Petrogenesis of the Campanian Ignimbrite: Implications for Crystal-Melt Separation and Open-System Processes from Major and Trace Elements and Th Isotopic Data

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ABSTRACT
The Campanian Ignimbrite is a large volume trachytic to phonolitic ignimbrite that was deposited at ~39.3 ka and represents one of a number of highly explosive volcanic events that have occurred in the region near Naples, Italy. Thermodynamic modeling using the MELTS algorithm reveals that major element variations are dominated by crystal-liquid separation at 0.15 GPa. Initial dissolved H₂O content in the parental melt is ~3 wt., and the magmatic system fugacity of oxygen was buffered along QFM + 1. Significantly, MELTS results also indicate that the liquid line of descent is marked by a large change in the proportion of melt (from 0.46 to 0.09) at ~884°C, which leads to a discontinuity in melt composition (i.e., a compositional gap) and different thermodynamic and transport properties of melt and magma across the gap. Crystallization of alkali feldspar and plagioclase dominates the phase assemblage at this pseudo-invariant point temperature of ~884 °C. Evaluation of the variations in the trace elements Zr, Nb, Th, U, Rb, Sm, and Sr using a mass balance equation that accounts for changing bulk mineral-melt partition coefficients as crystallization occurs indicates that crystal-liquid separation and open-system processes were important. Th isotope data yield an apparent isochron that is ~20 kyr younger than the age of the deposit, and age-corrected Th isotope data indicate that the magma body was an open-system at the time of eruption. Because open-system behavior can profoundly change isotopic and elemental characteristics of a magma body, these Th results illustrate that it is critical to understand the contribution that open-system processes make to magmatic systems prior to assigning relevance to age or timescale information derived from such systems. Fluid-magma interaction has been proposed as a mechanism to change isotopic and elemental characteristics of magma bodies, but an evaluation of the mass and thermal constraints on such a process suggests large-scale interaction is unlikely. In the case of the magma body associated with the Campanian Ignimbrite, the most likely source of the open-system signatures is assimilation of partial melts of compositionally heterogeneous basement composed of cumulates and intrusive equivalents of volcanic activity that has characterized the Campanian region for over 300 kyr.
INTRODUCTION

Recognition that chemical and physical gradients preserved in ignimbrites yield insight into pre-eruptive magma dynamics (e.g., Smith, 1979; Hildreth, 1979) has profoundly influenced the understanding of crustal magmatism. Studies during the last 25 years have revealed that, while the concept of reconstructing magma bodies from information about deposits is of fundamental value, significant challenges of interpretation are introduced by the dynamics of eruption (e.g., Spera, 1984; Wilson and Hildreth, 1997) as well as the panoply of mechanisms by which melt, exsolved volatile bubbles and crystals form, mix and unmix (e.g., Smith and Bailey, 1966; Hildreth, 1981; Worner and Schmincke, 1984a, 1984b; Bacon and Druitt, 1988). Accurate reconstruction of the pre-eruptive structure of the magmatic plumbing system depends upon integration of field data, multi-scale petrological and geochemical studies of the full range of erupted products, and theoretical modeling. Also, a comprehensive understanding of the processes responsible for generating the physical and chemical gradients requires an approach that blends descriptive and quantitative constraints.

Although significant progress has been made toward a holistic understanding of how large volume, intermediate to silicic composition crustal reservoirs form, two fundamental questions remain especially controversial: What processes quantitatively contribute to the major and trace element and isotopic heterogeneity of volcanic products of these large volume eruptions? And over what time scales do the associated magma bodies form and/or coalesce? The answers to these questions are different for different systems, but a detailed analysis that incorporates thermal, chemical and mass constraints for each system is prerequisite for making generalized observations about the behavior of magmatic systems.

In this contribution, we highlight the impact that crystal-liquid separation has on melt compositional evolution and particularly focus on trace element and Th isotope evidence for open-system processes in the magma body associated with the Campanian Ignimbrite (CI), a large volume pyroclastic deposit that outcrops in the vicinity of the densely populated city of Naples, Italy. This ~39.3 ka eruption is one of a number of explosive eruptions documented in the Campanian magmatic province, with the oldest dated at >300 ka (De Vivo et al., 2001). Thus, understanding the dynamics of the magma body associated with the CI, which is the largest identified eruption in the Mediterranean in the last 200 kyr (Barberi et al., 1978), will lend perspective to a much longer history of violent, destructive eruptions that have occurred
over timescales of at least $3 \times 10^5$ years. Our interpretations, which build on previous contributions (e.g., Fisher et al., 1993; Orsi et al., 1996; Civetta et al., 1997; Signorelli et al., 1999; De Vivo et al., 2001; Pappalardo et al., 2002; Rolandi et al., 2003), utilize thermodynamic and quantitative mass balance modeling of major and trace element data and semi-quantitative limits on Th and Sr isotopes to evaluate the role of crystal-melt separation, magma-fluid interaction, and assimilation of wallrock on the geochemical evolution of the CI. We find that the major element trends in the CI are dominated by crystal-melt separation. Based on results of detailed MELTS calculations (Ghiorso and Sack, 1995), we provide strong evidence for a dramatic episode of multi-phase crystallization, in which, over a very small temperature interval centered around $884 ^\circ C$, the proportion of residual melt in the system changes from $\sim 0.46$ to 0.09. The behavior of trace elements in the system is quantitatively evaluated using the major element results. One of the significant conclusions that emerges is that dramatic changes in phase assemblage that occur during isobaric fractionation yield large variations in bulk mineral-melt partition coefficients (bulk $K_{sm}$) over very small temperature intervals. Quantitative assessment of trace element concentrations using a mass balance equation that properly accounts for changing bulk $K_{sm}$ demonstrates the profound control solid-melt partitioning can have on trace element evolution as well as the challenges of interpretation (e.g., whether trace elements have been impacted by open-system processes or not) that emerge because, in some cases, published trace element mineral-melt partition coefficients (mineral-melt $K_{sm}$) vary significantly within a small compositional range. New Th isotope data, coupled with an evaluation of published Sr isotope data (Civetta et al., 1997), reveal evidence for open-system processes that most likely involve complex interaction between magma and intrusive equivalents of Campanian volcanics and/or cumulates formed in association with Campanian magmatism.

**PREVIOUS WORK**

**Regional Geology**

The Campanian Plain is a region of southern Italy that encompasses the Phlegrean Fields (Campi Flegrei - burning fields), which are located west of Naples (Figure 1a). The Plain is structurally located within a graben formed in Mesozoic carbonate of the southern Apennine Mountains, which border the Plain on the east and north. The graben formed during the Pliocene as a consequence of extension that occurred along the western margin of the Apennine chain,
resulting in subsidence along the Tyrrhenian coast (Scandone et al., 1991; Rosi and Sbrana, 1987). The Phlegrean Fields are characterized by a long history of magmatism dating back to at least 300 ka, based on Ar/Ar ages of xenocrystic sanidine identified in pyroclastic material sampled in the Campanian Plain (De Vivo et al., 2001). This region of southern Italy is famous not only for eruptions in the Phlegrean Fields, including the most recent eruption of Monte Nuovo in A.D. 1538, but also for the famed A.D. 79 eruption of Vesuvius that destroyed the villages of Pompeii and Herculaneum. Vesuvius most recently erupted in A.D. 1944. The volcanology of the Naples area has been of interest for centuries, particularly because of the vivid descriptions of the A.D. 79 eruption of Vesuvius by Pliny the Younger. Continued scrutiny of the volcanology and petrology of this area is warranted by the potentially lethal combination of eruption from either the Phlegrean Fields or Vesuvius, coupled with the densely populated, highly urbanized areas in and around Naples; this combination presents significant challenges for volcanic hazard mitigation.

**Volcanology and Geochronology of the Campanian Ignimbrite**

The Campanian Ignimbrite, a large volume (~150 km$^3$, Civetta et al., 1997, to ~200 km$^3$ DRE, Rolandi et al., 2003) trachytic-phonolitic ignimbrite, was originally distributed over ~30,000 km$^2$ in and around Naples, Italy (Fisher et al., 1993). While previous ages for the CI have been reported at ~37 ka (e.g., Deino et al., 1992; 1994), more recently, the deposit has been precisely dated at 39.28±0.11 ka by incremental heating and total fusion $^{40}$Ar/$^{39}$Ar geochronology (De Vivo et al., 2001). This age represents the weighted mean of results from eighteen alkali feldspar separates derived from representative units within the CI from a variety of geographic locations. Based on the detailed work of De Vivo et al. (2001), the CI is composed of up to 5 physically distinct units. The gray tuff unit of the CI grades upward into a yellow tuff, the color of which reflects secondary mineralization by zeolites. In several sections throughout the Campanian Plain, the gray tuff is overlain by a lithic breccia that grades upward into either a weakly stratified yellow tuff and/or an incoherent pyroclastic flow deposit. The lithic breccia is discontinuously exposed around the Campanian Plain, and in some locations, shows evidence of proximal depositional characteristics. Significantly, outcrops with proximal facies characteristics are distributed in a belt that runs parallel to the Tyrrhenian Sea, from Naples north to Massico Mountain (De Vivo et al., 2001). A basal pumice unit has also been
identified. Two samples of this unit are not included in the weighted mean age above; these samples yield ages of 40.16±0.21 ka and 41.02±0.26 ka. This unit may represent an event that is slightly older than that associated with the CI, or based on the behavior of the spectra, these ages more likely reflect incorporation of xenocrysts from lithic fragments (De Vivo et al., 2001).

The locations of the vent(s) of the CI are controversial, despite over a century of published inquiry on this topic (e.g., Scacchi, 1890). Barberi et al. (1978) noted that the NW-SE distribution of the ignimbrite is consistent with its eruption from a fissure associated with the Apennine front. Recent, more detailed work by De Vivo et al. (2001) and Rolandi et al. (2003) support this hypothesis; the characteristics and distribution of the lithic breccia and mapping of regions of maximum thickness of the CI suggest that the ignimbrite was fed from fissures, the locations of which are controlled by the local extensional tectonics associated with the evolution of the Apennine chain. Of interest to this hypothesis, a similar eruption mechanism has been proposed to explain the notable lack of caldera structures in the Sierra Madre Occidental (Mexico). Based on the size of this ignimbrite province, Swanson and McDowell (1984) estimate that 350 calderas equivalent in size to those found in the San Juan volcanic field would be required to accommodate the volume of erupted material, and yet, analysis by Aguirre-Díaz and Labarthe-Hernández (2003) indicates that fewer than 15 calderas have been identified. Aguirre-Díaz and Labarthe-Hernández (2003) propose that faults associated with Basin and Range extension acted as conduits through which large volumes of magma were explosively erupted. As part of the evidence cited in support of this hypothesis, the authors identify elongate patterns of co-ignimbrite lithic-lag breccia exposed adjacent to Basin and Range faults; such features are not unlike those in the Campanian region alluded to above.

An alternative hypothesis for the source of the CI is the Campi Flegrei caldera. Citing the distribution of the Breccia Museo, a lithic breccia interpreted to be associated with eruption of the CI, on opposite sides of a 12 km caldera, and evidence from drilling data, Rosi et al. (1983) suggest that eruption of the CI was associated with formation of a caldera. Later work by Rosi et al. (1996) used the distribution of proximal deposits of the CI to infer the location of the caldera, including specific locations for fault scarps formed upon collapse. Reconstruction of the size of the hypothesized caldera, coupled with an estimate of 700 m for average down drop, yields a collapse volume of 160 km$^3$, which accords well with the estimate of 150 km$^3$ for the CI by Civetta et al. (1997) and 200 km$^3$ by Rolandi et al., (2003), but is much larger than an earlier
estimate of 80 km$^3$ (Rosi et al., 1983; De Natale et al., 1991). Fisher et al. (1993) report anisotropy of magnetic susceptibility (AMS) measurements for samples from the CI that suggest the pyroclastic current flowed radially outward from the Phlegrean Fields area. Although this contribution does not explicitly address the source of the CI, these data have been cited as support for a source within the Campi Flegrei area (e.g., Civetta et al., 1997). Further AMS work (Ort et al., 1999) suggest that eruptions of Piperno Tuff were fed by a central vent north of Pozzuoli (Figure 1a), and tuffs that underlie the Breccia Museo may be related to eruptions from ring vents located on the northern and southern caldera margins. Rosi et al. (1996) note that all post-CI vents are located within the hypothesized caldera, but De Vivo et al. (2001) identify a unit located at Giugliano, 13 km outside of the identified caldera, with an age of 18.05±0.43 ka. Gravity and magnetic data provide supporting evidence for a ring structure in the Campi Flegrei area (Lirer et al., 1987; Scandone et al., 1991; Florio et al., 1999), but the associated eruptive event is still controversial; some attribute the structure to collapse associated with eruption of the Neapolitan Yellow Tuff (~12 ka, Lirer et al., 1987), whereas others attribute the caldera to eruption of the CI (Rosi et al., 1983). Another interpretation is that the depression is a nested caldera structure that formed in response to both eruptions (e.g., Orsi et al., 1996).

The Campanian Plain and Phlegraean Fields regions reflect a complex, integrated history of tectonic activity coupled with over 300 kyr of volcanism. Challenges presented by this complexity are exacerbated by exposure; many areas that may be critical to the interpretation of source are either covered by younger deposits and/or masked by intense urbanization. Resolution of the source controversy will require continued integrated volcanological, petrological and geophysical studies.

**Petrology and Geochemistry of the Campanian Ignimbrite**

The CI is a heterogeneous unit dominated by the compositional range phonolite to trachyte. Previously published ranges of major elements of single and composite pumice and glass from the ignimbrite include SiO$_2$ from 55.3 to 62.0 wt. % and MgO from 0.3 to 1.5 wt. % (Civetta et al., 1997, Pappalardo et al., 2002). A smaller number of samples of basal pumice, which is interpreted to represent Plinian fallout, has slightly higher SiO$_2$ concentrations, up to 62.4% (Signorelli et al., 1999). Matrix glass and glass inclusions from the basal pumice have SiO$_2$ and MgO (Signorelli et al., 1999) within the ranges cited above for pumice and glass from the
ignimbrite. Average compositions of melt inclusions in clinopyroxenes from a subset of samples presented in this study, analyzed by Webster et al. (2003), extend the range of SiO$_2$ and MgO; those denoted as low-MgO melt inclusions have average SiO$_2$ and MgO of 57.8 and 2.9 wt. %, respectively, whereas high-MgO melt inclusions have 51.0 and 7.6 wt %. Associated total alkalies for these melt inclusions extend the compositional range of melts of the CI event to basaltic trachyandesite (Figure 2a). The highly alkaline nature of pumice and glass of the CI is further illustrated by K$_2$O and Na$_2$O concentrations of 5.2 to 9.9 and 2.0 to 6.6 wt. %, respectively, among pumice, glass inclusions, and matrix glass (Civetta et al., 1997, Signorelli et al., 1999, Pappalardo et al., 2002, Webster et al., 2003).

Trace elements display a range of concentrations within the CI and its associated fallout deposit. For example, Sr varies from 17 to 777 ppm and Ba from 17 to 1111 ppm, and both show negative correlation with SiO$_2$. In contrast, elements such as Zr, Rb and Sm, are positively correlated with SiO$_2$, and also display marked ranges in concentration (Civetta et al., 1997; Pappalardo et al., 2002).

Analysis of pumice, glass and feldspar separates yield distinct Sr isotope values (Civetta et al., 1997, Pappalardo et al., 2002). $^{87}$Sr/$^{86}$Sr of pumice ranges from 0.70728 to 0.70746, with the isotopic ratio of associated glass typically within ±0.00002 of pumice. In contrast, most feldspar $^{87}$Sr/$^{86}$Sr are less radiogenic than pumice and are characterized by a relatively narrow Sr isotope range from 0.70730-0.70734 (Civetta et al., 1997). Exceptions to this range include one feldspar that has $^{87}$Sr/$^{86}$Sr of 0.70741 and is less radiogenic than its host pumice/glass, and one feldspar that has $^{87}$Sr/$^{86}$Sr of 0.70748 and is more radiogenic than its associated pumice.

The phenocryst assemblage of the CI is dominated by sanidine and includes clinopyroxene, plagioclase, biotite,apatite and spinel. Sanidine compositions range from Or$_{58}$ to Or$_{87}$, and no zoning was detected within individual crystals (Civetta et al., 1997, Pappalardo et al., 2002). Plagioclase compositions vary widely, from An$_{96}$ to An$_{25}$, and like sanidine, most crystals are compositionally homogeneous from core to rim (Civetta et al., 1997, Pappalardo et al., 2002). Clinopyroxene ranges from diopside to salite (Civetta et al., 1997; Webster et al., 2003), and detailed work by Webster et al. (2003) demonstrates that most clinopyroxene crystals are zoned, with higher MgO in the core. These authors note that the transition from higher to lower MgO is abrupt. Civetta et al. (1997) note that diopside is relatively rare in the clinopyroxene they analyzed, and the rims tend to be corroded.
Based on a variety of data, including those cited above, Civetta et al. (1997), Signorelli et al. (1999), Pappalardo et al. (2002), and Webster et al. (2003) propose models for the structure and petrogenetic evolution of the CI magma chamber. In this section, we briefly highlight ideas relevant to our study. Civetta et al. (1997) and Signorelli et al. (1999) hypothesize that the magma body was composed of two compositionally distinct layers of magma, separated by a compositional gap. Both contributions cite eruption dynamics and variable timing and extent of mixing between these two distinct layers to explain the geochemistry, petrology and spatial and temporal distribution of compositionally distinct units. The upper layer, which is regarded as compositionally homogeneous and more differentiated, evolved by crystal-liquid fractionation, as did the lower layer, which was modestly zoned. Sr isotope data are used to suggest that fluids interacted with the upper layer of the chamber, most likely after feldspar crystallized. Although the major element fractional crystallization model of Civetta et al. makes qualitative sense, there are some perplexing relationships among trace elements that hint at the need for a more detailed and realistic petrogenetic model. For example, an analysis using the reported initial and final melt concentrations for La, coupled with the observed partition coefficient of 0.3, indicates that removal of ~77% crystals is required; this amount of crystallization is much larger than the reported value of ~57%. The modeling results reported for Eu are also perplexing; the element’s variation from 2.2 to 1.8 ppm in initial to final magma, respectively, can not be described by a bulk partition coefficient of 0.9, as reported, because a bulk partition coefficient larger than 1 is required to accommodate the decrease in concentration as fractionation proceeds. The difference between the observed and calculated concentrations for Eu is reported to be 0, which implies a perfect match between the model and the observed data. Using the value of remaining melt calculated from the sum of the percentage of removed mineral phases (~57%), a bulk D of ~1.3 is required to accommodate the decrease in Eu from initial to final magma. An analysis of Ba, Sr and Sc also yields bulk partition coefficient values that are different from those reported. These incongruities, taken together, suggest that fresh insight can be gained by a more comprehensive treatment of the phase equilibria coupled explicitly and self-consistently to trace element analysis.

Based on their analysis of matrix glass and glass inclusion data from pumice from the Plinian fall deposit, Signorelli et al. (1999) suggest the occurrence of pre-eruptive magma mixing, stimulated by input of trachybasalt into pre-existing magma. In this view, crystal fractionation of
a variety of heterogeneous mixed magmas generated the evolved compositions. These authors also suggest that complexity in the distribution and compositional range of units within the fallout deposit precludes simple vertical stratification of layers in the magma body. Instead, they propose a vertically and laterally zoned body where compositional gradients are, in part, a function of distance from the source of mafic input. Thus, the degree of evolution increases as a function of distance from the source of mafic input. Unfortunately, it is impossible to test the validity of this model because the spatial distribution and eruptive history of the CI vent(s) are unlikely to ever be positively identified.

Webster et al. (2003) stress a role for magma mixing or mingling, and constraints provided by melt inclusion data indicate that mixing/mingling between more primitive and more evolved magma must have occurred shortly before eruption of the CI. Presence of MgO-rich melt inclusions in cores of diopsidic clinopyroxene led Webster et al. (2003) to suggest that these basaltic trachyandesite inclusions may represent primary mafic magma injected into the CI magmatic system; the compositional homogeneity of these inclusions also suggests that these primary magmas were likely derived from a common magmatic source(s). The compositional range of the low-MgO melt inclusions, from trachyandesite to trachyte, likely is a consequence of fractional crystallization, with or without mixing with primary magma.

Collectively, the models proposed by these authors emphasize roles for fractional crystallization, magma recharge and magma mixing/mingling, and contamination. Characterization of the chemical gradient(s) within the pre-eruptive CI magma body involves some (unspecified in detail) notion of vertical and/or lateral zonation. Despite these commonalities, central questions emerge from the earlier studies. These include quantitative analysis of the roles that crystal-melt separation, magma recharge and magma mixing/mingling, and crustal assimilation have in the evolution of the CI magma body, the relative timing of these processes as the magma body evolves, and the pre-eruptive structure of the magma plumbing system. The goal of our work is to quantify the aforementioned processes to the extent possible based on current descriptive knowledge of the products of the CI eruption. The current study is a preliminary examination of these issues; further details are presented elsewhere (Fowler et al., in preparation; Bohrson et al., in preparation).
METHODS

One hundred twenty five samples of the CI were obtained from approximately 30 localities throughout the Campanian Plain (Figure 1b). Based on the work of De Vivo et al (2001), each sample was recovered from one of the five distinct units (gray tuff, yellow tuff, incoherent unit, lithic breccia, and basal pumice) of the CI *sensu lato*. Sample types include bulk pumice or bulk rock (which includes pumice + matrix or matrix alone).

Analytical Methods for Major and Trace Element Data

Major, minor, and trace elements were determined either by the U.S. Geological Survey Laboratories (Reston, VA and Denver, CO) or by Activation Laboratories (Ancaster, Ontario, CA). Before grinding, bulk tuff and pumice samples were examined and any alteration was removed; the sample was then washed in deionized water. Grinding and powdering were done with either mild steel or alumina disks. Major element oxides were determined in representative aliquots by WD-XRF after fusion with lithium metaborate/tetraborate. Trace elements were determined by three methods. (1) Inductively-coupled plasma-mass spectrometry (ICP-MS) and inductively-coupled plasma-atomic emission spectrometry (ICP-AES) were done on solutions using a lithium metaborate/tetraborate fusion procedure before sample dissolution with multiple acids; (2) pressed power pellets were exposed to the appropriate X-rays necessary to fluoresce the element of interest using EDXRF, and (3) standard instrumental neutron activation analysis (INAA) technique after irradiation in the USGS "TRIGA" reactor. FeO was determined by titration, total sulfur reported as SO$_3$ was determined by combustion/infrared spectroscopy, Cl by selective ion electrode or INAA, F by selective ion electrode, LOI and H$_2$O$^{+/-}$ by gravimetric techniques, and CO$_2$ by infrared or colorimetric titration.

Calculation of Parental Melt Composition and Major Element Phase Equilibria Modelling

The motivation for applying detailed major element phase equilibria models is to have the ability to compare observed abundances with predictions based on closed system crystal-melt separation. Differences between predictions and observations then shed light on issues including not only the role of crystal-melt separation, but also the role of assimilation of hydrothermally-altered wallrock, lower crustal xenoliths, and/or meteoric fluids, the role of magma addition and mixing during recharge, as well the influence of mixing during high Reynolds number magma
withdrawal. Below, the methods used to reconstruct the parental melt composition, and an overview of the phase equilibria model (i.e., the MELTS algorithm) are described.

**Selection of parental melt composition**

Basaltic rocks that may correspond to CI parental compositions have not been identified in the Campanian Plain region; however, Webster *et al.* (2003) identified glass inclusions entrapped within host clinopyroxene phenocrysts, which are hereafter referred to as Webster Melt Inclusions (WMI). WMI VE1#3 from the high-MgO MI group is representative of the least evolved MI from this group and was therefore used as the basis for the parental melt composition. This sample was chosen, in part, because its incompatible trace element concentrations are lower than those of other high-MgO WMI from minimally deuterically-altered CI units (i.e., gray tuff, lithic breccia, and incoherent tuff). In particular, the concentrations of incompatible trace elements such as Ce, Th, and U are generally lower in sample VE1#3 than in other high-MgO WMI. While we recognize that the high-MgO inclusions have a range of compositions, we note that using a different WMI sample as the basis for the parental melt composition does not alter the main conclusions of the petrologic interpretations presented in later sections of the paper.

As noted by Watson (1976), reaction between trapped melt inclusions and their host crystals is generally expected. Because the high-MgO WMI are found within clinopyroxene phenocrysts, the effects of post-entrapment crystallization on the composition of sample VE1#3 were accounted for by addition of clinopyroxene. Reconstruction of the major element composition of the parental melt (RPM) is based on the mass balance relation \( y \overline{P}_i + (1 - y) \overline{MI}_i = \overline{RPM}_i \), using the major element compositions of WMI sample VE1#3 (\( \overline{MI}_i \)) and host pyroxene composition (\( \overline{P}_i \)) that corresponds to that of the WMI host crystal in sample VE1 (Webster *et al.*, 2003; Table 1). The value of \( y \), which is the extent of post-entrapment crystallization, was set to 0.2. We also used the method proposed by Kress and Ghiorso (2004) and found a similar result. Major element data for WMI VE1#3 and its clinopyroxene host, as well as the (hydrous) reconstructed parental CI melt (RPM) used as the initial condition in the MELTS isobaric simulations are given in Table 1. Also provided are the anhydrous reconstructed parental melt composition and the reconstructed concentrations for the trace elements, which are based on the measured abundances in MI VE1#3.
MELTS modeling

To calculate phase relations and major element variation diagrams, we used the MELTS algorithm (Ghiorso and Sack, 1995), which is a self-consistent, thermodynamic model of crystal-melt equilibria in which the system undergoes perfect separation of crystals from liquid. At specified pressure, temperature, and parental melt major element composition, the identity, composition, and proportion of phases in the multicomponent-multiphase system are computed in response to the extraction of enthalpy, both sensible and latent, from parental melt. To carry out the MELTS calculations, constraints on the system’s oxygen fugacity, pressure and initial (dissolved) parental melt H$_2$O content are needed. In order to determine the best-fit parameters for the CI magmatic system, over 100 MELTS simulations were carried out over a grid of oxygen fugacity, pressure, and water content. The quality of the MELTS results was evaluated by comparison between the predicted liquid line of descent, phase compositions and observed data. MELTS also predicts phase proportions, but we have not used these as a criterion because differential physical separation effects impact observed modal abundances. The density of fractionating phases varies widely, and both pre-eruptive and eruptive physical separation of crystals is expected and difficult to account for.

Trace Element Modeling

Based on the results of the phase equilibria calculations, it is possible to forward model the concentration of trace elements during the course of isobaric fractional crystallization. Deviations between calculated and observed compositions afford the possibility to better understand petrological processes controlling the magmatic evolution of the Campanian system. The starting point of a trace element assessment is the differential expression governing the concentration of a trace element in the melt as a function of the melt fraction during perfect crystal-liquid separation. For the moment, we ignore possible fractionation of trace elements into coexisting supercritical fluid. Although this assumption is implicitly made in many trace element studies, it may not always be tenable. The critical parameters governing the distribution of a trace element between solid–melt and supercritical fluid are the distribution ratio’s K$_{sm}$ and K$_{sf}$ (solid-melt and solid-fluid partition coefficients, respectively) and the rate of change of the mass fraction of fluid with respect to the mass fraction of melt during fractional crystallization.
In fact, the distribution of Rb, one of the trace elements used in this study, may be particularly sensitive to the existence of a fluid phase predicted to develop at \( T \approx 1127 \, ^\circ C \) during isobaric fractional crystallization at 0.15 GPa.

Ignoring the presence of a fluid phase, the well-known Rayleigh distillation mass balance relation in differential form is

\[
\frac{dC_m}{df_m} = \left( K_{sm} - 1 \right) \frac{C_m}{f_m}
\]  

(1)

which can be integrated

\[
\int_{C_m^\infty}^{C_m} \frac{dC_m}{C_m} = \int_1^{f_m} \left( K_{sm} - 1 \right) \frac{1}{f_m} df_m
\]

(2)

Because of the large differences in the instantaneous composition of solids being removed during fractional crystallization, the assumption that bulk solid-melt partition coefficient \( K_{sm} \) is constant is unacceptable. For example, \( K_{sm}^{Sr} \) as a function of fraction of melt \( (f_m(T)) \) calculated using mineral-melt partition coefficients (Table 2) and the proportion of phases returned from the MELTS simulation (Figure 4) is shown in Figure 3. Across the crystallization interval, bulk \( K_{sm}^{Sr} \) varies by \(~100\) from the liquidus, where olivine first saturates, down to the near solidus, where plagioclase is present. As another example, bulk \( K_{sm} \) of Th varies by a factor of \( \sim30\) over the crystallization interval. Our approach is to determine \textit{a priori} from MELTS the variation of bulk \( K_{sm} \) for each trace element as a function of \( T \) or, equivalently, \( f_m(T) \) and then to numerically integrate eq. (2) using a sequence of linear segmental parameterizations for \( K_{sm} \) as a function of \( f_m(T) \) (Figure 3). For a linear relationship between \( K_{sm} \) and \( f_m(T) \), eq. (2) can be integrated analytically; in practice, it is faster and just as accurate to perform the integration numerically using a fourth-order Runge-Kutta scheme (e.g., Spera and Bohrson, 2001).

In summary, trace element concentrations were calculated from the liquidus temperature where \( f_m(T) = 1 \) down to \( f_m(T) \approx 0.05 \) using the numerically-integrated form of eq. (2), taking explicit account of the variation in bulk \( K_{sm} \) for each trace element as a function of the fraction of remaining melt after removal of solids predicted from the MELTS simulation. The concentration
of a trace element is then calculated using the initial concentration values \( C_{m,0} \) for the \( i^{\text{th}} \) trace element listed in Table 1 and the numerically determined ratio \( C_m/C_m^0 \). As noted above, we neglect fractionation of an element into coexisting supercritical fluid phase in the results presented here, although for certain elements, specifically the alkalies (e.g., Rb; see Beswick, 1973) and for elements that strongly complex with halogens such as Cl, this assumption is suspect.

**Analytical Methods for Th Isotope Data**

Th isotopic analyses of 12 samples of the CI were performed at University of California, Los Angeles (UCLA), using a VG sector mass spectrometer equipped with a 30 cm electrostatic filter and a static collector array composed of a Faraday cup and an ion counting photomultiplier system. Thorium and Uranium were run as metals. Abundance sensitivity on this instrument during data collection was < 0.4 ppm at 1 amu. \(^{232}\text{Th}/^{230}\text{Th} \pm 2\sigma\) obtained on a standard solution and international reference samples are (1) University of California, Santa Cruz Th standard: 170587±0.26%, \((n=35)\), (cf. values of 17.03±9 x10\(^4\) and 17.05 x10\(^4\) reported in Reid, 1995); (2) AGV1 199040±0.20% \((n=5)\); (3) JB1 332302±0.96% \((n=5)\) (cf. values of 20.06 x10\(^4\) and 33.54 x10\(^4\) respectively, reported in Reid, 1995). U and Th concentrations were measured by isotope dilution using a \(^{229}\text{Th}-\) and \(^{233}\text{U}-\)enriched spike. Elemental purification was achieved using anion exchange resin and 7N HNO\(_3\).

**DESCRIPTION OF DATA**

**Major and Trace Elements**

Representative major element data are presented in Table 3. Consistent with numerous previous studies on the CI, pumice and bulk/matrix samples analyzed in this study are trachytic to phonolitic (Figure 2a). The typical phenocryst assemblage in pumice includes alkali feldspar, with lesser plagioclase and sparse to trace clinopyroxene, spinel, apatite, and biotite. Most samples are sparsely phryic; the maximum crystal content is \(~10\%\), and thus, although our samples (and some of those of Civetta et al. (1997)) are pumice, major and trace element signatures are dominated by melt compositions. As a consequence of zeolitization, samples of the yellow tuff have compositions distinct from the pumice and bulk/matrix samples and will not be plotted or discussed further in this contribution. Portrayed in Figure 2a are data for the high-
MgO and low-MgO melt inclusions of Webster et al. (2003), pumice and glass (by ICP) from Civetta et al. (1997) and matrix glass and clinopyroxene-hosted glass inclusions (by electron microprobe) from Signorelli et al. (1999). The Signorelli study focused on the Plinian phase of the eruption and therefore includes only data from the fall deposit (earliest part of the CI eruption).

Selected major oxide trends are illustrated in Figure 5a-d; all oxides are reported in wt. %. For most oxides, pumice and bulk samples are characterized by relatively coherent oxide-oxide trends. For example, SiO$_2$, Na$_2$O and MnO vs. MgO form relatively tight negatively correlated arrays. CaO, P$_2$O$_5$, FeO, and K$_2$O are positively correlated arrays, although two pumice samples have distinctly lower K$_2$O compared to other samples with equivalent MgO. Fe$_2$O$_3$, and Al$_2$O$_3$ vs. MgO trends are more scattered.

A subset of the trace elements analyzed for these samples was chosen for detailed discussion in this study: Zr, Nb, Th, U, Rb, Sr, and Sm. Selected MgO (wt. %) vs. element trends are illustrated in Fig. 6a-g; all trace elements are reported in ppm. These elements represent the range of element behavior in the CI. WMI trends for Zr, Nb, Th, and U show scattered changes in concentration at decreasing MgO. For these elements, a subset of the low-MgO group is characterized by enriched trace element abundances (~2-4x) compared to the remaining low MgO inclusions. These enriched melt inclusions have abundances similar to pumice with substantially less MgO. WMI Rb variations also show scattered changes with decreasing MgO, and the subset of low-MgO WMI noted above with more enriched abundances is absent. Sm has different behavior; concentrations among the WMI are generally similar to or higher than those of the pumice and glass/melt inclusions. For the elements discussed above, pumice and glass/melt show marked increases with decreasing MgO. Enrichment factors (defined as the ratio of element in the most MgO-rich pumice to least MgO-rich pumice) differ between the elements. Zr, Th, Nb, and U all have enrichment factors of ~6-8, whereas Rb and Sm have enrichment factors of 3-4. With several exceptions, Sr in the high-MgO WMI group is relatively enriched, compared to the low-MgO group. The pumice and glass/melt inclusion data form a relatively tight array that decreases with decreasing MgO.

Element-element trends for this subset of trace elements illustrate the systematics between U and Zr, Nb, Th, Rb, Sm, and Sr (Figure 7a-f). For U vs. Zr, Nb, and Th, WMI form relatively tight clusters. Four or five inclusions plot at higher concentrations of U vs. trace element; these
samples generally plot within the pumice and glass array, although several melt inclusions plot above the primary U vs. Zr array. With few exceptions, pumice and glass samples form tight, positively correlated arrays. U vs. Rb has systematics similar to those described above: a tight cluster of WMI and a well-correlated, positive array of pumice and glass. However, in contrast to the trends described above, the subset of WMI that plots at higher trace element concentrations fall slightly below the primary pumice and glass array. WMI exhibit variations of approximately a factor of 5 in Sm for a small range in U. Several samples, which plot at high U and Sm, are above the pumice and glass array, which is systematic and positively correlated. Like Sm, WMI have variable Sr over a small range of U (~factor of 5), and the high U melt inclusions plot below the pumice and glass array, which is somewhat scattered and broadly negatively correlated.

**Th Isotopes**

Twelve samples of the Campanian Ignimbrite were analyzed for Th isotopes and U, Th concentrations (Table 4). These samples are representative of the range of pumice and bulk rock compositions in our sample suite. They comprise 8 samples of gray tuff, (Sa-1a, Sa-1b, AFGI-1, AFGI-11, MP-1, ALT-1, VE-1, ICB-9), 2 samples of the lithic breccia (PONTIR, ICHB-6a), and two samples of the basal pumice (AFBP-1, AFBP-5).

Measured thorium activity ratios, \(^{230}\text{Th}/^{232}\text{Th}\), range from 0.936 to 0.996, and \(^{238}\text{U}/^{232}\text{Th}\) range from 0.881 to 1.190 (Figure 8a). Five samples are within 2.5% of secular equilibrium, 5 samples are enriched in \(^{238}\text{U}\) (up to ~16% enrichment), and 2 samples are \(^{230}\text{Th}\)-enriched (up to 8%). \(^{230}\text{Th}/^{238}\text{U}\) therefore vary from 0.837 to 1.08. Correlations with respect to \(^{230}\text{Th}/^{232}\text{Th}\) vs. \(^{238}\text{U}/^{232}\text{Th}\) and sample type (pumice vs. bulk; gray, basal pumice or lithic breccia) are lacking.

Measured Th isotope ratios were age-corrected using the mean \(^{40}\text{Ar}/^{39}\text{Ar}\) age of 39.28±0.11 ka reported in De Vivo et al. (2001). It is important to note that 6 of the 12 samples analyzed for Th isotopes were included in the dating study, and thus, the age constraints on the these samples and the deposit as a whole are precisely documented. Initial Th activity ratios, \(^{230}\text{Th}/^{232}\text{Th}\)_0, vary from 0.911 to 0.982, and \(^{230}\text{Th}/^{238}\text{U}\)_0 range from 0.767 to 1.115 (Figure 8b). Three samples are within 1.5% of secular equilibrium, 7 samples are \(^{238}\text{U}\)-enriched by up to ~23%, and
2 samples are $^{230}\text{Th}$-enriched by up to ~12%. The data plot as a relatively coherent linear, with a regression coefficient of 0.77.

Figures 8c and 8d illustrate variations between $(^{230}\text{Th})/(^{232}\text{Th})_o$ and Th (ppm) and U (ppm). Neither plot exhibits systematic relationships between activity ratio and concentration. The two samples with the lowest U and Th concentrations, PONTIR and ICHB-6a, identified as lithic breccias, have $(^{230}\text{Th})/(^{232}\text{Th})_o$ that range from ~0.91 to 0.95. Samples with higher abundances of Th and U exhibit a slightly greater range of $(^{230}\text{Th})/(^{232}\text{Th})_o$ from ~0.91 to 0.98.

DISCUSSION

Magma Chamber Processes

Ignimbrites have been interpreted as deposits that represent rapid evacuation of a magma chamber (e.g., Smith, 1979; Hildreth, 1981), and thus, the primary compositional and isotopic heterogeneity observed in the deposit reflects the range of magmas that were in the magma chamber just prior to evacuation. Such magmas form by processes that occur as melt forms and as melt+crystals+vapor ascend through and are stored in the crust. For our data set, comparison of the observed data with the MELTS model reveals that crystal-liquid separation played an important if not dominant role in developing the observed major element compositional heterogeneity. Detailed reconstructions of selected trace element trends highlights the critical control that phase assemblage and mineral-mineral partition coefficients ($K_{sm}$) have on melt trace element abundances. Imprecise knowledge of $K_{sm}$, in some cases, makes it difficult to ascertain the contribution from crystal-liquid separation, compared to other processes such as crustal assimilation, but several elements provide strong evidence for open-system processes. Th disequilibria data and published Sr isotope data (Civetta et al., 1997) support this suggestion by providing definitive evidence of open-system processes in the Campanian magma plumbing system.

Crystal-Liquid Equilibria: Major Element Discussion

The results of isobaric fractional crystallization starting from RPM composition listed in Table 1 are summarized in Figures 2b, 4 and 5a-5d. Best-fit MELTS parameters include pressure = 0.15 GPa, crystallization along the QFM+1 oxygen buffer, and initial dissolved water content
of the RPM of 3 wt. %, which is within the range of water contents measured on melt inclusions reported by Webster et al. (2003). The temperature interval used to compute the liquid line of descent is 0.5 °C. Figure 2b shows the calculated trend (anhydrous basis) on an alkali-silica diagram. Upon fractional crystallization of parental trachyandesite, the melt evolves to higher total alkali (K$_2$O + Na$_2$O) and higher silica. The most striking feature of this diagram is the presence of a compositional gap beginning at T ≈ 884 °C. This temperature defines a pseudo-invariant point in thermodynamic space that behaves practically like a eutectic point in a simple binary component system. That is, as heat (enthalpy) is isobarically extracted from the system, the fraction of melt changes from ~0.46 to ~0.09 essentially isothermally (T ≈ 884 °C), and melt simultaneously saturates in alkali feldspar, plagioclase and biotite. At this temperature, the melt composition and properties change rather abruptly. The difference in composition of the two distinct liquids across the gap is ~ 2 wt. % for Na$_2$O and Al$_2$O$_3$, ~1.5 wt. % for K$_2$O, 1 wt. % for SiO$_2$ and CaO (Figure 5) and ~0.5 wt. % for H$_2$O. In fact, across the gap, both the composition of the melt and the composition of the bulk magma (melt plus supercritical fluid) change rather significantly.

Figure 4 shows the abundance of the crystalline phases removed as a function of f$_m$(T). In addition to the rapid change in fraction of melt at the pseudo-invariant temperature, the other important features of Figure 4 are the following: (1) olivine is the liquidus phase; (2) melt saturates in H$_2$O (discrete supercritical fluid develops) at ~ 1127 °C; and (3) there is a 100 °C temperature interval dominated by clinopyroxene fractionation. The order of solids removal is olivine, clinopyroxene, spinel, apatite and then simultaneous removal of alkali feldspar, plagioclase and biotite at the pseudo-invariant point temperature, 884 °C.

In Figure 5a-d, MgO variation diagrams are shown for K$_2$O, Na$_2$O, Al$_2$O$_3$, and FeO. In each case, the MELTS predictions are in reasonable agreement with glass and pumice data, suggesting that crystal fractionation is the mechanism that dominates evolution of the major elements in the CI. The offset between the calculated and observed trend on the FeO-MgO diagram (Figure 5d) is most likely attributed to the imposition of a fixed oxygen buffer curve of QFM+1.

In summary, a reconstruction of the CI parental melt based on glass inclusions entrapped in clinopyroxene phenocrysts has been used as an initial condition to develop the liquid line of descent, assuming perfect closed system fractionation at fixed pressure (0.15 GPa or ~ 5 km depth) along the QFM+1 oxygen buffer. When one considers that the effects of assimilation are
not accounted for, comparison between predicted and observed data is reasonable and allows a ‘reference’ state to be defined, upon which a trace element analysis can be carried out.

Crystal-Liquid Equilibria: Trace Element Discussion

The goal of numerically modeling trace element trends generated by crystal-liquid equilibria is to quantitatively assess the degree of enrichment or depletion possible through separation of melt and solids. In this section, we integrate results of the best-fit MELTS model with the numerical formulation described above to reconstruct trace element abundances during crystal fractionation allowing for the change in bulk $K_{sm}$.

Results of the best-fit trace element models are illustrated in Figures 6 and 7. Before interpreting these trends in the context of the open- vs. closed-system question, it is useful to review the “robustness” of such model trends. A minimum of three types of input informs the final trace element results: the choice of parental composition, the phase proportions returned from the MELTS model, and the choice of mineral-melt $K_{sm}$. Several observations are relevant to the interpretations provided below. Variations in the parental composition will obviously lead to variations in trace element concentrations. The main impact changing the parental composition will have (all other modeling parameters being the same) will be to translate up or down the parts of the trend that are shown from ~10 wt. % MgO to ~2 wt. % MgO (Figure 6). The trajectory of the trends at lower MgO is primarily controlled by the bulk $K_{sm}$, particularly because the proportion of solids removed at this stage is so high. Thus, although some fine-tuning of the parental composition might improve the major element_trace element and/or trace element-trace element trends, given the range evident from the high MgO melt inclusions of Webster et al. (2003), it is unlikely that reasonable variations in the parental composition will drastically change the interpretations of trace element behavior. As noted above, the best-fit MELTS model is the result of approximately 100 simulations, which differ in detail but fundamentally return the same results: olivine and clinopyroxene at high temperatures (liquidus and sub-liquidus), followed by onset of apatite and spinel crystallization. At ~ 884°C, a large mass of crystals, dominated by alkali feldspar and plagioclase, form. Crystallization at this pseudoinvariant point is a feature of all of the MELTS results, as is onset of apatite formation. Thus, although the details of the MELTS model might change with further examination, the best-fit model, which is subject to the assumptions relevant to describing a magmatic system using the
MELTS approach, are robust. The final variable in the trace element modeling, which is the one that is perhaps the most problematic in producing robust results, is the choice of mineral-melt \( K_{sm} \). In this study, mineral-melt \( K_{sm} \) were chosen based on assessment of the range of values available in the Geochemical Earth Reference Model (GERM) Partition Coefficient compilation (http://earthref.org/). (All values in the GERM compilation are referenced, and references relevant to this study are included in Table 2). Inspection of the compilation for a particular phase and element, even within a restricted compositional range (e.g., silicic or basaltic), in most cases, reveals large differences in mineral-melt \( K_{sm} \) (e.g., Rb in basaltic plagioclase ranges from 0.016 to 0.3; Sr basaltic clinopyroxene ranges from 0.04 to 0.449; Th in apatite ranges from 1.6 to 41). In many cases, when applying partition coefficients to model a particular suite of rocks, it is difficult to develop independent criteria that allow a rational choice to be made among the values. The approach we adopted was to apply different \( K_{sm} \) from the compilation until the observed trends were suitably bracketed, and then final \( K_{sm} \) were chosen and the best-fit case was calculated. These best-fit cases are summarized in Figure 7. An example of bracketing is shown Figure 7a (U vs. Zr). One model trend (trend 1) plots above the observed trend, whereas the other model trend (trend 2) plots below. The critical point about these model trends is they have very different implications for understanding trace element variations. In the case of trend 2, the implication is that crystal-liquid separation cannot produce enrichments that are sufficient to describe the data. This implies the system was open, and therefore another process, such as crustal assimilation, was important. However, permissible changes in \( K_{sm} \) (based on available data) yield a trend (trend 1) that plots above the observed data. Trend 1 implies that crystal-liquid separation can produce concentrations that are more enriched than those observed. In this case, elements may have been scavenged from the magma, and such scavenging might be caused by transport of the element into a vapor phase, in the case of a vapor-saturated magma. In several cases (e.g., Th, Sm, Rb), application of the most extreme mineral-melt \( K_{sm} \) listed in the compilation that were relevant to the broad magma compositional range failed to yield model trends that reproduced or bracketed the data. In these cases, the model case shown is that which employs the most extreme, allowable \( K_{sm} \).

Figures 7a, b and f illustrate results for U vs. Zr, Nb, and Sr. For these elements, observed and model trends show similar systematics. This suggests, to a first-order, that the observed enrichments may be attributed to crystal-liquid separation. U, Zr, and Nb all behave
incompatibly, increasing in abundance with decreasing MgO (Figure 6a, b, d). At ~1.5 wt % MgO, the marked increase in observed and model abundances of these elements is interpreted to result from the large change in crystallinity associated with invariant point crystallization at ~884°C. Because $f_m(T)$ changes dramatically over a small temperature interval, the consequences on trace element abundances are profound. Sr is initially incompatible (i.e., increases in abundance with decreasing MgO, Figure 6g), and then, for $T< 884$ °C, Sr becomes compatible because plagioclase and alkali feldspar crystallize (Figure 7f).

Figures 7c and e illustrate model vs. observed results from U vs. Th and Sm. These elements provide an interesting window into the behavior of elements typically considered incompatible. In the case in which apatite is an important crystallizing phase, because the $K_{sm}$ for Th and Sm can be very high (e.g., order 2-90; e.g., Mahood and Stimac, 1990; Nagasawa, 1970), these elements will be very efficiently removed from the melt at $≈ 884$ °C. In the case of Th, the best-fit trace element trend uses the apatite-melt $K_{sm}$ that is least compatible of those reported (e.g., 1.6 of the range 1.6 to 41; Bea et al., 1994; Mahood and Stimac, 1990). The U-Th trend is positively correlated, indicating that Th is enriched during crystal-liquid separation, but the model trend is not as Th-enriched as the observed trend. Even with an apatite-melt Th partition coefficient of 1 (results not shown), Th is still not as enriched in the model as observed. Assuming the MELTS model is robust with respect to phase proportions, this result implies either that Th is not compatible in apatite, a result not supported by the partition coefficient database, or that Th may be impacted by open-system processes. (Because the MELTS and trace element modeling assume perfect fractional crystallization, it is possible that apatite did not effectively separate from its host melt. However, this explanation seems unlikely because $P_2O_5$ decreases with decreasing MgO, and Th increases as $P_2O_5$ decreases, suggesting apatite was fractionated). The case of Sm is more extreme because, compared to Th, it has much higher apatite-melt $K_{sm}$. The best-fit case illustrated in Figures 6f and 7e employed the lowest mineral-melt $K_{sm}$ in the GERM compilation (Table 2), and yet, the model trend grossly underestimates the observed Sm abundance; in fact, the model predicts that the melt will have almost no Sm. Although the detailed modeling is not yet complete, the LREE and other MREE in the CI behave similarly to Sm. Because these elements tend to be compatible (to varying degrees) in apatite, equivalent model systematics may emerge. Again, the model vs. observed results indicate either
that the Sm apatite-melt partition coefficient is highly inaccurate, or that most of the Sm is related to some open-system contribution.

Figure 7d shows the U vs. Rb results. The illustrated model trend employs mineral-melt $K_{sm}$ from the GERM compilation that are the most compatible for each phase; despite this, the model Rb trend grossly overestimates the observed abundances of Rb. This suggests that the GERM $K_{sm}$ are not relevant, that there is some yet unidentified trace phase that removed Rb, and/or that a separate process, such as interaction with a vapor, has removed Rb from the melt. The critical parameters governing the distribution of a trace element between solid, melt and supercritical fluid are the solid-melt ($K_{sm}$) and fluid-melt ($K_{fm}$) partition coefficients and the rate of change of the mass fraction of fluid ($f_f$) with respect to $f_m(T)$ during isobaric fractional crystallization. If the bulk partition coefficient for Rb between melt and vapor exceeds ~ 3, as it may based on laboratory experiments on sanidine and biotite (Beswick, 1973), then the discrepancy between the calculated trend assuming Rb is totally insoluble in the supercritical fluid and the observed trend can be rationalized. The role of melt-vapor fractionation is easily estimated. For insoluble behavior with $K_{fm}^{Rb} = 0$ and $K_{sm}^{Rb} = 0.5$ the situation is identical to standard solid-melt Rayleigh fractionation and enrichment in residual melt is expected $C_m^{Rb}/C_{m,o}^{Rb} \approx 2$. If however $K_{fm} = 5$ (i.e., Rb is decidedly soluble in fluid relative to melt), then the melt will be depleted in Rb such that $C_m^{Rb}/C_{m,o}^{Rb} \approx 0.1$. If this hypothesis of supercritical fluid fractionation is valid for Rb, one expects other geochemically similar elements will exhibit similar behavior. The study by Bohrson et al. (in preparation) addresses this issue further.

A final comment about all of the model trends is relevant to understanding magma chamber processes. The trace element mass balance model presented here represents perfect fractional crystallization and evaluates compositional changes in very small increments of fraction of melt. Pumice likely represent some integration of parcels of melt with distinct histories, and thus, some of the discrepancy between model and observed trends may be the result of magma and eruption dynamics that mix discrete masses of distinct-composition melt. An interesting test of this hypothesis would be to collect small spatial resolution data of glass in the pumice. Signorelli et al. (1999) represents just such a study because their glass data is the result of microprobe analyses, and thus, are small-spatial resolution samplings of the major element chemistry of the Campanian melt. In some cases, the MELTS model reproduces parts of the glass data trends. No trace element data are provided in the Signorelli et al. (1999) study, but the prediction would
be that the \textit{in situ} trace element data would fall close to or on the model trends, thus implying that the pumice analyses reflect mixing of melts that occurs in the chamber and/or upon eruption.

In summary, results of numerical trace element modeling indicate that Sm and Th are over-enriched compared to model values, suggesting these elements have been affected by processes other than simple equilibrium crystal-liquid separation. General trends for U vs. Nb, Zr, and Sr indicate that the abundances of these elements may be dominantly controlled by crystal-melt separation, but the range of $K_{sm}$ available in the literature does not preclude some contribution from other sources (i.e., open-system). Finally, the model predicts Rb should be more abundant in the Campanian samples, indicating that Rb may have been scavenged by vapor that was in equilibrium with melt.

**Open-System Processes: Th and Sr Isotopes**

Radiogenic isotopes are effective in identifying and quantifying open-system processes because isotopes of the same element are not fractionated by (high temperature) equilibrium crystal-liquid separation. Thus, for the closed-system case, $^{87}\text{Sr}/^{86}\text{Sr}$ and $(^{230}\text{Th})/(^{232}\text{Th})$ of melts will be the same as those of newly formed crystals. Likewise, in the case of a zoned magma body, all of the compositionally distinct masses of magma will share a common initial isotope ratio. The closed-system description assumes that the timescale of crystallization is short compared to the half-life of the parent isotope, and thus no (or insignificant) radiogenic ingrowth occurs \textit{during} the process. In the case of Rb, which has a half-life of $\sim4.9 \times 10^{10}$ yr, this assumption is robust for magmatic processes, except in rare cases in which Rb/Sr is extremely high. The half-life of $^{230}\text{Th}$ is relatively short ($\sim7.5 \times 10^{4}$ yr), and thus Th disequilibria have been studied in an attempt to understand crystal and magma residence and fractionation times.

$^{238}\text{U}/^{232}\text{Th}$ vs. $^{230}\text{Th}/^{232}\text{Th}$ is illustrated in Figure 8a. The striking observation related this figure is the relatively coherent linear array that the data define. Linear regression yields a correlation coefficient (R) of 0.82, and an apparent isochron age of $19.6 \pm 4.7$ ka. Such a result is problematic because the deposit (including 6 of the 12 samples analyzed for Th isotopes) has been precisely dated at $39.28 \pm 0.11$ ka (De Vivo et al., 2001). Age-corrected Th data are plotted in Figure 8b. \textit{The data clearly illustrate that the melts represented by pumice of the CI were not in Th isotopic equilibrium upon eruption.} The negative slope of the array also suggests that the system was open with respect to Th isotopes. The slope of the array is important because a
positively correlated array might be interpreted to reflect a magma residence time; in contrast, a negative array (in the absence of an open-system) would indicate timescales less than 0.

One of the interesting aspects of the Th isotope data is the relatively well-correlated trend in \( \frac{^{238}\text{U}}{^{232}\text{Th}} \) vs. \( \frac{^{230}\text{Th}}{^{232}\text{Th}} \). Despite this, simple correlations between age-corrected Th isotope ratio and concentration of U or Th are lacking (Figures 8c, d), as are correlations with other elements/oxides (not shown; e.g., MgO, Na2O, Zr, Nb). A good example of the lack of simple systematics is the observation that samples with very similar, high Th concentrations (AFBP-1, AFBP-5, MP-1, and ICB-9) have \( \frac{^{230}\text{Th}}{^{238}\text{U}} \) from ~0.91 to 0.97. Similarly, samples with low Th concentrations (PONTIR and ICHB-6a) have \( \frac{^{230}\text{Th}}{^{238}\text{U}} \) of ~0.95 and 0.91, respectively. These observations collectively preclude simple two-component mixing as the explanation for the Th isotopic signatures.

The interpretation of the open-system history of Th in the magma body is further complicated by the following observations: (1) there are no systematic correlations between elements or oxides and the degree of disequilibrium, \( \frac{^{230}\text{Th}}{^{238}\text{U}} \). This, taken together with the range of U, Th vs. \( \frac{^{230}\text{Th}}{^{232}\text{Th}} \) noted above, means it is difficult to reliably identify the least contaminated sample or establish the systematics of U-Th fractionation during differentiation. (2) Examination of the \( \frac{^{238}\text{U}}{^{232}\text{Th}} \) of the high-MgO WMI indicates they are heterogeneous (0.45 to 1.36) and have a range that encompasses and exceeds those of the CI samples. If this range represents potential fractionation that has affected less differentiated melts of the Campanian system, then it is difficult to systematically define characteristics of U-Th fractionation in more differentiated melts. That is, it is unclear if the range is \( \frac{^{238}\text{U}}{^{232}\text{Th}} \) in the pumice was inherited from heterogeneous parental magmas, is due to differentiation processes, or both. (3) Although the number of samples analyzed for Th is somewhat restricted, there does not appear to be any correlation between \( \frac{^{230}\text{Th}}{^{238}\text{U}} \) or \( \frac{^{230}\text{Th}}{^{238}\text{U}} \) and sample locality.

Sr isotope data for Campanian samples published by Civetta et al. (1997) include acid-leached data for pumice, glass and feldspar. Figure 9 illustrates the systematics of \( ^{87}\text{Sr}/^{86}\text{Sr} \) vs. Sr concentration (by ICP) in the pumice. Note that no Sr concentration data are available for the glass and feldspar data, so Figure 9 is intended to illustrate pumice Sr isotope-concentration systematics and provide a visual comparison of \( ^{87}\text{Sr}/^{86}\text{Sr} \) for pumice, glass and feldspar from the same sample. Observations and interpretations relevant to this discussion from Civetta et al.
(1997) include (1) samples were acid leached, and residue and leachate (with only a few exceptions) yielded similar $^{87}$Sr/$^{86}$Sr; thus the authors conclude it is unlikely that the range in pumice $^{87}$Sr/$^{86}$Sr is the result of post-eruptive alteration. (2) Pumice $^{87}$Sr/$^{86}$Sr are broadly correlated with Sr concentration; the least Sr-rich samples are those with the most radiogenic $^{87}$Sr/$^{86}$Sr. (3) Feldspars exhibit isotopic disequilibrium with pumice. For most feldspar, $^{87}$Sr/$^{86}$Sr range is small, and feldspar signatures are less radiogenic than pumice or glass. Exceptions include two samples that have relatively radiogenic $^{87}$Sr/$^{86}$Sr; these are associated with pumice that has relatively low Sr concentration (Figure 9).

The hypothesis that was favored by Civetta et al. (1997) to explain the disequilibria and the change in $^{87}$Sr/$^{86}$Sr among the pumice (including the systematic relationship with Sr concentration) was contamination after feldspar formation. They call on a model that potentially involves interaction between hydrothermal fluids and magma prior to eruption. The authors indicate that selective assimilation of 20% of a seawater-like fluid can explain the range of $^{87}$Sr/$^{86}$Sr in the pumice. Citing the same data set, Pappalardo et al. (2002) note that this interaction could occur on the timescales of seconds. These authors reference Palacz and Wolff (1989), which provides (among other types of data) Sr isotopes on the Granadilla Pumice, Tenerife. Feldspar $^{87}$Sr/$^{86}$Sr range from 0.70314-0.70318, and vigorous acid-leached pumice range from 0.7032-0.7052. Thus, like the Campanian data set, there is Sr isotope disequilibria between feldspar and acid-leached glass. The model of Palacz and Wolff posits vesiculating magma and hydrothermal fluids (with high $^{87}$Sr/$^{86}$Sr) interact just prior to or during eruption. Limited diffusion of Sr occurs into the bubble walls before quenching. Palacz and Wolff (1989) suggest that diffusion at magmatic temperatures is fast enough to impart radiogenic signatures on the timescale of eruption.

Tracer diffusion of Sr at 900 °C in CI melt containing several wt. % dissolved H$_2$O is estimated at ~10^{-13} m$^2$/s (Spera, 2000). The characteristic timescale for Sr diffusive transport, $\tau_{Sr}$ ~ $\delta^2$/D, where $\delta$ is a diffusion length scale, is $\tau_{Sr}$ ~ 10 s for micron scale. Although this timescale is small, its significance with respect to isotopic exchange of Sr during eruption is not clear. The concentration of Sr in CI melt (>20 ppm) exceeds the Sr concentration in seawater (~9 ppm), so diffusion of seawater Sr into melts is not suggested. If concentrated brine interacts with the magma, the chemical potential gradient might possibly allow for Sr transport into the melt. But there is a huge energy requirement for fluid heating, and once subsolidus temperatures are
reached, Sr diffusion slows dramatically. For a diffusion event of one-day duration at 900 °C, the diffusion scale is 0.1 mm—this seems rather small.

Magma-fluid interaction has been provided as an explanation for open-system signatures in Phlegrean Fields as well as other locations (e.g., Hildreth et al., 1984; Clocchiatti et al., 1988; Villemant, 1988; Michaud, 1995; Villemant et al., 1996). Several observations, some of which are noted in papers referenced above, are relevant to this hypothesis. First, any proposal that invokes addition of fluid to a magma body must grapple with the fluid conditions therein. It is unlikely that fluid will flow into a fluid-saturated magma because of lack of a H₂O chemical potential gradient (e.g., Taylor, 1974; 1977; 1980; 1986). Second, fluids need to come to total or partial thermal equilibrium with magma at temperatures of ~ 900 °C to 1100 °C and must therefore be heated considerably from shallow meteoric values of ~ 100 °C to 200 °C. For fluids at crustal temperatures, such heating requires enthalpy delivered from the magma body. A simple calculation of energy balance places reasonable limits on the mass of fluid that can be involved in such an interaction. For a single mass of magma (i.e., no recharge), the maximum energy available to heat crustal fluid is the sum of the sensible and latent heat. For a magma similar in composition and properties to the Campanian (T_{liq} = 1236°C; T_{solid} = 866°C, ΔH = 396 kJ/kg, C_{pm} = 1484 J/kg K) and heat capacity of supercritical H₂O of 4 kJ/kg K, the maximum fluid to magma ratio is ~0.3. We note that this is an extreme case because the calculation assumes all of the thermal potential of the magma body is used for heating of initial cool fluid and the chamber must crystallize fully, thus rendering an eruption impossible. However, if we neglect these extreme limitations for purposes of illustration, a third constraint, one of mass balance, can be constructed for magma-fluid interaction. In this case, we use the Sr isotope characteristics of the Campanian samples of Civetta et al. (1997). Using a nominal feldspar ⁸⁷Sr/⁸⁶Sr value of 0.70731 as an initial value and the range of Sr concentration and ⁸⁷Sr/⁸⁶Sr from the pumice, the required fluid to magma ratios to invoke the observed isotopic shift range from ~0.3 to ~0.9. To decrease the high water to magma ratio to ~0.3 (the approximate limit from thermal balance), the concentration of Sr in a hydrothermal fluid would have to be 3x that in seawater, assuming seawater-like ⁸⁷Sr/⁸⁶Sr of ~ 0.709.

Although it is unlikely that the Th isotopes characteristics of the Campanian samples are due to magma-fluid interaction, particularly because the best-fit MELTS model indicates the Campanian magmatic system was vapor saturated in the compositional range represented by the
ignimbrite samples included in this study, it is instructive to examine the mass balance arguments because the concentration of Th is seawater is orders of magnitude less than that found in typical igneous rocks. Seawater has a variable but high to extremely high $^{230}\text{Th}/^{232}\text{Th}$ (4-300, Roy-Barman et al., 1996). Despite this, large water to magma ratios are typically required to produce isotopic changes in magmas because of the very low (picograms/gram) concentration of Th in typical seawater. For example, for an average $^{230}\text{Th}/^{232}\text{Th}$ of 100 and a Th concentration of $\sim 0.008$ ppb (the highest reported for either seawater or mid-ocean ridge hydrothermal fluids (Chen et al., 1986; Chen, 1987)), water to magma ratios required to produce a $^{230}\text{Th}/^{232}\text{Th}$ range from $\sim 0.91$ to 0.98, assuming the magma has $\sim 11$ ppm Th, are on the order of tens to hundreds. Clearly such interactions are not possible based on thermal constraints noted above, and even if such interaction could occur, these high water to magma ratios would predict seawater-like Sr isotopes (~0.709) in CI pumice, which is not observed.

In summary, hypotheses that invoke fluid-magma interaction must be evaluated in the context of chemical potential gradients for fluid, and allowable thermal (energy) and mass balances. Because some magmas, at least for part of their evolution, are fluid saturated (indeed the model CI parental magma volatile saturates at $\sim 1127^\circ\text{C}$), it is unlikely that fluid will enter the magma in the first place. Even if this constraint is relaxed, the high heat capacity of fluid requires a great deal of energy be extracted from the magma body to heat it from the ambient crustal to magmatic temperatures. Such demanding thermal requirements imply high degrees of crystallization, which, because of the physical changes that accompany crystal formation (e.g., increase in viscosity), may impact the eruptability of the body. Finally, fluids are typically characterized by low concentrations of elements compared to most rocks. Simple mass balance calculations like those above can therefore provide limitations on hypotheses that invoke fluids to explain chemical and isotopic variations in magmas. In the case of the CI, we conclude that it is highly unlikely that the open-system signatures are due to direct interaction between magma and fluid.

The explanation for the Th and Sr isotopic heterogeneity may lie in interaction between magma and wallrock, which might include intrusive parts of the long-lived Campanian magmatic system. Several lines of evidence bear on such an open-system model. Characterization of U-Th disequilibria associated with products (tephra, lava and cumulate nodule) of the 1994 eruption of
Vesuvius (Black et al., 1998) demonstrate that whole-rocks and mineral phases (leucite, biotite, pyroxene, and a magnetic separate) are dominated by \((^{230}\text{Th})/(^{232}\text{Th})\) similar to or lower than the CI samples (Figure 8b). \((^{238}\text{U})/(^{232}\text{Th})\) ranges from Th-enriched to U-enriched, and some samples show relatively extreme behavior (e.g., tephra biotite = 5.1 (not shown); cumulate magnetic separate = 0.65). The cumulate is interpreted as being composed of phases that are cogenetic with the 1944 magma or that represent an earlier stage of magmatism on Vesuvius. Beneath Vesuvius, it is likely that there are intrusive equivalents of the 1944 erupted products, because typical intrusive to extrusive relationships (Crisp, 1984) predict that large masses of magma remain in the crust relative to those erupted. Thus, if cumulates and intrusive equivalents present in the magma storage-transport system of Vesuvius undergo in-situ decay, wallrock that is isotopically heterogeneous and in some cases, characterized by extreme \((^{230}\text{Th})/(^{232}\text{Th})\) and \((^{238}\text{U})/(^{232}\text{Th})\), may be present.

Although we recognize the character of the wallrock beneath the Campanian region might be different from that beneath Vesuvius, the similarity in \((^{230}\text{Th})/(^{232}\text{Th})\) of the 1944 Vesuvius samples and our Campanian samples lends support to the possibility of similar basement beneath the Campanian region. Fedele et al. (this issue) provide some constraints on the nature of cumulate material beneath the Campanian region. They describe trachytic xenoliths from the Breccia Museo (a unit erupted in the Campanian Plain) that are interpreted to represent crystal accumulations on the associated magma chamber walls and floor. In addition to feldspar and clinopyroxene (among other phases), these xenoliths are characterized by a spectrum of accessory minerals such as U-bearing thorite, and U and REE-bearing phosphates. Many of these accessory minerals have typical hydrothermal textures and have been interpreted to reflect interaction between solids and hydrothermal fluids. As a consequence, whole-rock trace element data of these nodules show concentrations of elements such as U, Th, Zr, and REE that are, in some cases, similar to those of the pumice in the CI. (E.g., Zr abundances in nodules range from 285 to 658; Th ranges from 20 to 48). Using the whole-rock nodule U and Th data, \((^{238}\text{U})/(^{232}\text{Th})\) ranges from \(~0.4\) to 1.3, which encompasses and exceeds \((^{238}\text{U})/(^{232}\text{Th})\) of the CI samples. Although no \((^{230}\text{Th})/(^{232}\text{Th})\) are available for these samples, if the range is similar to those in this study and the Vesuvius study, then aging of such material will provide basement that is isotopically heterogeneous. In addition, the nodules may provide a source of trace elements and
if extensive hydrothermal interaction has affected basement rocks, then their Sr isotope signatures would be displaced toward the value of modern seawater, ~0.709.

A reasonable hypothesis regarding the open-system signatures of the CI system is that magmas interacted with heterogeneous wallrock composed of cumulates and intrusive equivalents of the volcanic products exposed in the Campanian region. Sr isotope disequilibria between feldspar and pumice/glass suggest that assimilation occurred largely during feldspar growth, particularly because of the two feldspar samples that have relatively high $^{87}\text{Sr}/^{86}\text{Sr}$; assuming these signatures are primary, these feldspars would not have such elevated signatures if assimilation occurred strictly after feldspar growth. Figures 8c and 8d may provide additional evidence that assimilation occurred as the magma body was undergoing crystal-liquid separation. These figures illustrate that, despite the relatively systematic relationship shown on the age-corrected isochron diagram (Figure 8b), there is no simple correlation between Th, U concentration and isotope ratio. This precludes two-component mixing, and our attempts to model such data arrays with energy-constrained assimilation-fractional crystallization (EC-AFC, Spera and Bohrson, 2001; Bohrson and Spera, 2001) failed to reproduce the isotope-concentration relationships. The EC-AFC formulation does not model zoning in magma bodies, and therefore, the failure of the model to reproduce the observed trends may be tied to the compositional heterogeneity that is produced as the magma body evolves. The Th, U vs. isotope array may reflect assimilation in a magma body that is undergoing compositional zonation. Thus, as feldspar (and other phases) form, the residual liquid becomes compositionally zoned. At the same time, heterogeneous basement that has been heated to its solidus or above can partially melt and be incorporated into this evolving magma body (Figures 8c, d). Thus, magmas with distinct Th and U concentrations interact with partial melts of heterogeneous basement to yield this compositionally complex suite of samples.

The idea that assimilation is occurring as the magma body is zoning may also be supported by the Sr concentration-isotope data of Civetta et al. (1997). Examination of Figure 9 (and other element vs. $^{87}\text{Sr}/^{86}\text{Sr}$ trends not shown) shows that there are pumice samples that range in Sr concentration from ~650 ppm to 100 ppm. $^{87}\text{Sr}/^{86}\text{Sr}$ of these vary from 0.70733 to 0.70735, which is likely to be close to reproducibility. Thus, this implies that magmas with very different Sr concentrations have similar $^{87}\text{Sr}/^{86}\text{Sr}$. Likewise, pumice with ~100 ppm Sr range in $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.70733 to 0.70745. We do note the general trend of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ with decreasing
Sr concentration; such a trend is consistent with general mass balance constraints for assimilation affecting low-Sr magmas. However, the ranges cited above highlight potential complexity of such a process. Like U, Th vs. \((^{230}\text{Th})/(^{232}\text{Th})\), there seem to be complex relationships between isotopic and elemental signatures. This may provide support for the idea that assimilation occurred as magma chamber zoning and crystal growth occurred.

The hypothesis that partial melts of cumulates and intrusive equivalents of magmas that have erupted on the Campanian Plain represent a potential assimilant may also be consistent with the trace element data. Trace element numerical model results provide poor fits for Sm and Th, which strongly implicates open-system processes. Some open-system contribution to Nb, Zr, and U are permissible, based on the modeling results. Partial melting of rocks similar to the nodules studied by Fedele et al. (this issue) as well as intrusive material hypothesized to be present in the magmatic storage-transport system would contribute trace elements to the evolving magma body.

Detailed quantification of the proposed model is precluded for several reasons. First, the highly heterogeneous nature of the basement, coupled with the uncertainty in the uncontaminated magma composition, introduces challenges in defining the end-members of the assimilation-fractional crystallization process. The trace element analysis illustrates how sensitive the closed-system trace element trends are to choice of mineral-melt partition coefficients; because of this, it is difficult to identify the contribution that open-system processes makes to trace element mass balance. Finally, the mass, species (trace element and isotope), and energy conservation equations for a system that is zoning as it evolves have not yet been formulated. Previous work (Spera and Bohrson, 2001, 2002, 2004; Bohrson and Spera, 2001, 2003) has demonstrated that energy-constrained assimilation-fractional crystallization can lead to non-monotonic element-isotope trends, and thus, full understanding of the systematics of the CI data may require formulation of conservation equations that examine the effects of open-system processes on a zoned magma body.

**SUMMARY OF MODEL, RELATIONSHIP TO PREVIOUS WORK AND OPEN QUESTIONS**

Based on the results of MELTS simulations, crystal-liquid separation played a critical role in the evolution of the Campanian magma body. Of particular interest is the occurrence of a
compositional gap, which is a consequence of a nearly isothermal crystallization at ~884°C. Several authors (e.g., Civetta et al., 1997; Pappalardo et al., 2002) have identified a compositional gap in the CI that was used in support of the idea that the magma chamber included two compositionally distinct layers that mixed during eruption. We suggest that the compositional gap is a consequence of the process of crystal-liquid separation, as predicted by the phase equilibria results discussed earlier.

The crystallization event at ~884°C caused drastic changes in the state of the magmatic system: ~40% crystallization took place over a small temperature interval, which led to a decrease in the proportion of residual melt from ~0.46 to 0.09. Most oxide and element trajectories show distinct changes in response to this event. MELTS results indicate that, as crystallization proceeds, the phase assemblage evolves, which leads to drastic changes in bulk solid-melt partition coefficients. Numerical modeling, based on a mass balance equation that accommodates changes in bulk partition coefficients, yielded some model trends that effectively reproduced observed trends. In other cases, model trends provide evidence of processes other than closed system crystallization. As a result of the MELTS modeling and implementation of a mass balance equation that correctly accommodates changes in bulk partition coefficients, the critical need for better constraints on mineral-melt partition coefficients is highlighted. Several examples shown here illustrate that, because of the permissible range of mineral-melt partition coefficients, it is difficult to constrain whether open-system processes have impacted the behavior of particular trace elements. This limitation seriously hampers attempts to quantify the evolution of the magmatic system.

$(^{230}\text{Th})/(^{232}\text{Th})$ vs. $(^{238}\text{U})/(^{232}\text{Th})$ yield an apparent isochron of 19.6± 4.7 ka, which is approximately 20 ka younger than the eruption age of the deposit. The regression coefficient for this array is 0.87, which indicates good correlation between $(^{230}\text{Th})/(^{232}\text{Th})$ vs. $(^{238}\text{U})/(^{232}\text{Th})$. Because precise and independent age evidence is available, it is clear that this linear array does not have significance with respect to the eruption age. Because Th, as well as other isotope systems, have been used to provide information about timescales associated with formation of magma bodies, our results indicate that the effects that open-system magmatic processes have on the species (isotope) balance must be assessed prior to assigning relevance to timescale information derived from these systems. This result also points to the value of acquiring
independent age or time scale information, and thus highlights the critical need for studies that integrate constraints from a range of perspectives.

Age-corrected Th isotope data suggest the magma body was open with respect to Th, and published Sr data (Civetta et al., 1997) are consistent with this. Fluids have been hypothesized to play a role in generating the open-system signature in the CI (Civetta et al., 1997; Pappalardo et al., 2002), but thermal and mass balance analysis suggests that assimilation of basement rock is more likely. Th isotopic data for Vesuvius (Black et al., 1998), and U-Th data for cumulate nodules from the Breccia Museo (Fedele et al., this issue) suggest that isotopically heterogeneous basement may reside beneath the Campanian Plain. Assimilation of partial melts of such basement may contribute isotopic and elemental heterogeneity to the CI magmas. Accessory phases in the nodules from the Breccia Museo (Fedele et al., this issue) suggest that hydrothermal fluids may have affected these rocks, and thus it is possible that the assimilant bears a hydrothermal imprint. Oxygen isotopes should reveal more about this, as would Nd isotopes; in the case of oxygen, some deviation from magmatic values would be expected. However, because the abundance of Nd is so low in typical seawater-like fluids (and other hydrothermal fluids), Nd isotopes may be dominated by a magmatic signature.

Finally, constraints on the timing of assimilation were suggested by Civetta et al. (1997) based on Sr isotope disequilibria. They hypothesized that assimilation occurred after feldspar formation. Phase equilibrium modeling however indicates that both alkali feldspar and plagioclase precipitate continuously from 884°C to the solidus. Thus, if fluids interacted with melt at supersolidus temperatures, feldspar should record the contamination event. Reevaluation of those data, coupled with complex trends in Th isotope-U, Th concentration space and Sr isotope-Sr concentration space introduces the possibility that assimilation occurred as the magma body was zoning. Thus, crystal growth, zoning in the melt and assimilation may have occurred simultaneously. Additional work on mineral phases would better elucidate the complex question of timing.

Better understanding of the behavior of magma chambers undergoing compositional zoning, crystallization, assimilation, eruption, and even recharge hinge, in part, on conservation models that accommodate mass, species and energy constraints. These types of models, coupled with characterization of volcanic products at a range of scales, hold great promise for improving our ability to develop comprehensive images of crustal magmatic systems.
ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1: (a) Simplified map of the Campanian Plain after De Vivo et al. (2001). (b). Locations of outcrops sampled for this study.

Figure 2: (a) Alkali-silica diagram using classification scheme of Le Maitre et al. (1989). Symbols are shown in legend. High-MgO melt inclusions of Webster et al. (2003) are dominantly basaltic trachyandesite and low-MgO melt inclusions are mostly trachyandesite to trachyte. Samples containing the clinopyroxene-hosted melt inclusions from the Webster et al. (2003) study are a subset of samples presented in this work. Most samples of the CI are trachyte
to phonolite. Some samples, denoted as the yellow tuff unit, show depletions in alkalies. In addition to data from this study, also included are glass and pumice data from Civetta et al. (1997), and melt inclusion and glass data from Signorelli et al. (1999). (b) Alkalies-silica diagram with result of the best-fit MELTS model shown for comparison. Best-fit MELTS calculation was run in increments of 0.5°, and therefore each black square represents a temperature decrease of 0.5°. The MELTS curve is annotated with temperatures, including the MELTS-predicted compositional gap between 884 and 883° C. Note that MI data from Signorelli et al. (1999) and Webster et al. (2003) are not expected to lie on the predicted liquid line of descent due to post-entrapment crystallization. See text for discussion.

Figure 3: Fraction of residual melt, \( f_m(T) \), vs. bulk partition coefficient for Sr, bulk \( K_{sm}^{Sr} \). The heavy black line is the computed partition coefficient based on the solid assemblage predicted from MELTS and the partition coefficients listed in Table 2. The \( K_{sm}^{Sr} \) vs. \( f_m(T) \) relationship is broken into 5 linear piecewise continuous segments as indicated by the line segments in gray in order to carry out the numerical integrations for the trace element evolution.

Figure 4: \( f_m(T) \) vs. \( T \) (°C) for MELTS simulation of the reconstructed parental composition for the Campanian Ignimbrite. Fields represent cumulative proportion of mineral phases as saturation occurs. Note the distinct change in \( f_m(T) \) at the point in which plagioclase and alkali feldspar become liquidus phases: \( f_m(T) \) changes from ~0.46 to 0.09 at \( T \sim 884°C \). See text for discussion.

Figure 5: MgO (wt. %) vs. (a) K₂O (wt. %), (b), Na₂O (wt. %), (c) Al₂O₃ (wt. %), (d) FeO (wt. %). Symbols are the same as those in Figure 2. Best-fit MELTS model shown by black trends, and each black square represents a temperature decrease of 0.5°. Gap in trends represents change in composition between 884° C and 883° C.

Figure 6: MgO (wt. %) vs. (a) Zr, (b) Nb, (c) Th, (d) U, (e) Rb, (f) Sm, (g) Sr. All trace elements in ppm. Symbols are the same as those in Figure 2. Best-fit MELTS model shown by grey trends, and each grey square represents a temperature decrease of 0.5°. Gap in trends represents change in composition between 884° C and 883° C. MELTS trend after
compositional gap not shown on (e), but arrow shows trajectory of trend at 884°C, which begins at 1255 ppm Rb.

Figure 7: U (ppm) vs. (a) Zr, (b) Nb, (c) Th, (d) Rb, (e) Sm, (f) Sr. Symbols are the same as those in Figure 2. Best-fit MELTS model shown by grey trends, and each grey square represents a temperature decrease of 0.5°. In (a), trends 1 and 2 illustrate bracketing of observed trend based on use of variable mineral-melt partition coefficients, which are reported in Table 2. See text for discussion.

Figure 8: (a) $^{238}$U/$^{232}$Th vs. measured $^{230}$Th/$^{232}$Th for 12 samples of the CI. Analyses plot as a relatively well-correlated linear array (R = 0.82), which gives an apparent age of 19.6±4.7 ka. Note that this is ~20 kyr younger than the 39.28±0.11 ka age of the deposit (De Vivo et al., 2001). (b) $^{238}$U/$^{232}$Th vs. $^{230}$Th/$^{232}$Th. Samples, which were all age-corrected to 39.28±0.11 ka, plot on a relatively well-correlated linear array (R = 0.77) characterized by a negative slope. (c) Th (ppm) vs. $^{230}$Th/$^{232}$Th. (d) U (ppm) vs. $^{230}$Th/$^{232}$Th. In both (c) and (d), note lack of simple correlation between isotope ratio and concentration. Also shown are arrows to qualitatively illustrate effects of crystal-liquid separation, and possible mixing lines between fractionating melt and partial melts of heterogeneous wallrock characterized by relatively low $^{230}$Th/$^{232}$Th. See text for discussion of qualitative open system model.

Figure 9: Sr (ppm) vs. $^{87}$Sr/$^{86}$Sr of pumice, glass and feldspar data of Civetta et al. (1997). Symbols shown in legend. Note disequilibrium between feldspar, pumice and glass and the general trend defined by decreasing Sr (ppm) and increasing $^{87}$Sr/$^{86}$Sr. Arrow shows qualitative effect of assimilation of wallrock with relatively radiogenic Sr isotope signature.
Table 1a: Major Element Data for Melt Inclusion and Host Clinopyroxene Used in Reconstruction of Parental Melt

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Table 1b: Reconstructed Parental Melt Composition used in Best-Fit MELTS Model

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Compositions used in MELTS modeling based on sample VE1#3 (Webster et al., 2003). Recalculated VE1#3 composition for X = 0.2. See text for discussion.
Table 2a: Mineral-Melt Distribution Coefficients used in Trace Element Modeling for T > feldspar-in (~884°C)

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<th>Olivine</th>
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<td>0(^a)</td>
<td>0.02</td>
<td>1.3</td>
<td>8, -, 20, 21</td>
</tr>
<tr>
<td>Zr</td>
<td>0.12</td>
<td>0.71</td>
<td>0.06</td>
<td>0.64</td>
<td>7, 11, 19, 4</td>
</tr>
<tr>
<td>Nb</td>
<td>0.12</td>
<td>0.7</td>
<td>0.11</td>
<td>0.64(^b)</td>
<td>8, 5, 3, -</td>
</tr>
<tr>
<td>Sm</td>
<td>0.75</td>
<td>0.01</td>
<td>0.02</td>
<td>4.5</td>
<td>17, 15, 2, 21</td>
</tr>
<tr>
<td>Th</td>
<td>0.03</td>
<td>0.10</td>
<td>0.02</td>
<td>1.6</td>
<td>8, 11, 20, 12</td>
</tr>
<tr>
<td>U</td>
<td>0.04</td>
<td>0.11</td>
<td>0.04</td>
<td>1.8</td>
<td>1, 11, 19, 10</td>
</tr>
</tbody>
</table>

\(^a\) Distribution coefficient for Zr in spinel not reported GERM compilation; estimated to be 0.
\(^b\) Distribution coefficient for Nb in apatite not reported GERM compilation; estimated using distribution coefficient for Zr.

Table 2b: Mineral-Melt Distribution Coefficients for Zr used to Calculate Trends 1 and 2 for T > feldspar-in (~884°C)

<table>
<thead>
<tr>
<th>Element</th>
<th>Clinopyroxene</th>
<th>Spinel</th>
<th>Olivine</th>
<th>Apatite</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr Trend 1</td>
<td>0.12</td>
<td>0.71</td>
<td>0.06</td>
<td>0.1</td>
<td>7, 11, 19, -</td>
</tr>
<tr>
<td>Zr Trend 2</td>
<td>0.12</td>
<td>0.71</td>
<td>0.06</td>
<td>0.64</td>
<td>7, 11, 19, 4</td>
</tr>
</tbody>
</table>
Table 2c: Mineral-Melt Distribution Coefficients used in Trace Element Modeling for T < feldspar-in (~884°C)

<table>
<thead>
<tr>
<th>Element</th>
<th>Alkali</th>
<th>Feldspar</th>
<th>Plagioclase</th>
<th>Biotite</th>
<th>Apatite</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>0.66</td>
<td>0.52</td>
<td>5.3</td>
<td>0.40</td>
<td>16, 20, 3, 12</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>3.9</td>
<td>2.8</td>
<td>0.31</td>
<td>2.1</td>
<td>16, 16, 3, 21</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>0.069</td>
<td>0.08</td>
<td>0.205</td>
<td>2.0</td>
<td>3, 20, 20, 12</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>0.15</td>
<td>0.57</td>
<td>9.5</td>
<td>2.0^</td>
<td>3, 3, 13, -</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>0.02</td>
<td>0.13</td>
<td>0.26</td>
<td>20.7</td>
<td>18, 10, 6, 12</td>
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</tr>
<tr>
<td>Th</td>
<td>0.02</td>
<td>0.008</td>
<td>0.31</td>
<td>1.6</td>
<td>18, 10, 20, 10</td>
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</tr>
<tr>
<td>U</td>
<td>0.04</td>
<td>0.014</td>
<td>0.08</td>
<td>1.8</td>
<td>18, 10, 20, 10</td>
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</tr>
</tbody>
</table>

^Distribution coefficient for Nb in apatite not reported in GERM compilation; estimated using distribution coefficient for Zr.

Table 2d: Mineral-Melt Distribution Coefficients for Zr used to Calculate Trends 1 and 2 for T < feldspar-in (~884°C)

<table>
<thead>
<tr>
<th>Element</th>
<th>Alkali</th>
<th>Feldspar</th>
<th>Plagioclase</th>
<th>Biotite</th>
<th>Apatite</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr Trend 1</td>
<td>0.03</td>
<td>0.09</td>
<td>0.205</td>
<td>0.1</td>
<td>13, 20, 20, -</td>
<td></td>
</tr>
<tr>
<td>Zr Trend 2</td>
<td>0.36</td>
<td>0.36</td>
<td>0.59</td>
<td>2</td>
<td>9, 13, 3, 12</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Selected Major and Trace Element Abundance Data for Samples of the Campanian Ignimbrite

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>PontIR</th>
<th>IC-HB6a</th>
<th>ALT-1</th>
<th>SA-1b</th>
<th>SA-1a</th>
<th>AFGI-11</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pumice</td>
<td>pumice</td>
<td>bulk</td>
<td>bulk</td>
<td>pumice</td>
<td>pumice</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>58.26</td>
<td>58.37</td>
<td>60.15</td>
<td>60.88</td>
<td>60.95</td>
<td>61.34</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>0.43</td>
<td>0.46</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>18.81</td>
<td>18.85</td>
<td>18.57</td>
<td>18.94</td>
<td>18.93</td>
<td>18.98</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1.89</td>
<td>2.22</td>
<td>2.32</td>
<td>2.75</td>
<td>2.54</td>
<td>1.71</td>
</tr>
<tr>
<td>FeO</td>
<td>2.44</td>
<td>2.12</td>
<td>1.44</td>
<td>1.01</td>
<td>1.08</td>
<td>1.89</td>
</tr>
<tr>
<td>MnO</td>
<td>0.10</td>
<td>0.10</td>
<td>0.16</td>
<td>0.17</td>
<td>0.12</td>
<td>0.19</td>
</tr>
<tr>
<td>MgO</td>
<td>1.44</td>
<td>1.38</td>
<td>0.92</td>
<td>0.79</td>
<td>0.79</td>
<td>0.68</td>
</tr>
<tr>
<td>CaO</td>
<td>4.09</td>
<td>4.02</td>
<td>3.23</td>
<td>2.64</td>
<td>2.46</td>
<td>2.17</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>2.66</td>
<td>2.61</td>
<td>4.44</td>
<td>4.23</td>
<td>4.40</td>
<td>4.63</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>9.18</td>
<td>9.18</td>
<td>7.53</td>
<td>7.74</td>
<td>7.90</td>
<td>7.62</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.27</td>
<td>0.25</td>
<td>0.18</td>
<td>0.16</td>
<td>0.15</td>
<td>0.09</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.05</td>
<td>0.08</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.01</td>
</tr>
<tr>
<td>Cl</td>
<td>0.24</td>
<td>0.26</td>
<td>0.42</td>
<td>0.09</td>
<td>0.08</td>
<td>0.11</td>
</tr>
<tr>
<td>F</td>
<td>0.10</td>
<td>0.09</td>
<td>0.15</td>
<td>0.11</td>
<td>0.16</td>
<td>0.06</td>
</tr>
<tr>
<td>Nb$^b$</td>
<td>21</td>
<td>20</td>
<td>64</td>
<td>70</td>
<td>55</td>
<td>87</td>
</tr>
<tr>
<td>Rb</td>
<td>225</td>
<td>230</td>
<td>315</td>
<td>340</td>
<td>305</td>
<td>361</td>
</tr>
<tr>
<td>Sm</td>
<td>6.4</td>
<td>6.3</td>
<td>11.6</td>
<td>12.7</td>
<td>9.6</td>
<td>9.85</td>
</tr>
<tr>
<td>Sr</td>
<td>760</td>
<td>800</td>
<td>355</td>
<td>265</td>
<td>270</td>
<td>202</td>
</tr>
<tr>
<td>Th</td>
<td>11.8</td>
<td>11.8</td>
<td>34.8</td>
<td>36.7</td>
<td>27.4</td>
<td>37.8</td>
</tr>
<tr>
<td>U</td>
<td>3.5</td>
<td>3.4</td>
<td>9.5</td>
<td>10.3</td>
<td>7.4</td>
<td>12.5</td>
</tr>
<tr>
<td>Zr$^a$</td>
<td>166</td>
<td>164</td>
<td>420</td>
<td>455</td>
<td>350</td>
<td>521</td>
</tr>
</tbody>
</table>

$^a$Major elements in wt. %
$^b$Trace elements in ppm
Table 3: Selected Major and Trace Element Abundance Data for Samples of the Campanian Ignimbrite (cont.)

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>VE-1</th>
<th>AFGI-1</th>
<th>AFBP-1</th>
<th>AFBP-5</th>
<th>MP-1</th>
<th>ICB-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Type</td>
<td>bulk</td>
<td>pumice</td>
<td>pumice</td>
<td>pumice</td>
<td>pumice</td>
<td>pumice</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>60.74</td>
<td>61.12</td>
<td>60.12</td>
<td>60.58</td>
<td>60.61</td>
<td>61.53</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.46</td>
<td>0.46</td>
<td>0.47</td>
<td>0.45</td>
<td>0.43</td>
<td>0.44</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>18.73</td>
<td>18.74</td>
<td>19.93</td>
<td>19.08</td>
<td>18.63</td>
<td>18.96</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.49</td>
<td>2.80</td>
<td>1.11</td>
<td>0.88</td>
<td>1.80</td>
<td>3.08</td>
</tr>
<tr>
<td>FeO</td>
<td>1.05</td>
<td>0.79</td>
<td>2.30</td>
<td>2.52</td>
<td>1.39</td>
<td>0.23</td>
</tr>
<tr>
<td>MnO</td>
<td>0.20</td>
<td>0.21</td>
<td>0.24</td>
<td>0.23</td>
<td>0.23</td>
<td>0.20</td>
</tr>
<tr>
<td>MgO</td>
<td>0.62</td>
<td>0.59</td>
<td>0.46</td>
<td>0.42</td>
<td>0.40</td>
<td>0.38</td>
</tr>
<tr>
<td>CaO</td>
<td>2.25</td>
<td>2.19</td>
<td>1.79</td>
<td>1.71</td>
<td>1.75</td>
<td>1.76</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>5.20</td>
<td>5.32</td>
<td>5.39</td>
<td>5.54</td>
<td>6.39</td>
<td>5.78</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>7.20</td>
<td>7.26</td>
<td>6.86</td>
<td>7.34</td>
<td>7.12</td>
<td>7.04</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.12</td>
<td>0.09</td>
<td>0.04</td>
<td>0.05</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.03</td>
<td>0.02</td>
<td>0.05</td>
<td>0.03</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Cl</td>
<td>0.74</td>
<td>0.30</td>
<td>0.74</td>
<td>0.67</td>
<td>0.84</td>
<td>0.23</td>
</tr>
<tr>
<td>F</td>
<td>0.17</td>
<td>0.03</td>
<td>0.23</td>
<td>0.26</td>
<td>0.31</td>
<td>0.28</td>
</tr>
<tr>
<td>Nb$^b$</td>
<td>93</td>
<td>101</td>
<td>112</td>
<td>114</td>
<td>114</td>
<td>104</td>
</tr>
<tr>
<td>Rb</td>
<td>380</td>
<td>362</td>
<td>356</td>
<td>406</td>
<td>420</td>
<td>375</td>
</tr>
<tr>
<td>Sm</td>
<td>13.8</td>
<td>14.8</td>
<td>15.6</td>
<td>15.1</td>
<td>14.8</td>
<td>14.1</td>
</tr>
<tr>
<td>Sr</td>
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<td>128</td>
<td>101</td>
<td>44</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>Th</td>
<td>46.1</td>
<td>47.3</td>
<td>52.9</td>
<td>51.3</td>
<td>54.0</td>
<td>51.4</td>
</tr>
<tr>
<td>U</td>
<td>14.0</td>
<td>16.5</td>
<td>16.2</td>
<td>17.4</td>
<td>16.3</td>
<td>16.3</td>
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<tr>
<td>Zr</td>
<td>580</td>
<td>591</td>
<td>671</td>
<td>665</td>
<td>670</td>
<td>630</td>
</tr>
</tbody>
</table>
Table 4: Selected Major and Trace Element and Th Isotopic Data for Samples of the Campanian Ignimbrite

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>MgO (wt. %)</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
<th>Th/U</th>
<th>232(^{\text{Th}})/230(^{\text{Th}}) (x 10^4)^a</th>
<th>((^{238}\text{U})/(^{232}\text{Th}))^b</th>
<th>((^{230}\text{Th})/(^{232}\text{Th}))^b</th>
<th>((^{230}\text{Th})/(^{238}\text{U}))^b</th>
<th>((^{230}\text{Th})/(^{232}\text{Th}))_o^c</th>
<th>((^{230}\text{Th})/(^{238}\text{U}))_o^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>PONTIR pumice</td>
<td>1.44</td>
<td>3.62</td>
<td>11.22</td>
<td>3.10</td>
<td>19.39</td>
<td>0.979</td>
<td>0.958</td>
<td>0.979</td>
<td>0.950</td>
<td>0.970</td>
</tr>
<tr>
<td>ICHB6a pumice</td>
<td>1.38</td>
<td>3.63</td>
<td>11.10</td>
<td>3.06</td>
<td>19.86</td>
<td>0.993</td>
<td>0.936</td>
<td>0.942</td>
<td>0.911</td>
<td>0.917</td>
</tr>
<tr>
<td>ALT-1 bulk</td>
<td>0.92</td>
<td>10.56</td>
<td>33.24</td>
<td>3.15</td>
<td>19.40</td>
<td>0.964</td>
<td>0.958</td>
<td>0.994</td>
<td>0.956</td>
<td>0.992</td>
</tr>
<tr>
<td>Sa-1b bulk</td>
<td>0.79</td>
<td>9.63</td>
<td>33.17</td>
<td>3.44</td>
<td>19.53</td>
<td>0.881</td>
<td>0.952</td>
<td>1.080</td>
<td>0.982</td>
<td>1.115</td>
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<tr>
<td>Sa-1a pumice</td>
<td>0.79</td>
<td>8.49</td>
<td>27.34</td>
<td>3.22</td>
<td>19.52</td>
<td>0.943</td>
<td>0.952</td>
<td>1.010</td>
<td>0.956</td>
<td>1.014</td>
</tr>
<tr>
<td>AFGI-11 pumice</td>
<td>0.68</td>
<td>13.84</td>
<td>41.75</td>
<td>3.02</td>
<td>18.93</td>
<td>1.006</td>
<td>0.980</td>
<td>0.977</td>
<td>0.972</td>
<td>0.967</td>
</tr>
<tr>
<td>VE-1 bulk</td>
<td>0.62</td>
<td>14.18</td>
<td>39.74</td>
<td>2.80</td>
<td>18.90</td>
<td>1.083</td>
<td>0.984</td>
<td>0.908</td>
<td>0.940</td>
<td>0.868</td>
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<tr>
<td>AFGI-1 pumice</td>
<td>0.59</td>
<td>12.99</td>
<td>41.08</td>
<td>3.16</td>
<td>19.47</td>
<td>0.959</td>
<td>0.955</td>
<td>0.995</td>
<td>0.953</td>
<td>0.993</td>
</tr>
<tr>
<td>AFBP-1 pumice</td>
<td>0.46</td>
<td>14.96</td>
<td>49.45</td>
<td>3.31</td>
<td>19.45</td>
<td>0.918</td>
<td>0.956</td>
<td>1.041</td>
<td>0.972</td>
<td>1.059</td>
</tr>
<tr>
<td>AFBP-5 pumice</td>
<td>0.42</td>
<td>16.26</td>
<td>49.31</td>
<td>3.03</td>
<td>19.16</td>
<td>1.000</td>
<td>0.970</td>
<td>0.970</td>
<td>0.957</td>
<td>0.956</td>
</tr>
<tr>
<td>MP-1 pumice</td>
<td>0.40</td>
<td>18.13</td>
<td>48.44</td>
<td>2.66</td>
<td>18.83</td>
<td>1.139</td>
<td>0.987</td>
<td>0.867</td>
<td>0.921</td>
<td>0.809</td>
</tr>
<tr>
<td>ICB-9 pumice</td>
<td>0.38</td>
<td>18.13</td>
<td>46.24</td>
<td>2.55</td>
<td>18.65</td>
<td>1.190</td>
<td>0.996</td>
<td>0.837</td>
<td>0.912</td>
<td>0.767</td>
</tr>
</tbody>
</table>

a \(232\text{Th}/230\text{Th}\) represent averages of at least 2 replicates except for samples PONTIR and ICHB6a, which are represented by only 1 analysis. Average in-run analytical precision for Th isotope analyses ranges from 0.23% to 0.49%. Typical reproducibility for Th isotope ratios is 1.5% or less. Typical reproducibility for U/Th is 2%.

b Activity ratios denoted by parentheses and calculated using the following decay constants: \(\lambda_{232} = 4.9475 \times 10^{-11} \text{ yr}^{-1}\); \(\lambda_{230} = 9.1952 \times 10^{-6} \text{ yr}^{-1}\); \(\lambda_{238} = 1.55125 \times 10^{-10} \text{ yr}^{-1}\) and using the weighted mean \(232\text{Th}/230\text{Th}\).

cAge of 39.28 (±0.11) ka, determined by incremental heating and total fusion \(^{40}\text{Ar}/^{39}\text{Ar}\) geochronology (De Vivo et al., 2001) used for age correction on all samples.
Table 5: Characteristics Predicted by Best-Fit MELTS Model of Melts at Pseudoinvariant Point

<table>
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<th>FeO</th>
<th>MgO</th>
<th>MnO</th>
<th>CaO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
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<th>H$_2$O</th>
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Lithic breccia deposit at the top of Campanian Ignimbrite (39 ka)

Breccia deposit underlying Campanian Ignimbrite (39 ka)

Neapolitan Yellow Tuff (12 ka) caldera (Lirer et al., 1987; Scandone et al., 1991; Florio et al., 1999)

Acerra depression

Fault identified by geological and geophysical data

Campanian Ignimbrite inferred caldera (Orsi et al., 1996)

Fig.1: Simplified geologic map of the Campania Plain
Figure 2; Bohrson et al., 2005
Figure 3; Bohrson et al., 2005
Figure 5; Bohrson et al., 2005
Figure 6; Bohrson et al., 2005
Figure 7; Bohrson et al., 2005
Figure 8, Bohrson et al.
Figure 9, Bohrson et al.