



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 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.

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1. 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 [$D_i = x_{\text{LS}}^{\text{cpx}}(I)/x_{\text{LS}}^{\text{melt}}(I)$ on a weight basis] is generally assumed to be constant for magma modelling. However, this simple approximation does not take into account 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 ($X_{\text{Mg}}^{\text{M1}}$), Mg-number of the melt [$\text{Mg\#}^{\text{melt}} =$

$X_{\text{Mg}}^{\text{melt}} / (X_{\text{Fe}}^{\text{melt}} + X_{\text{Mg}}^{\text{melt}})$], 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 $X_{\text{Na}}^{\text{M2}}$ due to the higher incorporation of Na^+ in M2 with increasing P , for example via the hypothetical end-member $\text{Na}_{0.5}\text{REE}_{0.5}\text{MgSi}_2\text{O}_6$. 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 $X_{\text{Al}}^{\text{iv}}$ and $X_{\text{Mg}}^{\text{M2}}$, and negatively correlated with T and H_2O dissolved in the melt. Gaetani et al. (2003) attributed the decrease of D_{REE} with increasing H_2O 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

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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.

2. 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 (D'Antonio, 2011; Marianelli et al., 2006; Pabst et al., 2008; Signorelli et al., 2001; Webster et al., 2003).

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 1080 °C (Fedele et al., 2009; Fowler et al., 2007; Fulignati et al., 2004; Marianelli et al., 2006; Masotta et al., 2013). Melt inclusion measurements and hygrometric predictions indicate a melt–water concentration ranging from 3 to 6 wt.% (Marianelli et al., 2006; Mollo et al., 2015b; Signorelli et al., 2001; Webster et al., 2003). 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 and Mastrolorenzo, 2012; Pappalardo et al., 2008).

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 ~1000 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).

3. Analytical methods

Field emission gun scanning electron microscope (FE-SEM) images and electron probe micro analyses (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 s. 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.

4. 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

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