and $D_0^{3+}$ is the ratio of $X^{M_2}_{REE}$ to $X^{melt}_{REE}$. Using these parameters, the equilibrium constant (6) was rearranged as:

$$K_{ex}^{3+} = \frac{D_0^{3+}X^{M_1}_{Mg}}{Mg\#^{melt}}$$

(7)

If $\Delta H_T^0$, $\Delta S_T^0$, and $\Delta V$ refer to the differences in thermodynamic properties between pure melt and pure crystal, it was found that:

$$\Delta H_T^0 - T\Delta S_T^0 + P\Delta V - \frac{1}{2} \left( \frac{\partial\Delta V}{\partial P} \right)P^2 = RT \ln \left( \frac{D_0^{3+}X^{M_1}_{Mg}}{Mg\#^{melt}} \right)$$

(8)

The regression analysis of REE data from literature provided the best fit of the thermodynamic parameters on the left side of the reaction (8):

$$RT \ln \left( \frac{D_0^{3+}X^{M_1}_{Mg}}{Mg\#^{melt}} \right) - 7,050P + 770P^2 = 88,750 - 65.644T$$

(9)

When the dataset from the Campi Flegrei is used to test the equation (9), all the strain-free partition coefficients are successfully predicted (Fig. 7), and the regression analysis of measured vs. predicted values of $D_0^{3+}$ yields a very high correlation coefficient ($R^2 = 0.997$) and low standard error of estimate (SEE = 0.048). To account for the dependence of $D_i$ (Fig. 3) and $D_0^{3+}$ (Fig. 5) on the amount of aluminium in the tetrahedral site of clinopyroxene, Wood and Trigila (2001) re-fitted
the original calibration dataset of $D_0^{3+}$ by adding Al$^{iv}$ as predictor to the $P$ and $T$ parameters previously employed. It was found, however, that the tetrahedral aluminium is not statistically significant for the predictive equation (9) and that $D_0^{3+}$ is adequately described in terms of pressure and temperature only. Moreover, when the value of $D_0^{3+}$ is modelled after Wood and Blundy (2001) assuming local charge balance between REE in the M2 site and adjacent Al$^{iv}$ within clinopyroxene (i.e., $[REE]^{ps}/[X^{3+}]$, where $[X^{3+}]$ is the proportion of M2 sites charge-balanced by a 3+ cation), we found that the ability prediction of equation (9) does not substantially change ($R^2 = 0.997$ and SEE = 0.046; Fig. 7). On the other hand, Wood & Blundy (1997) assumed for simplicity that the activity of REE in the melt is equal to its concentration, thus ignoring that the melt structure may potentially control $D_0^{3+}$. Indeed, data plotted on Fig. 6a seems to suggest that $X^{melt}_{REE}$ is better described by $[REE]^{melt}/[Ca^{2+}/(M^++M^{2+})]^{melt}$ rather than the simple concentrations of REE in the melt. Therefore, we have incorporated the melt structure parameter into the predictive equation (9) but the regression analysis of measured vs. predicted values did not provide any improvement for the prediction of $D_0^{3+}$ ($R^2 = 0.994$ and SEE = 0.063; Fig. 7). The same conclusion was reached in recent studies for the partitioning of REE and Y between clinopyroxene/orthopyroxene and picritic/basaltic melts (Yao et al., 2012; Sun and Liang, 2012, 2013). This finding is apparently in contrast with the effects of $[NBO/T]^{melt}$ and $[Ca^{2+}/(M^++M^{2+})]^{melt}$ on the lattice-free partition coefficient (Fig. 6). One possible explanation is that, for moderately to highly depolymerized magmas, $[NBO/T]^{melt}$ is constantly higher than the threshold value of 0.4 (cf. Sun and Liang, 2012), whereas its value is persistently lower than 0.2 for polymerized magmas (Fig. 6a). On the other hand, due to the strong rival effects of $X^{iv}_{Al}$, $P$, and $T$, no obvious correlations are found between $[Ca^{2+}/(M^++M^{2+})]^{melt}$ and $D_0^{3+}$ when pressure, temperature, and clinopyroxene components change at the same time (cf. Huang et al., 2006). As these parameters are to some extent interdependent, it is not easy to differentiate between their relative influences over a broad range of crystallization conditions and compositions (crystal and melt). It can be concluded that the role of melt chemistry is to reduce the number of melt sites onto which REE can be accommodated. Thus, the melt structure can
potentially control the partitioning of trace elements over a wide spectrum of melt compositions (Fig. 6). However, for an isolated bulk melt composition, the final value of the REE partition coefficient is also determined by the relative (rival) effects of pressure, temperature and mineral chemistry.

Using a calibration dataset specific to basaltic compositions, Wood and Blundy (1997) found that \( P \) and \( T \) closely describe the variance of \( E \) according to the regression equation (3), whereas \( X_{Al}^{M1} \) and \( X_{Cu}^{M2} \) are the best predictors for \( r_0 \), as provided by the best fitting equation (4). Further nonlinear regression calculations performed by Sun and Liang, (2012) and Yao et al. (2012) on a more recent basaltic dataset provided that \( X_{Mg}^{M2} \) and \( X_{Al}^{M1} \) can also be suitable predictors for \( r_0 \).

Due to the strong relationship between \( E \) and \( r_0 \), Wood and Blundy (1997) preferred to estimate the value of Young’s modulus using only \( P \) and \( T \). Conversely, an intrinsic trade-off between \( E \) and \( r_0 \) was also found by Sun and Liang, (2012) that favoured calculating \( E \) as a linear function of \( r_0 \). The authors demonstrated that the dependence of \( E \) and \( r_0 \) on the same clinopyroxene components does not weaken the predictive power of the lattice strain model. However, in multiple linear regression analyses some variables may closely describe the variance of the dataset, whereas some others may generate a set of predictions with low degrees of freedom that lead to strong data overfitting. Therefore, variables that do not improve the fit must be identified and removed from a model.

Through an algorithm based on the Mallows’ \( Cp \) statistic, we have performed systematic permutations of a number of independent variables to derive the best predictive models for \( r_0 \), and \( E \). Mallows’ \( Cp \) is expressed as (Hair et al., 1995):

\[
Cp = \frac{RSS_k}{RSS_p} - n + 2p \tag{10}
\]

\( RSS_k \) is the ratio of the residual sum of squares of all predictors \( k \), \( RSS_p \) is the residual sum of squares of only \( p \) of the \( k \) predictors, and \( n \) is the number of observations. Mallows’ \( Cp \) is a measure
of the bias in a model: if the type and number of selected predictors \( p \) (including the constant term in linear regression) are sufficient to provide a good description of the data, then \( C_p \) has values as close as possible to \( p \). The independent variables used for permutations were \( X_{Al}^{iv} \), \( X_{Al}^{M1} \), \( X_{Ca}^{M2} \), \( X_{Na}^{M2} \), \( X_{Mg}^{M2} \), \( [Ca^{2+}/(M^{2+}+M^{2+})]^{melt} \), \( [NBO/T]^{melt} \), \( P \) and \( T \). Results are reported in Table 6S together with the mean squared error (MSE), \( R^2 \), \( p \), and \( C_p \). The Mallows’ \( C_p \) statistic indicates that \( E \) and \( r_0 \) are both primary influenced by the same variables (i.e., \( X_{Ca}^{M2} \) and \( X_{Mg}^{M2} \)), corroborating the observation of Sun and Liang (2012) that \( E \) is indeed linearly correlated to \( r_0 \) (\( R^2 = 0.968 \)). In contrast, the temperature, pressure and melt composition have minor effects on these parameters, as would be expected given (a) these are crystal-chemical parameters and (b) that the thermal expansivity of the M2 site is relatively small for the temperature range considered here (Nimis, 1999). Therefore, using \( X_{Ca}^{M2} \) and \( X_{Mg}^{M2} \) as independent variables, we have performed a multiple linear regression analysis of the data from the Campi Flegrei to derive an improved predictive model for \( E \) (Fig. 8a):

\[
E = -82.35 + 636.56 X_{Ca}^{M2} - 253.29 X_{Mg}^{M2}
\] (11)

The statistics (\( R^2 = 0.967 \) and SEE = 4.72) of the equation (11) are much better than those observed for the original equation (3) when \( T \) and \( P \) of trachy-phonolitic magmas are used as input data (\( R^2 = 0.495 \) and SEE = 17.78). Through the same approach, we have also derived a predictive model for \( r_0 \) (Fig. 8b):

\[
r_0 = 1.0231 + 0.0278 X_{Ca}^{M2} - 0.0101 X_{Mg}^{M2}
\] (12)

The equation (12) produces an improved fit to the data of the Campi Flegrei (\( R^2 = 0.954 \) and SEE = 0.002). Conversely, clinopyroxene compositions from trachytes and phonolites provide low
statistics for $X_{Al}^{M1}$ and $X_{Cu}^{M2}$ ($R^2 = 0.552$ and $SEE = 0.007$), as predictors of the original equation (4).

It is apparent that the uncertainty measured for the recalibrated equations (11) and (12) is reasonably low due to the restricted bounds of the calibration dataset that, in turn, closely describe the crystallization conditions and compositions of magmas at Campi Flegrei (Fig. 1 and Table 1S). On the other hand, the original equations (3) and (4) of Wood and Blundy (1997) were calibrated using primitive compositions obtained prevalently at high-temperatures that, in turn, do not reproduce the variability internal to the trachy-phonolitic dataset. For example, the percentage error of $E$ predicted by the equation (3) increases as the temperature decreases (Fig. 9a) due to the fact that thermal conditions below 1,100 °C are not adequately represented into the calibration dataset of Wood and Blundy (1997). Fig. 9a shows that this is valid either to natural alkaline differentiated magmas from this study or to experimental basaltic compositions equilibrated at relatively low temperatures (data from experiments of Green et al., 2000 and Adam and Green, 2006). Conversely, Fig. 9b shows that the equation (11) has a very low percentage error of $E$ at temperatures below 1,050 °C, but the error progressively increases with temperature, although $T > 1,100$ °C are rarely recorded by alkaline differentiated products. This simple test clearly makes the recalibrated equations (11) and (12) not suitable for high-temperature primitive magmas. We also observe that values of $E$ and $r_0$ from basaltic and more differentiated compositions are scattered through the literature, consequently, the global regression analysis of these data did not provide statistically significant parameters applicable over a wide range of temperatures, pressures, and compositions.

In the online supplementary material, we provide an Excel spreadsheet in which equations (9), (11), and (12) are incorporated, and that can be used to predict $D_{REE}$ and $D_Y$ through major element analyses of clinopyroxene in equilibrium with trachy-phonolitic magmas. In Fig. 10a we have compared the standard error of estimate of each partition coefficient predicted by (i) the original model of Wood and Blundy (1997), (ii) the Excel spreadsheet from this study, and (iii) the parameterized model of Sun and Liang (2012). It is worth noting that this latter model was
calibrated specifically to basaltic systems. With respect to the original model of Wood and Blundy (1997), our recalibrated model offers little improvements in the prediction of $D_{\text{LREE}}$, whereas its accuracy is remarkably high for most of the $D_{\text{HREE}}$ values. Conversely, the model of Sun and Liang (2012) is affected by a systematic uncertainty in the prediction of $D_{\text{LREE}}$. This is not surprising if we consider that the model was parameterized over crystallization conditions and compositions rather different to those presented in this study. However, in the case of $D_{\text{Tm}}$, $D_{\text{Yb}}$ and $D_{\text{Lu}}$, the standard error of estimate is found to be lower than that of other models. This is due to the fact that the model of Sun and Liang (2012) tends to overestimate the value of $E$ that, in turn, reduces the width of the partitioning parabola with minor effects on trace elements having low ionic radii. For example, measured vs. predicted values for $D_{\text{Ce}}$ (Fig. 10b) and $D_{\text{Yb}}$ (Fig. 10c) show that partition coefficients for larger LREE cations predicted by the model of Sun and Liang (2012) deviate significantly from the one-to-one line, whereas partition coefficients for smaller HFSE cations approach to the one-to-one line much better than those predicted by other models (see also Table 7S for the whole dataset).

Applications to the Campanian Ignimbrite

As anticipated from the preceding discussion, the dependence of trace element partitioning on $P$, $T$, and composition (crystal and melt) results in a variety of $D_i$ values. However, most of the petrological models from literature assume for simplicity that $D_i$ is independent on the physicochemical conditions of system, despite such an assumption is unlikely during crystallization of natural magmas. In order to clearly demonstrate the importance of considering the change of $D_i$ for a better understanding of magmatic differentiation, we have selected four natural clinopyroxene-melt pairs representative of the internal compositional variability of the Campanian Ignimbrite eruption (data from Civetta et al., 1997 and Arienzo et al., 2009). These data yield $\Delta D_{\text{Hd}}$ between 0.01 and 0.12 suggestive of near-equilibrium crystallization conditions (Mollo et al., 2013a), but are...
also characterized by distinct features in terms of $P$, $T$, and composition (Table 8S). In particular, thermometers and barometers of Masotta et al. (2013) suggest that the natural clinopyroxene-melt pairs equilibrated at 100-300 MPa and 914-982 °C, in agreement with previous estimates from petrological (e.g., Fulignati et al., 2004; Marianelli et al., 2006; Fowler et al., 2007) and geophysical (e.g., Zollo et al., 2008) studies. As discussed above, the effect of pressure on trace element partitioning between clinopyroxene and melt can be considered negligible at shallow crustal depths.

On the other hand, there is a well-documented inverse correlation between the concentration of water dissolved in the melt and $D_{\text{REE}}$ (cf. Blundy et al., 2002; Gaetani, 2004; Sun and Liang, 2012). For trachytic and phonolitic compositions, it is not clear to what extent H$_2$O can influence $D_{\text{REE}}$ during magma differentiation. Undoubtedly, the macroscopic effect of increasing water is to depress the liquidus temperature of the melt (Putirka, 2008). However, we have already tested that a water change of ±2 wt.% in trachytic and phonolitic magmas corresponds to a negligible temperature variation of ±12 °C. According to Mollo and Masotta (2014), low $\Delta$DiHd values allow to (1) minimize significantly the uncertainty of barometers and thermometers, and (2) find a good correspondence between the crystallization temperature of magma and the geochemical evolution of clinopyroxene. This latter point is better explained in Fig. 11a where $Mg^{\#}_{\text{Mg}}$ correlates positively with $T$, evidencing the relative effects of temperature and clinopyroxene composition on trace element partitioning. Only when magnitudes of these two opposing effects are reciprocally compensated, a set of nearly constant partition coefficients can be expected. Otherwise, temperature and clinopyroxene composition dominate over the final value of $D_n$, hence controlling the partitioning of trace elements during magma crystallization (e.g., Sun and Liang, 2012). Each symbol plotted on Fig. 11a refers to the value of $D_0^{3+}$ predicted using the Excel spreadsheet from this study. $D_0^{3+}$ increases from 0.67 to 0.91 with decreasing both $T$ and $Mg^{\#}_{\text{Mg}}$. In this view, the whole range of values calculated for $D_{\text{REE}}$ and $D_Y$ has been used as input data for the Rayleigh fractional crystallization equation (FC):
\[ C_l^{FC} = C_0 F^{(D-1)} \]  

Where \( C_l^{FC} \) is the concentration of an element in remaining melt during fractional crystallization, \( C_0 \) is the concentration of the trace element in parental liquid (starting composition), \( D_i \) is the partition coefficient of the trace element of interest whose value changes as a function of the physicochemical conditions of the system (see below), \( F \) is the fraction of melt remaining during crystallization. At the beginning of the modelling, low degrees of clinopyroxene fractionation (i.e., 3\%, 5\%, 7\%, and 9\%) have been considered to constrain its early effect as liquidus phase on the geochemical signature of magma. Stepwise calculations were performed changing the clinopyroxene composition and temperature at each step of fractionation (Fig. 11a), in order to derive a set of four different partition coefficients rather than one single value. In Fig. 11b, modelled Ce and Y concentrations are compared with those of rock samples from the Campanian Ignimbrite. Notably, the ratio of Ce/Y for the Campanian Ignimbrite eruption changes significantly from 0.21 to 0.33, in contrast to what would be expected for igneous products sharing a common parental magma. This discrepancy is reconciled by the nonlinear trajectory of the cpxFC vector that is controlled by the variation of the partition coefficient. Thus, at the early stage of clinopyroxene crystallization, the incorporation of variable proportions of Ce and Y into the crystal lattice provides explanation for the strong variability of the natural dataset. According to Civetta et al. (1997), the internal differentiation of the Campanian Ignimbrite can be addressed to the fractionation of \(<10\% \) and \(~50\% \) of clinopyroxene and feldspar, respectively. Considering that Ce and Y are highly incompatible in feldspar \( (D_{Ce} = 0.039 \) and \( D_Y = 0.017; \) Larsen, 1979), further fractional crystallization steps have been developed accounting for the segregation of 50\% of feldspars from the solidifying magma. Notably, due to the highly incompatible behaviour of Ce and Y, feldspar fractionation may only increase the REE content in magma but cannot control the internal REE variability of the Campanian Ignimbrite eruption. Modelling results are aligned along four different FC trajectories (i.e., from \(^{kfs}FC1\) to \(^{kfs}FC4\)) that faithfully reproduce the entire differentiation path of
the Campanian Ignimbrite, from lowest to highest Ce/Y ratios (Fig. 11a). Clearly, the constancy of
the clinopyroxene-melt partition coefficient would yield only one single FC trend that, in turn, is
inadequate to reproduce in full the complex trace element pattern of natural products. Therefore, the
process responsible for the heterogeneous REE concentrations of the Campanian Ignimbrite
products is twofold: (1) the early fractionation of clinopyroxene at relative high temperature and (2)
the subsequent fractionation of feldspars during the final stage of magma cooling (cf. Fowler et al.,
2007). Additional complexities, including crystallization of other phases (oxides, biotite, apatite)
and partial cumulate mush remelting (e.g., Wolff et al., 2015) can further explain some of the trace
element variations observed in the Campanian Ignimbrite.

Conclusions

Coherently with previous natural and experimental studies, we documented that the partitioning of
trace elements between clinopyroxene and trachy-phonolitic melts can be addressed to (1) the entry
of REE+Y and HFSE in the M2 and M1 sites, respectively, due to substitution of Si^{4+} with Al^{iv}, (2)
the increased net charge on the M1 site that causes divalent TE to become less compatible within
clinopyroxene crystal lattice, (3) a charge-balanced cation substitution reaction reflecting an
increased ease of locally balancing the excess charge as the number of surrounding tetrahedrally-
coordinated aluminium atoms increases, and (4) the effect of changes in melt structure that increase
the number of large sites critically important to accommodating large REE cations. On the other
hand, we tested that the incorporation of additional crystallochemical parameters (assuming local
charge balance between REE in the M2 site and adjacent Al^{iv}) and melt structure parameters (given
as the ratio of non-bridging oxygens to tetrahedral cations and/or the ratio of molar calcium to the
sum of monovalent and divalent cations) into the lattice strain model of Wood & Blundy (1997) did
not provide any improvement for its ability prediction. This is due to the strong rival effects of
pressure, temperature, and crystal/melt parameters. Therefore, over a broad range of crystallization
conditions and crystal/melt compositions, it is not possible to differentiate between the relative influence of each single parameter on REE+Y partitioning. As a consequence, no obvious correlations are found when the physicochemical conditions of the system change at the same time. According to the lattice strain theory, we observe that, $D_{0}^{3+}$, $r_{0}$ and $E$ can be successfully predicted once $T$, $P$, $X_{Cu}^{Mg}$ and $X_{Mg}^{Mg}$ are known for trachy-phonolitic compositions. On this basis, we updated the existing partitioning equations to derive a self-consistent model for trachy-phonolitic magmas. The application of this model to natural products from the Campanian Ignimbrite, the largest caldera-forming eruption at the Campi Flegrei, reveals that the complex REE pattern of magma can be successfully described by the stepwise fractional crystallization of clinopyroxene and feldspar where the clinopyroxene-melt partition coefficient changes progressively as a function of the physicochemical conditions of the system.

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**Figure captions**

Fig. 1. The compositions of host melts and clinopyroxene phenocryst cores from this study are compared with those of natural products at Campi Flegrei in terms of total alkali vs. silica of the melt (a), ΣHREE vs. ΣLREE of the melt (b), Di vs. Hd of clinopyroxene, and (c) ΣHREE vs. ΣLREE of clinopyroxene. Natural data from Villemant (1988), Civetta et al. (1997), Fulignati et al. (2004), Marianelli et al. (2006), Fedele et al. (2007), Pappalardo et al. (2002; 2008), and Arienzo et al. (2009).

Fig. 2. Example of the textural features of clinopyroxene phenocrysts from this study. (a) Backscattered electron images show that crystals are euhedral and complex zoning patterns are absent. Microprobe compositional profiles reveal the occurrence of some chemical heterogeneities
at the crystal-melt interface. (b) Diffusive boundary layer occurs into the glass next to clinopyroxene rims showing Al and Na enrichments (see also data in Table 5S).

Fig. 3. Plots of partition coefficients for HFSE (Ti, Zr, Nb, Ta), REE (La) and TE (Co) vs. Al$^{iv}$. Data from this study have been compared with those from literature to highlight the dependence of $D_i$ on Al$^{iv}$.

Fig. 4. Plots of partition coefficients for REE and Y vs. ionic radii (data from Shannon 1976) for the samples object of this study. The near parabolic dependence found by Onuma et al. (1968) dictates the distribution of the data. The lines show fits to the lattice strain model of Blundy and Wood (1994). Fit parameters are listed in Table 4S. The agreement of our data with the model emphasizes the importance of lattice strain in controlling REE and Y partitioning at equilibrium crystallization conditions.

Fig. 5. Plots of $D_0^{3+}$ for clinopyroxene-melt partitioning of REE vs. Al$^{iv}$ content in clinopyroxenes from this study and previous works. $D_0^{3+}$ is calculated through the lattice strain model of Blundy and Wood (1994).

Fig. 6. Plot of $D_0^{3+}$ for clinopyroxene-melt partitioning of REE vs. $NBO/T$ of the melt. (a) Our data for trachy-phonolitic melts are compared with those from literature obtained for highly polymerized silicic melts, and moderately-to-poorly polymerized silicic melts. According to Gaetani (2004) and Huang et al. (2006) the melt structure have a significant influence on partition coefficients for $[NBO/T]^{melt}$ values higher than 0.4. (b) Plot of $D_0^{3+}$ for clinopyroxene–melt partitioning of REE vs. $[Ca^{2+}/(M^{+}+M^{2+})]^{melt}$, where $M^{+}$ and $M^{2+}$ are Na$^{+}$+K$^{+}$ and Fe$^{2+}$+Ca$^{2+}$+Mg$^{2+}$, respectively. The negative correlation between $D_0^{3+}$ and $[Ca^{2+}/(M^{+}+M^{2+})]^{melt}$ confirms the reliability of Eqn. (2)
favouring large structural sites critically important to accommodating large trace element cations in the melt.

Fig. 7. Clinopyroxene-melt pairs from this study, Pappalardo et al. (2008) and Fedele et al. (2009) have been used as input data for the original equation for $D_0^{3+}$ derived by Wood and Blundy (1997). New predictors have been also introduced in this equation, i.e., $[REE]^{\text{cpx}}/[X^{\text{cpx}}]$ (after Wood and Blundy, 2001) and $[REE]^{\text{melt}}/[Ca^{2+}/(M^+ + M^{2+})]^{\text{melt}}$. The analysis of predicted vs. measured values indicates that these new predictors do not offer improvements for the ability prediction of the original equation of Wood and Blundy (1997).

Fig. 8. Clinopyroxene-melt pairs from this study, Pappalardo et al. (2008) and Fedele et al. (2009) have been used as input data for the original equations for (a) $E$ and (b) $r_0$ derived by Wood and Blundy (1997). The analysis of predicted vs. measured values indicates that these equations are affected by a high uncertainty. The best fitting equations have been derived through the regression analysis of trachy-phonolitic data using $X_{Ca}^{M^2}$ and $X_{Mg}^{M^2}$ as predictors.

Fig. 9. The predictive equations for $E$ from (a) Wood and Blundy (1997) and (b) this study have been tested using trachy-phonolitic (this study, Pappalardo et al., 2008 and Fedele et al., 2009) and basaltic (Green et al., 2000 and Adam and Green, 2006) data. For the original equation of Wood and Blundy (1997), the percentage error of $E$ increases with decreasing temperature. The opposite occurs for the equation from this study showing low ability prediction for high-temperature basaltic magmas.

Fig. 10. $D_{\text{REE}}$ and $D_{\text{Y}}$ “measured” in this study are compared with those “predicted” by the original model of Wood and Blundy (1997), the parameterized model of Sun and Liang (2012) for basaltic compositions, and the recalibrated model from this study for trachy-phonolitic compositions. (a)
Comparison of the standard error of estimate. (b) Comparison of $D_{Ce}$ values as representative of partitioning of larger LREE cations. (c) Comparison of $D_{Yb}$ values as representative of partitioning of smaller LREE cations.

Fig. 11. Natural clinopyroxene-melt pairs from the Campanian Ignimbrite have been used as input data for the thermobarometer of Masotta et al. (2013) and the trace element model presented in this study. (a) Temperature vs. $Mg^{\#}_{\text{cpx}}$ diagram shows that the geochemical evolution of clinopyroxene parallels the decreasing temperature of magma. Each symbol plotted on the diagram refers to the value of $D_{0}^{3+}$ predicted using the Excel spreadsheet from this study. $D_{0}^{3+}$ is found to increase from 0.60 to 0.85 with decreasing both $T$ and $Mg^{\#}_{\text{cpx}}$. (b) Ce vs. Y diagram showing the geochemical evolution of the Campanian Ignimbrite modelled through the Rayleigh fractional crystallization equation. At the beginning of the modelling, low degrees of clinopyroxene fractionation (i.e., 3%, 5%, 7%, and 9%) have been considered. Stepwise calculations were performed changing the clinopyroxene composition and temperature at each step of fractionation. Modelled Ce and Y concentrations were used to draw the $\text{cpxFC}$ vector. Fractional crystallization calculations were further developed accounting for the segregation of ~50% of K-feldspar from the solidifying magma. Modelling results are aligned along four different FC trajectories (i.e., from $\text{kfsFC1}$ to $\text{kfsFC4}$).
Figure 5

- Silicic alkaline aluminous melts
- Trachytic and phonolitic melts
- Ultramafic and mafic melts

- This study
- ▲ Mollo et al. (2013)
- ✗ Fedele et al. (2009)
- ◇ Pappalardo et al. (2008)
- ◊ Huang et al. (2006)
- ◊ Gaetani (2004)
- ✗ Wood and Trigila (2001)
- ▲ Gallahan and Nielsen (1992)
- ▲ MacKay et al. (1986; 1994)
Figure 10

(a) Standard error of estimate

(b) D_{Ce} predicted vs. D_{Ce} measured (ppm)

(c) D_{Yb} predicted vs. D_{Yb} measured (ppm)

Legend:
- This study
- Sun and Liang (2012)
- Wood and Blundy (1997)

D values of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu
Values of $D_0^{3+}$ predicted using clinopyroxene-melt pairs from the Campanian Ignimbrite eruption:

- **□**: 0.91
- **▲**: 0.85
- **●**: 0.73
- **◆**: 0.67

**Figure 11**

(a) Temperature °C vs. Mg#\textsubscript{cpx}.

(b) Y (ppm) vs. Ce (ppm) for the Campanian Ignimbrite eruption, showing geochemical variability.

- Feldspar fractionation (50%)
- Clinopyroxene fractionation (9%)
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Cpx-melt D model for trachy-phonolitic compositions
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