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Phase Equilibria Constraints on the Chemical and Physical Evolution of the Campanian Ignimbrite

SARAH J. FOWLER¹*, FRANK J. SPERA¹, WENDY A. BOHRSON², HARVEY E. BELKIN³ AND BENEDETTO DE VIVO⁴

¹DEPARTMENT OF EARTH SCIENCE AND INSTITUTE FOR CRUSTAL STUDIES, UNIVERSITY OF CALIFORNIA, SANTA BARBARA, SANTA BARBARA, CA 93106, USA

²DEPARTMENT OF GEOLOGICAL SCIENCES, CENTRAL WASHINGTON UNIVERSITY, ELLENSBURG, WA 98926, USA ³956 NATIONAL CENTER, US GEOLOGICAL SURVEY, RESTON, VA 20192, USA

⁴DIPARTIMENTO DI SCIENZE DELLA TERRA, UNIVERSITÀ DI NAPOLI FEDERICO II, 80134 NAPOLI, ITALY

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The Campanian Ignimbrite is $a > 200 \text{ km}^3$ trachyte-phonolite pyroclastic deposit that erupted at 39.3 ± 0.1 ka within the Campi Flegrei west of Naples, Italy. Here we test the hypothesis that Campanian Ignimbrite magma was derived by isobaric crystal fractionation of a parental basaltic trachyandesitic melt that reacted and came into local equilibrium with small amounts (5–10 wt%) of crustal rock (skarns and foid-syenites) during crystallization. Comparison of observed crystal and magma compositions with results of phase equilibria assimilation-fractionation simulations (MELTS) is generally very good. Oxygen fugacity was approximately buffered along QFM + 1 (where QFM is the quartzfayalite-magnetite buffer) during isobaric fractionation at 0.15 GPa $(\approx 6 \text{ km depth})$. The parental melt, reconstructed from melt inclusion and host clinopyroxene compositions, is found to be basaltic trachyandesite liquid (51.1 wt% SiO₂, 9.3 wt% MgO, 3 wt% H₂O). A significant feature of phase equilibria simulations is the existence of a pseudo-invariant temperature, $\sim 883 \,^{\circ}C$, at which the fraction of melt remaining in the system decreases abruptly from ~ 0.5 to < 0.1. Crystallization at the pseudo-invariant point leads to abrupt changes in the composition, properties (density, dissolved water content), and physical state (viscosity, volume fraction fluid) of melt and magma. A dramatic decrease in melt viscosity (from 1700 Pa s to \sim 200 Pa s), coupled with a change in the volume fraction of water in magma (from ~ 0.1 to 0.8) and a dramatic decrease in melt and magma density acted as a destabilizing eruption trigger. Thermal models suggest a timescale of ~ 200 kyr from the beginning of fractionation

until eruption, leading to an apparent rate of evolved magma generation of about 10^{-3} km³/year. In situ crystallization and crystal settling in density-stratified regions, as well as in convectively mixed, less evolved subjacent magma, operate rapidly enough to match this apparent volumetric rate of evolved magma production.

KEY WORDS: assimilation; Campanian Ignimbrite; fractional crystallization; magma dynamics; phase equilibria

INTRODUCTION

Variations in physical and chemical properties of intermediate to silicic magmas are the result of a complex array of processes that occur in the source and in crustal-level magma reservoirs. In the case of erupted magmas, additional complications may be introduced during magma withdrawal from compositionally heterogeneous bodies. Documenting, and where possible quantifying, magma chamber processes leads to a description of how and why physical and chemical gradients form in magma bodies and also informs the debate about the origin and evolution of continental crust. The timescales over which intermediate to silicic magmas form, evolve and amalgamate are also critical, particularly because such chronological information may improve eruption assessment and mitigation efforts. Among the

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most exciting endeavors in the current study of evolved magmatic systems is integration of these two fundamental topics; that is, documenting the duration of discrete but definable processes that contribute to the formation, evolution, and, where relevant, eruption of these systems. A challenging goal of such an approach includes realistic representation of the physical and chemical nature of magma bodies in space and time.

The wide range of processes that affect the formation and evolution of evolved magmatic systems complicates realization of such a goal. Crystal-liquid separation and partial melting appear to be important mechanisms for generating chemical and physical diversity (e.g. Bacon & Druitt, 1988; DeSilva & Wolff, 1995; Bohrson & Reid, 1997; Bryan et al., 2002; Costa & Singer, 2002), but careful studies over the last 25 years have revealed that a number of other mechanisms are also viable. Among these are incorporation of crustal materials, both melt and solids (Duffield et al., 1995; Bindemann & Valley, 2001; Reagan et al., 2003; Bacon & Lowenstern, 2005; Zellmer et al., 2005), magma recharge/magma mixing or mingling (e.g. Bryan et al., 2002; Nakagawa et al., 2002; Sumner & Wolff, 2003), remobilization of magmatic 'mush' zones (e.g. Murphy et al., 2000; Bachmann & Bergantz, 2003; Wilson et al., 2005), and inclusion of cumulates (e.g. Reubi & Nicholls, 2005; Zellmer et al., 2005). A critical observation is that in many cases, two or more of these processes may act simultaneously, thus complicating efforts to define and quantify magmatic evolution. Even when the chemical effects of a process can be reliably identified, a comprehensive physical description of the process often remains elusive. A good example of this is the important, but still incompletely understood, mechanism of crystal-liquid separation. Gas-driven filter pressing (Sisson & Bacon, 1999), Stokes' or hindered settling (Bachmann & Bergantz, 2004), compaction (Bachmann & Bergantz, 2004), and in situ marginal porous mush crystallization (McBirney et al., 1985; Trial & Spera, 1990) are plausible physical mechanisms that have been proposed and quantitatively examined for separation of melt and crystals. The complicated nature of magmatic systems suggests that each of these mechanisms may play a role, but detailed application of governing physical principles is not yet routine in the study of magma bodies. Further, physical descriptions of processes such as crustal assimilation and magma recharge and mixing are also incomplete. Although deciphering the processes that lead to chemical evolution in magma bodies remains a challenge, an associated and equally significant undertaking is documentation of the physical properties of magma (melt + crystals + supercritical fluid) at each stage of evolution. The physical state of magma is intricately linked not only to the processes that affect it but also to its ultimate fate as intrusive or extrusive rock.

Implicit in the pursuit of understanding magmatic evolution is deciphering the chronology of events as magma forms and evolves. Particularly in the last 15 years, insightful applications of radiogenic isotope systematics (e.g. Christensen & DePaolo, 1993; Reid et al., 1997; Davies & Halliday, 1998; Charlier et al., 2003; Reagan et al., 2003), diffusion (e.g. Zellmer et al., 1999; Costa et al., 2003; Morgan et al., 2004), and magma transport and kinetic phenomena (e.g. Mangan, 1990; Spera et al., 1995; Higgins, 1996; Bergantz, 1999) have enhanced understanding of magmatic timescales, which have been shown to vary by several orders of magnitude ($<10^{1}$ to 10^{6} years). Improved precision and spatial resolution in studies involving radiogenic isotopes (e.g. Reid et al., 1997; Lowenstern et al., 2000), and the benefit of larger, faster computers and better algorithms that allow more detailed dynamical models of magma transport have provided constraints that were lacking even a decade ago. Along with the significant analytical and computational advances, however, come challenges of interpretation. The question of what magmatic timescales mean in the context of the mass, chemical, and thermal evolution of magma bodies is central to these studies, but the answers are not straightforward. In the case of isotope data, application of a particular system to address timing may be complicated by opensystem processes that may be very difficult to recognize. In addition, studies based on diffusion and magma transport are limited by imperfect knowledge of material properties and associated kinetic factors that affect the rates of, for example, elemental diffusion or heat flow. A particularly promising approach for documenting timescales of processes involves integrated studies that attempt to document the timescales of magma chamber processes by independent means.

In this paper, we examine processes that gave rise to the Campanian Ignimbrite, a 39.28 ka (De Vivo et al., 2001) trachytic to phonolitic ignimbrite erupted near Naples, Italy. By applying constraints from phase equilibria embodied within the MELTS thermodynamic model (Ghiorso & Sack, 1995), we document the major element evolution and associated changes in physical properties of this magmatic system, where isobaric multiphase liquid-crystal separation is a dominant process and wall-rock assimilation plays a secondary role. A key aspect of our results includes identification of a pseudoinvariant temperature along the liquid line of descent. That is, at $\approx 883^{\circ}$ C, the system undergoes marked changes in crystallinity, melt composition including volatile content, viscosity, and density. The behavior of the system at this point has fundamental implications regarding the origin of the Campanian Ignimbrite and may provide a triggering mechanism for this ignimbrite and possibly other volatile-rich, low-pressure pyroclastic style eruptions. Because MELTS tracks the enthalpy of the system along



Fig. 1. (a) Simplified geological map of the Campanian Plain. Grey region in inset shows approximate location of Campania in Italy (modified from De Vivo *et al.*, 2001). The Neapolitan Yellow Tuff (Lirer *et al.*, 1987; Scandone *et al.*, 1991; Florio *et al.*, 1999) caldera is indicated. (b) Typical stratigraphic column of the Campanian Ignimbrite (modified from De Vivo *et al.*, 2001).

the liquid line of descent, application of a simple heat transport model provides time constraints on the duration of magmatic activity, including estimates of the durations of crystallization for individual mineral phases. Such temporal context provides one approach for evaluating the meaning of timescale information derived from other types of studies.

GEOLOGICAL SETTING

The Campi Flegrei Volcanic Field covers an area of $\sim 2000 \text{ km}^2$ west of Naples, Italy, and forms part of the Campanian Plain, a region located within a graben of Mesozoic carbonates (Fig. la). Formation of the graben as a consequence of extension along the western margin of the Apennine Mountains led to the opening of the Tyrrhenian Sea in the Pliocene–Quaternary (Rosi & Sbrana, 1987; Acocella *et al.*, 1999). Eruption of the Campanian Ignimbrite (CI) at $39\cdot28\pm0.11 \text{ ka}$ (De Vivo *et al.*, 2001) is regarded as the dominant event in the history of the Campi Flegrei Volcanic Field and, via its

influence on northern hemisphere and perhaps global climate, may have played a role in human evolution, particularly the replacement of the Neanderthals by modern *Homo sapiens sapiens* (Fedele *et al.*, 2003). In addition to the CI, explosive eruptions have been documented in the Campanian Plain at >300 ka, ~205 ka, ~184 ka, ~157 ka, and ~18 ka (De Vivo *et al.*, 2001; Rolandi *et al.*, 2003).

The CI is a grey, phenocryst-poor, unwelded to partially welded trachytic-phonolitic ignimbrite with a minimum bulk volume of ~310 km³ (~200 km³ Dense Rock Equivalent; DRE) and initial areal distribution of ~30 000 km² (Rolandi *et al.*, 2003). There are four distinct pyroclastic flow units (Rosi *et al.*, 1996; De Vivo *et al.*, 2001) overlying a volumetrically subordinate basal fallout deposit (Fisher *et al.*, 1993; Rosi *et al.*, 1996; De Vivo *et al.*, 2001). In some sections of the CI, the Gray Tuff lies beneath a Lithic Breccia that grades upward into a weakly stratified Yellow Tuff and/or an incoherent pyroclastic flow deposit (Upper Incoherent Tuff). The Yellow Tuff has been modified through secondary mineralization, notably by zeolites. The Lithic Breccia is discontinuously exposed around the Campanian Plain, and in some locations, shows evidence of proximal depositional characteristics (De Vivo *et al.*, 2001). A schematic cross-section of the CI is presented in Fig. 1b; detailed stratigraphic sections of localities from which the samples studied as part of this investigation were taken have been given by De Vivo *et al.* (2001).

Debate persists about the location of vents of the CI. Some workers advocate eruptions from quasilinear fissures controlled by regional fault systems (e.g. Di Girolamo, 1968, 1970; Milia *et al.*, 2000, 2003; De Vivo *et al.*, 2001; Rolandi *et al.*, 2003). In particular, work by De Vivo *et al.* (2001) has identified proximal depositional characteristics and an elongate pattern in the distribution of the Lithic Breccia. An alternative hypothesis posits an association with a caldera ring fracture system located within the Campi Flegrei Volcanic Field (e.g. Rosi & Sbrana, 1987; Fisher *et al.*, 1993; Rosi *et al.*, 1999; Signorelli *et al.*, 1999) or elsewhere in the Campanian Plain (e.g. Scandone *et al.*, 1991; Orsi *et al.*, 1996).

ANALYTICAL METHODS

Major and minor elements were determined on fused glass disks by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF) using the method described by Taggart et al. (1987) at the US Geological Survey laboratories, Denver, CO and at Activation Laboratories, Ancaster, Ontario, Canada. 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. The titration technique used for FeO determination was that of Peck (1964). CO₂ was determined coulometrically (Engleman et al., 1985). Total H₂O was determined by Karl-Fischer titration (Jackson *et al.*, 1987). H_2O^- was calculated by weight loss after heating at 110°C for a minimum time of 1h (Shapiro, 1975). H_2O^+ is thus calculated from the difference between total H_2O and H_2O^- . Loss on ignition (LOI) is the weight loss after heating over the temperature range 925–1050°C. Total sulfur reported as SO3 was determined by the combustion-IR spectroscopy method described by Kirschenbaum (1983). Fluorine was determined by the selective-ion electrode method of Kirschenbaum (1988), and chlorine was determined by either selective-ion electrode (Aruscavage & Campbell, 1983) or by instrumental neutron activation analysis (Hoffman, 1992).

Quantitative electron microprobe analyses of major and minor elements in feldspar were obtained by WD-XRF, using a JEOL JXA-8900 five-spectrometer, fully automated electron microprobe analyzer. Analyses were made at 15 keV accelerating voltage and 20 nA probe current measured with a Faraday cup; counting times on both peak and background varied from 20 to 120 s, with a 5 µm probe spot. The analyses were corrected for electron beam matrix effects, instrumental drift and deadtime using a Phi-Rho-Z algorithm (CITZAF; Armstrong, 1995) as supplied with the JEOL JXA-8900 electron microprobe. Relative accuracy of the analyses, based upon comparison between measured and published compositions of standard reference materials, is ~1–2% for oxide concentrations >1 wt% and ~5–10% for oxide concentrations <1 wt%. Elements analyzed as oxides and their detection limits (wt%) at 3 σ are as follows: MgO (0.01), Al₂O₃ (0.03), SiO₂ (0.03), CaO (0.02), FeO (total) (0.03), Na₂O (0.03), K₂O (0.01), BaO (0.04), SrO (0.04), and P₂O₅ (0.02).

PETROGRAPHY AND MAJOR ELEMENT COMPOSITIONS

Our study is based upon 77 stratigraphically oriented pumice or bulk-rock (pumice + matrix) samples that cover a wide geographical area and include examples from each of the four ignimbrite units and the basal pumice (Fig. la and b). The locations and volcanological framework of these samples have been presented by De Vivo et al. (2001) and Bohrson et al. (2006). Here, we present an overview of the petrography and describe the major element composition of the Gray Tuff, Lithic Breccia, Incoherent Tuff, and Basal Pumice. Because samples of the Yellow Tuff have undergone secondary alteration, which is obvious in hand sample, they are not discussed here. We also utilize data from several published studies on single and bulk pumice, glass, and melt inclusions (Civetta et al., 1997; Signorelli et al., 1999; Pappalardo et al., 2002a, 2002b; Webster et al., 2003).

Petrography and mineral compositions

The crystallinity of CI ash-flow tuff and Plinian fall (Basal Pumice) is low (average crystallinity $\sim 3 \text{ vol. }\%$; maximum crystallinity $\sim 10 \text{ vol. }\%$). The typical phenocryst assemblage includes alkali feldspar, with lesser plagioclase and sparse to trace clinopyroxene, spinel, apatite, and biotite. Based on analyses of Civetta et al. (1997), some clinopyroxene exhibits modest compositional zoning, whereas spinel and biotite are nearly homogeneous. Based on several hundred microprobe analyses of feldspar (Table 1; see also Electronic Appendix 1, available for downloading at http://www.petrology.oxfordjournals.org), the Or component of alkali feldspar ranges from 44 to 88. Alkali feldspar compositions exhibit a bimodal distribution with a sub-maximum near Or₈₅₋₉₀ and a larger peak at Or₅₅₋₆₅ (Fig. 2a). In some cases, crystals are modestly zoned from higher Or cores to lower Or rims. Plagioclase typically exhibits the most intracrystal variation. An content varies from ~ 20 to 90 and, based on

Sample	п	SiO ₂	AI_2O_3	FeO	MgO	CaO	BaO	SrO	Na ₂ O	K ₂ 0	P_2O_5	Sum	An	Ab	Or
AFGI-1.D.core	2	64.85	19.74	0.22	0.01	0.74	d.l.	0.05	4.03	10.45	d.l.	100.07	3.6	35.6	60.8
AFGI-1.D.rim	2	65·41	20.05	0.19	d.l.	0.82	d.l.	d.l.	5.58	8.09	d.l.	100.12	4.0	49·1	46.9
AFGI-1.L	4	55·12	28.21	0.59	0.05	10.27	d.l.	0.08	5.17	1.05	0.02	100.54	49.2	44.8	6.0
AFGI-4.D	2	49.70	32.15	0.58	0.03	14.68	d.l.	0.12	3.08	0.25	0.02	100.60	71.5	27.1	1.5
AFGI-4.1.core	2	63·27	19.77	0.21	d.I.	0.44	0.99	0.29	1.46	13.99	0.02	100.43	2.2	13.3	84.4
AFGI-4.1.rim	1	65.31	19.63	0.17	d.I.	0.50	d.l.	0.06	4.23	10.42	d.I.	100.32	2.4	37.2	60.3
AFGI-5A.G.incl	1	46.75	33.12	0.60	0.04	16.34	d.l.	0.26	2.31	0.18	0.02	99.62	78.8	20.2	1.0
AFGI7.E.incl	3	59.98	25.14	0.39	0.01	6.33	d.l.	0.04	6.97	1.67	d.I.	100.53	30.2	60.3	9.5
ALT-2.G	4	45.65	34.61	0.66	0.04	17.88	d.l.	0.41	1.22	0.23	0.02	100.71	87·8	10.9	1.3
ALT-2.H	3	65·10	19.72	0.24	0.01	0.84	d.l.	d.l.	3.78	10.76	0.02	100.48	4.1	33.4	62·5
COD-3.E	3	63.58	19.26	0.22	d.I.	0.42	1.15	0.34	1.22	14.05	d.I.	100.24	2.2	11.4	86.5
COD-3.F.core	3	45.96	33.71	0.65	0.04	16.93	d.l.	0.28	1.38	0.24	d.I.	99·20	85.8	12.7	1.5
COD-3.F.rim	1	48.35	32.36	0.64	0.05	15.27	d.l.	0.24	2.18	0.49	0.02	99.60	77·2	19.9	2.9
ICB-11.B.core	1	61.81	19.84	0.19	d.I.	0.64	2.08	0.91	2.01	11.91	d.I.	99.39	3.5	19.7	76·8
ICB-11.B.rim	2	63.59	19.51	0.21	d.I.	0.56	0.54	0.57	2.11	12.79	d.I.	99.86	2.9	19.5	77.7
ICB-11.F.core	2	51.95	30.28	0.55	0.04	13.43	d.l.	0.14	3.73	0.68	d.I.	100.79	64·0	32.2	3.8
ICB-11.F.rim	1	54.47	28.34	0.52	0.04	11.15	d.l.	0.07	4.59	1.13	0.02	100.33	53.6	39.9	6.5
ICB-15.C	3	64.92	19.16	0.21	d.I.	0.72	d.l.	d.l.	3.31	11.38	d.I.	99.70	3.6	29.5	66·9
ICB-15.D.core	2	64·10	19.42	0.28	d.I.	0.75	0.43	0.18	3.55	10.80	0.02	99·51	3.7	32.1	64·2
ICB-15.D.rim	1	52·10	29.21	0.71	0.06	11.95	0.07	0.35	4.37	0.35	0.03	99·18	58.9	39.0	2.0
ICB-4.D.core	3	60.02	24.73	0.39	0.02	6.16	d.l.	0.04	6.97	1.71	d.I.	100.03	29.6	60.6	9.8
ICB-4.D.rim	2	65.73	19.48	0.24	d.I.	0.57	d.l.	d.l.	5.33	8.63	d.I.	99.97	2.8	47.1	50·1
PM-1.D.core	2	60·13	24.60	0.42	0.02	6.44	d.l.	0.05	6.82	1.73	d.I.	100.20	30.9	59·2	9.9
PM-1.D.intermediate	1	60.99	23.05	0.71	0.02	5.01	d.l.	d.l.	6.32	3.72	d.I.	99.82	24.0	54.8	21.2
PM-1.D.rim	1	64·13	20.07	1.08	0.01	2.12	d.l.	d.l.	5.12	7.26	d.l.	99.79	10.6	46.3	43·2
PM-1.E.incl	3	49.14	32.34	0.49	0.01	15.63	d.l.	0.24	2.70	0.19	d.I.	100.75	75.4	23.5	1.1

Table 1: Representative compositional data for feldspars, Campanian Ignimbrite

n, number of analytical points arithmetically averaged. d.l., detection limit as given in text. Iron determined as FeO but assumed to be trivalent in cation normalization. Mean oxide standard deviation (1 σ) of 18 averaged analyses for *n*>1: SiO₂ 0.29, Al₂O₃ 0.18, FeO 0.03, MgO 0.01, CaO 0.20, BaO 0.12, SrO 0.03 Na₂O 0.17, K₂O 0.17, P₂O₅ 0.01.

available data, plagioclase exhibits trimodality with local maxima at An_{80-90} and An_{50} , and an absolute modal maximum at An_{30} (Fig. 2b). In some cases, sieved-textured calcic cores are surrounded by more potassic rims. Mean linear (equivalent size) dimensions for clinopyroxene, spinel, apatite, biotite, alkali feldspar and plagioclase are 0.60, 0.30, 0.09, 0.75, 1.56 and 0.50 mm, respectively, based on analysis of several hundred crystals.

Petrochemistry

Previous studies (e.g. Civetta *et al.*, 1997; Signorelli *et al.*, 1999; Pappalardo *et al.*, 2002*a*, 2002*b*) show that CI pumice and bulk-rock samples are dominantly trachyte and phonolite (Fig. 3). Also plotted in Fig. 3 are CI glass and pumice data from Civetta *et al.* (1997) and basal pumice glass and melt inclusion data from

Signorelli *et al.* (1999). Because the crystallinity of CI ashflow tuff and basal pumice fall is low, whole-rock, pumice and glass compositions are compositionally similar. Figure 3 also illustrates the loss of alkalis during zeolitization of the Yellow Tuff facies. Because these samples clearly show effects of non-magmatic processes, samples of the Yellow Tuff facies will not be considered further in this study (marked with an open circle in Fig. 3).

Also included in Fig. 3 are data for clinopyroxene-hosted melt inclusions (MI) studied by Webster *et al.* (2003) (marked with + in the figure). These MI data were collected from a subset of samples presented in the present study. Webster *et al.* (2003) identified two groups of MI: high-MgO and low-MgO. The high-MgO MI data extend the compositional range of the CI dataset to basaltic trachyandesite and have been interpreted by Webster *et al.* (2003) as possibly representing parental or



Fig. 2. (a) Fraction vs Or for alkali feldspar in the Campanian Ignimbrite (n = 130). (b) Fraction vs Ab for plagioclase in the Campanian Ignimbrite (n = 65).

at least close to parental magma. These MI data will be described in more detail in the next section, where we use them to reconstruct a parental melt that is then used as a starting point in phase equilibria calculations.

Selected major oxide trends of CI data on MgO variation diagrams are presented in Fig. 4a–f, and representative major element data are presented in Table 2. All major element data are presented in Electronic Appendix 2 (available at http:// www.petrology.oxfordjournals.org). For most oxides,

pumice and bulk samples are characterized by relatively coherent oxide-oxide trends, and no systematic differences in these two sample types are evident. SiO₂, Na₂O, and MnO (not shown) vs MgO form relatively tight negatively correlated arrays, whereas in general, CaO, P₂O₅ (not shown), FeO, and K₂O are positively correlated arrays. Al₂O₃ vs MgO forms a relatively tight cluster that lacks negative or positive correlation. In most cases, glass and melt inclusion data from the basal pumice (Signorelli et al., 1999) extend the major element compositional ranges compared with pumice and bulk-rock, consistent with compositional zonation defined by differences between basal pumice fall deposits and later-erupted pyroclastic flow deposits. Discussion of the computed trends in Fig. 4 is reserved for a later section of this paper. Although the thermodynamic calculations do self-consistently determine H₂O solubility, the volatile content of CI pumice and whole-rock samples measured today provides little constraint on volatiles at depth. All comparisons between predicted and observed compositions are consequently made on an anhydrous basis unless stated explicitly.

PHASE EQUILIBRIA CONSTRAINTS: MELTS MODELING

Phase equilibria constraints on major element changes in magma during crystallization form a fundamental starting point in the discussion of magma compositional evolution. MELTS is a rigorous thermodynamic model of crystal-liquid equilibria that uses experimentally derived data on the compositions of coexisting solid and magmatic silicate liquid phases at specified temperatures, pressures, and oxygen fugacities to calibrate models for the compositional dependences of thermodynamic potentials for mineral and silicate liquid phases. As heat is extracted and the temperature drops in a system, phase identities, compositions, and proportions are calculated. The MELTS algorithm is based on classical equilibrium thermodynamics and has been extensively reviewed elsewhere (Ghiorso & Sack, 1995; Asimow & Ghiorso, 1998). Below we provide a brief summary of points that are relevant to the present study.

Application of MELTS to natural systems

From a practical perspective, using MELTS to model the evolution path of cooling magma requires specification of the initial state of a system and constraints under which evolution proceeds. Initial conditions define the starting temperature, temperature step, pressure, and a parental composition including an initial water concentration. In this study we have chosen the liquidus temperature as the starting temperature; MELTS computes a liquidus temperature based on the specified initial liquid



Fig. 3. Iotal alkalis-silica diagram using classification scheme of Le Maitre *et al.* (1989). Symbols and data sources are shown in the legend. Melt inclusion samples from Webster *et al.* (2003) include: AR-I, MO-2, VE-I, SA-I (High-MgO group) and ALT-I, SA-I, ICB-12E, SP-3, SFC-2, SP-2 (Low-MgO group). Because samples of the Yellow Tuff unit are affected by zeolitization and show depletions in alkalis, they are excluded from further consideration. RPM, reconstructed parental melt.

composition and pressure. An end temperature is selected by comparison of MELTS results and observed data. A system ferric/ferrous ratio must be defined, either from FeO/Fe₂O₃ analyses or from total Fe, in which case selection of an oxygen fugacity distributes iron in the liquid and solids between FeO and Fe₂O₃ according to the specified temperature and pressure. The constraints specify a reaction path in which the system is closed or open to mass transfer within standing magma (fractional or equilibrium crystallization) or from wall-rock to standing magma (assimilation). Pressure may be held constant or may vary along some P-T path. An oxygen fugacity constraint path may be defined. These and a number of additional issues must be considered when using MELTS to explore the consequences of magmatic evolution in natural systems.



Fig. 4. Campanian Ignimbrite MgO vs oxide (wt%) variation diagrams showing CI data trend and MELTS simulation results. Filled grey circles, pumice and bulk tuff samples from this study and Civetta *et al.* (1997); ×, glass and melt inclusion data from Civetta *et al.* (1997) and Signorelli *et al.* (1999). As a result of probable reaction, the clinopyroxene-hosted melt inclusions presented in Fig. 3 (Webster *et al.*, 2003) provide no basis for comparison, and therefore are not included here. MELTS results represent evolution of reconstructed parental melt by closed-system fractionation (blue line, CSF with fO_2 along QFM+1 buffer; green dot-dot-dash line, CSF with fO_2 fixed at QFM) and open-system assimilation-fractionation (red dashed line, OSAF with fO_2 along QFM+1). Pressure is fixed



Fig. 4. Continued

at $\overline{0.15}$ GPa and the initial water concentration is 3 wt% in all simulations. Assimilant was added at 1000°C (note the discontinuity in the liquid line of descent), so at T > 1000°C (>~15 wt% MgO), the trend is equivalent to the CSF (QFM +1) case. Decreasing wt% MgO corresponds to decreasing magma temperature. Temperature step for CSF (QFM +1) trend is 0.5°C, and is 5°C for CSF (QFM) and OSAF trends. The termination of each MELTS trend is labelled ($f_m = 0.05$), as are the solid phase saturation temperatures. OI, olivine; Cpx, clinopyroxene; Sp, spinel; Ap, apatite; Fsp, alkali and plagioclase feldspar; bio, biotite. Hereafter, 'best-case' is defined as CSF (QFM +1), wherein parental melt is RPM, pressure is 0.15 GPa, initial water concentration is 3 wt%, and fO_2 is along QFM +1 buffer. (See text for details.) (a) MgO vs SiO₂. (b) MgO vs K₂O. (c) MgO vs Na₂O. (d) MgO vs Al₂O₃. (e) MgO vs CaO. (f) MgO vs FeO.

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Sample	PontiR	IC-HB6a	ICB-8	ALT-1	SA-1a	SA-1b	AFGI11	VE-1	AFGI1	ICB-13	MP-1	ICB-9	ICB9GTa
SiO ₂ wt%	58.26	58.37	59·41	60·15	60.95	60.88	61.34	60.74	61.12	61.14	60.61	61.53	62.56
TiO ₂	0.47	0.47	0.46	0.47	0.43	0.47	0.46	0.46	0.46	0.44	0.43	0.44	0.42
Al ₂ O ₃	18.81	18.85	18.66	18.57	18.93	18.94	18.98	18.73	18.74	18.79	18.63	18.96	18.59
Fe ₂ O ₃	1.89	2.22	1.69	2.32	2.54	2.75	1.71	2.49	2.80	3.15	1.80	3.08	3.15
FeO	2.44	2.12	2.30	1.44	1.08	1.01	1.89	1.05	0.79	0.26	1.39	0.23	0.24
MnO	0.10	0.10	0.12	0.16	0.12	0.17	0.19	0.20	0.21	0.20	0.23	0.20	0.22
MgO	1.44	1.38	1.11	0.92	0.79	0.79	0.68	0.62	0.59	0.50	0.40	0.38	0.37
CaO	4.09	4.02	3.41	3.23	2.46	2.64	2.17	2.25	2.19	2.30	1.75	1.76	1.77
Na ₂ O	2.66	2.61	3.25	4.44	4.40	4.23	4.63	5.20	5.32	5.48	6.39	5.78	5.40
K ₂ 0	9.18	9.18	8.94	7.53	7.90	7.74	7.62	7.20	7.26	7.09	7.12	7.04	6.67
P ₂ O ₅	0.27	0.25	0.24	0.18	0.15	0.16	0.09	0.12	0.09	0.14	0.09	0.08	0.05
SO ₃	0.05	0.08	0.03	<0.01	<0.01	<0.01	0.01	0.03	0.02	0.03	<0.01	<0.01	0.01
CI	0.24	0.26	0.27	0.42	0.08	0.09	0.11	0.74	0.30	0.36	0.84	0.23	0.35
F	0.10	0.09	0.11	0.15	0.16	0.11	0.06	0.17	0.03	0.13	0.31	0.28	0.07
-0=F,Cl	0.10	0.10	0.11	0.16	0.09	0.07	0.05	0.24	0.08	0.14	0.32	0.17	0.11
LOI 925°C	1.06	1.04	0.65	0.37	0.44	1.03	1.36	1.44	1.17	0.93	0.70	0.35	0.79
CO ₂	<0.01	<0.01	n.a.	<0.01	<0.01	<0.01	n.a.	<0.01	n.a.	n.a.	<0.01	<0.01	n.a.
H_2O^+	0.98	0.88	0.96	0.21	0.25	0.64	n.a.	0.56	n.a.	<0.01	0.13	0.06	n.a.
H_2O^-	0.17	0.19	0.14	0.17	0.16	0.28	n.a.	0.43	n.a.	0.19	0.09	0.07	n.a.
Fe ₂ O _{3T} (anhydrous)	4.60	4.57	4.25	3.93	3.75	3.88	3.80	3.66	3.68	3.44	3.35	3.34	3.42
FeO_{T} (anhydrous)	4.14	4.12	3.82	3.53	3.37	3.49	3.42	3.30	3.31	3.10	3.01	3.00	3.08

Table 2: Selected major element analyses of the Campanian Ignimbrite

All analyses calculated on an anhydrous and CO_2 -free basis. S was determined as total S and recalculated to SO_3 . Fe_2O_3 was calculated from a direct determination of FeO and total Fe determined as Fe_2O_3 . < values were not detected at that lower limit. n.a., not analyzed.

Thermodynamic properties database

Compared with data from our investigation of some seven natural explosive volcanic systems, MELTS effectively predicts oxide concentrations for liquids during fractional crystallization, from the liquidus down to low melt fraction ($\sim 0.03-0.04$). However, predicted CaO and K₂O concentrations are systematically displaced from observed data by up to ~ 3 wt%. The discrepancy for CaO can probably be attributed to understabilization of clinopyroxene (M. Ghiorso, personal communication, 2006). The problem with K_2O may be due to a lack of experimental data to calibrate the thermodynamic model that describes alkali feldspar-liquid equilibria (M. Ghiorso, personal communication, 2006). The calibration of the activity of the K-component in the liquid may give a value that is too high, resulting in overprediction of the stability of alkali feldspar that is manifest in a reduction of liquid K₂O concentrations.

Lack of accounting for CO_2

MELTS currently does not have a thermodynamic model for CO_2 solubility. However, the solubility of CO_2

in melt is minimal (Holloway, 1976) and we show through MELTS-based consideration of carbonate assimilation (discussed below) that carbonate assimilation probably was not an important factor in the petrogenesis of the CI.

Application of MELTS to modelling of the CI

In this study, all MELTS models are based on minimization of Gibbs free energy along an isobaric path of decreasing temperature and decreasing system enthalpy. We have imposed model constraints regarding the liquid oxidation state. Only the total Fe has been used as an input; FeO and Fe₂O₃ quantities in evolving liquid reflect ferric/ferrous ratios relative to the quartz-fayalitemagnetite (QFM) buffer. The mode of crystallization is fractional crystallization, whereby crystals, once crystallized, are chemically isolated (no further reaction allowed) from silicate liquid. We performed MELTS equilibrium crystallization calculations and found the results to be significantly off mark compared with CI geochemical data. The low average crystal content of the CI supports the occurrence of fractional crystallization. Chemical fractionation does not presuppose that crystals are physically removed from magma, although this may indeed occur (see below). It is obvious but still critical to note that isobaric removal of heat is the process driving fractional crystallization, a fact that facilitates construction of a timescale for petrological evolution (see below) that can be related to independent timescales derived from other constraints.

To document the pre-eruptive state of the CI magmatic system, we performed ~110 MELTS crystal fractionation calculations for a range of potential parental compositions, pressures (0.1-0.5 GPa), oxygen fugacities (QFM - 1 to)OFM + 3), and initial water concentrations (1, 2 and 3) wt%). The goal of these calculations is to develop bounds for the intensive thermodynamic parameters of pressure, oxygen fugacity and initial dissolved water content for a range of possible parental compositions that lead to the compositionally evolved CI liquid array depicted in Fig. 4. Each isobaric computation begins above the liquidus temperature and continues along a closed-system fractionation (CSF) path. Crystallization simulations were terminated at a minimum fraction of melt (f_m) equal to 0.05. The 'best-case' set of intensive variables for a given starting composition was chosen based on comparison of MELTS predictions with observed pumice, glass and bulk-rock major element compositions, and comparison of predicted and observed phenocryst compositions. MELTS also predicts mineral proportions, but we have not used these as a criterion for model evaluation because of likely complications introduced by physical processes in the magma reservoir (e.g. separation of crystals and melt within the evolving magma body and during eruption) that may physically separate crystals from melt as well as each other.

Below, we present the results of sensitivity tests for a selected parental composition to demonstrate the effects of varying initial water content, pressure, and oxygen fugacity. We then present and discuss the bestcase results.

ESTIMATION OF CAMPANIAN IGNIMBRITE PARENTAL MAGMA COMPOSITION

The search for a representative CI parental melt composition is aided by the presence of MI found within clinopyroxene phenocrysts (Webster *et al.*, 2003). Webster and co-workers found a group of high-MgO (\sim 7 wt%) MIs with \sim 53 wt% average SiO₂ (Fig. 3) that represent a first approximation to the parental CI melt (Webster *et al.*, 2003). A better approximation of

the parental melt composition comes from recognition that the MIs within clinopyroxene phenocrysts are evidently saturated with respect to pyroxene and hence are related to the CI parental melt by reaction with their clinopyroxene host (i.e. clinopyroxene removal). As demonstrated by Watson (1976), MIs within multiple cotectic phases (e.g. plagioclase, olivine and clinopyroxene) can be related to a unique parental melt through a simple graphical construction. Unfortunately, the procedure developed by Watson could not be implemented here because MIs analyzed by Webster et al. (2003) are found solely in clinopyroxene. An attempt to reconstruct the parental composition following the method of Kress & Ghiorso (2004) failed to converge adequately essentially for the same reason; trapped MIs within multiple phases are needed to robustly reconstruct the parental liquid. Although, in principle, MIs within a single phase could be used, small uncertainties in activity-composition relations in monoclinic pyroxenes are too large to generate robust solutions. Similarly, detailed experimental data on the temperature and composition dependence of diffusivity of relevant species (Van Orman et al., 2001) necessary to implement the method proposed by Cottrell *et al.* (2002) are, unfortunately, not currently available. In light of these issues, we have had to invoke a less exact procedure.

Our method of parental melt reconstruction is based on two assumptions. The first is that the incompatible trace element concentration of the parental magma is lower than any other liquid related to it by crystal fractionation. Fortunately, trace element abundances have been measured in the high-MgO MIs (Webster et al., 2003), so these can be ordered by their incompatible trace element concentrations. MI sample VE1#3 has incompatible trace element concentrations that are generally lower than those of other high-MgO MIs from minimally altered CI units (i.e. Gray Tuff, Lithic Breccia, and Incoherent Tuff). In particular, concentrations of trace elements incompatible in clinopyroxene, including Ce, Th, Sm, and Nb, are lower in VE1#3 than in other high-MgO MIs by factors of $\approx 1.5-2$. The second assumption is that a simple pyroxene-addition method can account for the effects of post-entrapment MI crystallization. The composition of clinopyroxene added to an analyzed MI corresponds to that of the MI host crystal taken from Webster *et al.* (2003). The reconstructed parental melt (RPM) is based on the mass balance relation

$$\phi \,\hat{C}_{\rm cpx} + (1 - \phi)\hat{C}_{\rm MI} = \hat{C}_{\rm RPM} \tag{1}$$

where ϕ represents the mass fraction of host clinopyroxene added to the observed MI and \hat{C}_j represents the oxide composition vector of host clinopyroxene phenocrysts (cpx), MI and RPM, respectively. We used a range of ϕ values to construct an array of reasonable parental melt starting compositions (e.g. for VE1#3, $\phi = 0.1, 0.2, 0.3$, and 0.4). A ϕ value of zero corresponds to the assumption that an MI is unmodified by reaction with its clinopyroxene host. Using this procedure, we performed approximately 15 MELTS simulations using as starting data the high-MgO MIs with low incompatible trace element concentrations (VE1#3 was the lowest of the group). For each MI studied, a range of reconstructed parental compositions was generated to test the quantitative effects of variable clinopyroxene addition (i.e. different ϕ). Isobaric fractional crystallization simulations were then carried out for fixed values of oxygen fugacity, dissolved H₂O concentration, and pressure for each RPM composition. Higher ϕ values result in higher proportions of magnesian phases crystallizing along the liquid line of descent, but major element paths are generally similar for ϕ values in the range ~0.15–0.4. A parent composition based on $\phi = 0.2$ best describes the observed major element data. Figure 5 compares the results of closed-system isobaric fractionation simulations based on two distinct parental melt compositions: unmodified MI VE1#3 with $\phi = 0$ and VE1#3 with $\phi = 0.2$. Both numerical simulations were carried out under the following conditions: pressure of 0.15 GPa, initial water content of 3 wt%, and oxygen fugacity fixed at the QFM+1 buffer. The liquid line of descent based on VE1#3 with $\phi = 0.2$ corresponds more closely to observed CI glass compositions than the results based on the unmodified VE1#3composition. In both cases, there is a 'jump' or compositional discontinuity in the predicted sequence of liquids. This phenomenon is discussed in detail below. For now, the important point is that unmodified VE1#3composition does not produce evolved liquids that fit observations (shaded field in Fig. 5). For example, in the VE1#3 ($\phi = 0$) case at low MgO values, the trend and the field for the CI data do not overlap (Fig. 5a). Al₂O₃ for the VE1#3 ($\phi = 0$) simulation also completely misses the CI field (Fig. 5b). This comparison clearly illustrates that a recalculated parental composition provides a better estimate of the parental magma for the CI. Although VE1#3 with $\phi = 0.2$ provides the best correspondence to the CI data, similar results are found for other high-MgO MIs with ϕ values in the range 0.15-0.4. Based on these and additional numerical simulations of isobaric CSF, we conclude that the composition giving rise to fractionation trends most like those exhibited by the eruptive products of the CI is VE1#3 with $\phi = 0.2$. For the remainder of this paper, this is referred to as the RPM. Table 3 presents the major element compositions of MI VE1#3, its host clinopyroxene, and the RPM of VE1#3 with $\phi = 0.2$ (anhydrous).



Fig. 5. Comparison of closed-system fractional crystallization (CSF) cases for two parental melt compositions: reconstructed parental melt composition (RPM) (see text for further details) and unmodified melt inclusion (VE1#3, black crosses). Melt inclusion data from Webster *et al.* (2003). All other model parameters are the same as the best case defined in Fig. 4. Shaded region represents field for all CI data, and phase-in abbreviations are as in Fig. 4. (a) MgO vs SiO₂. (b) MgO vs Al₂O₃. The RPM composition performs much better, as noted by overlap of the CSF (RPM) trend and data field at low concentration of MgO; trend for unmodified melt inclusion does not overlap data field. The temperature at which the discontinuity occurs in the CSF (RPM) trend is $T_{\rm inv}$, the temperature at which multiple phases simultaneously saturate.

Table 3: Major element compositions of MI VE1#3, its host clinopyroxene, and the RPM of VE1#3 with $\phi = 0.2$ (anhydrous)

Oxide	SiO ₂	TiO ₂	AI_2O_3	FeO	MgO	MnO	CaO	K ₂ 0	Na ₂ O	P ₂ O ₅
VE1										
Host cpx	52·49	0.37	2.13	3.96	16.48	0.12	24.28	0	0.17	0
VE1#3 measured	52.78	1.03	14.53	5.82	7.82	0.07	9.88	5.16	2.07	0.84
<i>VE1#3</i> RPM	52.72	0.90	12.05	5.45	9.55	0.08	12.76	4.13	1.69	0.67

Compositions used in MELTS modelling based on sample VE1 3 (Webster *et al.*, 2003). Cpx, clinopyroxene; RPM, recalculated VE1#3 composition via addition of 20% by mass of cpx to MI [ϕ = 0.2; see equation (1)].

PHASE EQUILIBRIA CONSTRAINTS ON THE CHEMICAL EVOLUTION OF THE CAMPANIAN IGNIMBRITE Results of closed-system fractional (CSF) crystallization MELTS simulations

In this section, we summarize results of numerous MELTS simulations of CSF to illustrate the effects of varying the initial H₂O content, oxygen fugacity, and pressure on the calculated liquid line of descent and on phase relations. This is followed by a detailed comparison of observed and predicted liquid and solid (clinopyroxene, spinel, alkali feldspar, and plagioclase) phase compositions. The conclusion is that a liquid of RPM composition plus 3 wt% H₂O undergoing closed-system isobaric fractionation at $\sim 6 \text{ km}$ depth at between the QFM and QFM+1 oxygen buffer conditions provides a good first-order model for derivation of the CI magma.

Effects of varying initial water concentration

The influence of initial water concentration on the fractional crystallization path of the CI was examined via isobaric (0.15 GPa) fractional crystallization simulations based on a parent melt of RPM and oxygen fugacity defined by the QFM +1 buffer for 1, 2, and 3 wt% initial H₂O. The results, presented in Fig. 6a and b, show that for 1 and 2 wt% initial H₂O, SiO₂ vs MgO trends do not intersect the data field for the CI; at low MgO, predicted SiO₂ is much lower than observed. In contrast, at the lowest MgO values, Al₂O₃ greatly exceeds observed concentrations. A key difference between the 1 wt% H₂O and the 3 wt% H₂O case concerns the behavior of feldspar



Fig. 6. Results of numerical experiments designed to examine CSF paths with variable initial water content. All other conditions are identical to those of the best case defined in Fig. 4, and phase-in abbreviations are as in Fig. 4. Grey squares, best case at 3 wt% H₂O; triangles, 2 wt% H₂O; black crosses, 1 wt% H₂O. Shaded region represents field for all CI data. (a) MgO vs SiO₂. (b) MgO vs Al₂O₃. Water contents $\approx 3 \text{ wt}\%$ are required to describe the CI data and produce phenocrysts consistent with the CI assemblage.

at lower melt fractions. An initial water concentration of 1 wt% H₂O leads to stabilization of both feldspar phases at higher temperatures, with crystallization of plagioclase beginning at a higher temperature (1010°C) than that of alkali feldspar (965°C). In contrast, for the 3 wt% case, both feldspars saturate at the same temperature (~883°C), and the abundance of both feldspar phases increases progressively with decreasing temperature. At the lowest melt fraction ($f_{\rm m} = 0.05$), the total proportion of feldspar is lower (0.37) in the 1 wt% case than in the 3 wt% H₂O case (0.40) and, as a consequence, the liquid is characterized by greater Al₂O₃ enrichment and SiO₂ depletion (Fig. 6a and b). In the 1 wt% H₂O case, a rhombohedral oxide phase (ilmenite) appears at low melt fraction, which is inconsistent with the observed phase assemblage. Although not shown in Fig. 6, for cases in which initial dissolved water contents range from 4 to 6 wt%, calculated differentiation trends and the predicted phase assemblage do not agree with observed features of the CI. We therefore conclude that dissolved H₂O contents around 3 wt% are most realistic for the initial dissolved water content of the RPM. The dramatic difference in behavior of the liquid line of descent at low melt fraction clearly shows that water contents around 3 wt% are required to best match CI data.

Effects of varying pressure

To explore effects of changing pressure, we compared results produced at fixed oxygen fugacity (QFM + 1) and 0·10, 0·15, 0·30, and 0·50 GPa. Results for the latter three pressures are presented in Fig. 7. An initial water concentration of 3 wt% was chosen, except in the case of the 0·10 GPa model, in which 3 wt% water supersaturates the system at the mineral liquidus. An initial water concentration of 2·6 wt% was chosen to set the system at water saturation at this low pressure.

The 0.30 and 0.50 GPa cases vield different phase assemblages at lower melt fraction when compared with the lower pressure cases of 0.10 and 0.15 GPa. The 0.30 and 0.50 GPa cases have leucite as a fractionating phase (Fig. 7b and c), a phase never observed in the CI. Compared with the 0.15 GPa case, where alkali feldspar and plagioclase saturate at $\approx 883^{\circ}$ C (Fig. 7a), at 0.30 and 0.50 GPa the onset of feldspar crystallization occurs at lower temperatures ($\approx 845^{\circ}$ C in both cases), and with increasing pressure the mass fraction of feldspar crystallized in the first temperature increment of feldspar crystallization decreases (Fig. 7). As a consequence, compared with the 0.15 GPa case, isobaric fractionation at higher pressure yields SiO₂ concentrations that are lower and Al₂O₃ concentrations that are substantially higher than the CI. An additional factor leading to SiO₂ depletion at higher pressures is an increase in the calculated ratio of alkali feldspar to plagioclase in the first increment of feldspar crystallization (~2.3 at 0.15 GPa,

~5.5 at 0.30 GPa, and ~148.2 at 0.50 GPa). Although liquid compositions are similar for the 0.10 and 0.15 GPa cases, the concentration of SiO₂ is lower in the 0.10 GPa case because the proportion of feldspar over the first increment of feldspar crystallization is 2% lower.

The misfit of oxide data, coupled with the mismatch between observed and predicted phases, eliminates the possibility that the CI magma evolved at pressures of 0.30 GPa or higher. Results for the 0.10 GPa case are very similar to those for the 0.15 GPa case. However, at low melt fraction, the concentration of SiO₂ is lower in the 0.10 GPa case and therefore, the 0.15 GPa case more closely approximates the range of SiO₂ observed in the CI. We conclude that the major phase of crystal fractionation to generate CI composition melt took place at relatively low pressure (\approx 0.15 GPa) corresponding to a depth of about 6 km.

Effects of varying oxygen fugacity

With pressure and initial water concentration values fixed at 0.15 GPa and 3 wt%, respectively, we performed additional calculations to examine the effects of varying oxygen fugacity (QFM -1, QFM, QFM +1, QFM +2, and QFM + 3). The results illustrate the strong influence of oxygen fugacity on the relative stability of Fe²⁺- and Fe³⁺-bearing phases. Olivine is the liquidus phase in all computations described in this study, but with oxygen fugacity constrained to follow the QFM -1 buffer curve, crystallization of fayalitic olivine is also predicted at low melt fraction and makes up ~7.5% of the end $(f_{\rm m} = 0.05)$ phase assemblage. In comparison, at QFM+1 and QFM + 3, olivine is stable only at high melt fraction $(f_{\rm m} > 0.9)$. The decreasing abundance of olivine with increasing fO_2 leads to stabilization of clinopyroxene and a slightly higher final clinopyroxene content (~44% at QFM + 3, ~42% at QFM -1). More oxidizing conditions naturally lead to stabilization of spinel at higher temperatures and slight increases in the mass proportion of spinel [0.01 at QFM - 1 to 0.03 at QFM + 3of the end $(f_m = 0.05)$ phase assemblages]. Differences in spinel stability lead to differences in SiO₂ and FeO concentrations; Fig. 8a and b summarizes these differences for all of the five oxygen fugacity cases. In the QFM + 3case, the relatively high abundance of spinel and onset of spinel crystallization at higher temperature leads to corresponding shifts in melt SiO₂ and FeO contents. Maximum SiO₂ concentrations are ~1.5 wt% higher than in the QFM+1 case, whereas the maximum difference in FeO contents is $\sim 3 \text{ wt\%}$, with the QFM + 3 having the lower value. In contrast, the lower abundance of spinel in the QFM -1 case leads to predictions of melt SiO₂ concentrations that are lower than those of the 0.15 GPa case by a minimum of \sim 1.5–2 wt%; in addition, at the lowest melt fraction ($f_{\rm m} = 0.05$), FeO is higher by >1 wt%.



Fig. 7. Phase proportions as a function of temperature for MELTS simulations of variable pressure. All other conditions are identical to those of the best case defined in Fig. 4. Ap, apatite; Bio, biotite; Cpx, clinopyroxene; Cr, corundum; Gt, garnet; Ksp, alkali feldspar; Leuc, leucite; Ms, muscovite; Ol, olivine; Pl, plagioclase feldspar; Qz, quartz; Rh-ox, rhombohedral oxide; Sp, spinel. T, temperature. Best cases at (a) 0.15 GPa, (b) 0.30 GPa, and (c) 0.50 GPa. The high-pressure simulations produce solids that are not observed in the CI phenocryst assemblage.

The choice of oxygen buffer for the best case, which we define as between QFM and QFM +1, is most influenced by the behaviors of SiO₂ and FeO; the poor correlation between observed and model trends for QFM -1, QFM +2 and QFM +3 demonstrates that these oxygen buffers are not relevant. We conclude that the fugacity of oxygen during isobaric fractionation between QFM and QFM +1 gives the closest agreement between the numerical simulation and CI compositions.

Best-case closed-system fractional crystallization model

Based on the comparisons described above, the most plausible parental starting composition involves the anhydrous composition given in Table 3 plus \sim 3 wt% H₂O. This starting composition undergoes fractional crystallization along the QFM to QFM+1 oxygen buffer at 0.15 GPa. For simplicity, the following discussion is based on the QFM+1 results. Here we provide a detailed comparison between this particular case, hereafter referred to as CSF, and observations.

Mineral identities and abundances and the temperature at which water saturates for CSF along the liquid line of descent are summarized in Fig. 7a. Olivine is the liquidus phase ($T_{\text{liq}} = 1235^{\circ}\text{C}$) followed by clinopyroxene, H₂O, spinel and apatite at 1162°C, 1127°C, 1078°C and 1018°C, respectively. Significantly, at 883°C, alkali feldspar,



Fig. 8. Results of numerical experiments designed to examine CSF paths for variable fO_2 . All other conditions are identical to those of the best CSF case defined in Fig. 4. Shaded region represents field for all CI data. Grey squares, best CSF case with fO_2 along QFM +1; black zig-zag line, QFM -1; dash-dot-dot line, QFM; dotted line, QFM +2; long-dashed line, QFM +3. (a) MgO vs FeO. (b) SiO₂ vs Na₂O+K₂O. It should be noted that for the best CSF case, the liquid composition just below T_{inv} lies within the CI data field.

plagioclase, and biotite appear simultaneously and crystallize along with apatite, spinel and clinopyroxene. At and below 883°C, crystallization is dominated by the growth of alkali feldspar and, to a lesser extent, plagioclase. A small modal amount of olivine ($\sim 5\%$ by mass) is predicted to crystallize during the first $\sim 100^{\circ}$ C of cooling. With the exception of olivine (not reported in the CI), the CSF predictions match observed phases (alkali feldspar, plagioclase, clinopyroxene, biotite, spinel, and apatite) very well. Olivine crystals are not found as phenocrysts in the CI perhaps because, as the first phase to crystallize from the parental melt of low viscosity, settling has been especially efficient. Calculated liquid compositions of the CSF define trends that reflect removal of these mineral phases and are plotted in Fig. 4. Because the oxygen buffer is interpreted to lie between QFM and QFM +1, Fig. 4 shows results for both buffers. Concentrations of SiO₂, K_2O , Na_2O , and Al_2O_3 initially increase with decreasing MgO, reflecting olivine fractionation, and continue to increase as clinopyroxene, spinel, and apatite join the fractionating phase assemblage. The increase in SiO₂ concentration becomes more gradual when clinopyroxene replaces olivine, but then increases sharply when spinel appears. CaO contents rise until clinopyroxene appears, then decrease sharply with further cooling. FeO decreases slightly in the early stages of crystallization, but decreases markedly with spinel crystallization. Whereas results using the QFM buffer more closely track observed FeO, the QFM +1 buffer yields SiO₂ that extends to higher values, and therefore, more closely approximates the observed range of SiO₂.

Perhaps the most striking feature of the CSF calculation results is the abrupt change in melt composition (i.e. a compositional gap) at 883°C (Fig. 4). Within a degree or so of this temperature, identified here as the pseudo-invariant temperature, T_{inv} , melt simultaneously saturates in alkali feldspar, plagioclase and biotite, leading to a dramatic decrease in $f_{\rm m}$, from 0.46 to 0.09 (Fig. 7a). That is, a major increment of crystallization occurs essentially at a single temperature. At this pseudo-invariant point, the specific enthalpy of the system changes in response to the 'wave' of crystallization. Major element shifts in melt composition at $T_{\rm inv}$ are ~2 wt% for Na₂O and Al₂O₃, ~1.5 wt% for K₂O, ~1 wt% for SiO₂ and CaO, and ~0.5 wt% for H₂O (Fig. 4). For $T < T_{inv}$ SiO₂ and Na₂O concentrations in the melt continue to increase as a result of feldspar fractionation and the increase in Na₂O becomes particularly steep. K_2O , Al_2O_3 , FeO and CaO decrease at $T < T_{inv}$ Compositional changes at T_{inv} are associated with physical changes [e.g. in the density and viscosity of water-saturated melt and magma (melt + supercritical fluid)] that have important dynamical consequences (discussed below).

As shown in Fig. 4, predicted CSF trends in melt composition agree fairly well with pumice or bulk-rock, and glass data for most oxides. Because the clinopyroxene-hosted MIs of Webster *et al.* (2003) have reacted with host clinopyroxene, they do not lie on the liquid line of descent and therefore MI data are not included in Fig. 4. Calculated and observed concentrations are in favorable agreement for SiO₂, Na₂O, Al₂O₃, FeO, and MgO. The CSF trends for CaO are higher than observed by $\sim 0.5-3.5$ wt%; the misfit of predicted vs observed data is discussed in the section on open-system processes.

Because MELTS generates equilibrium mineral composition data for each step along the liquid line of descent, a further test of the robustness of a MELTS fractionation computation is comparison of observed and predicted compositions of phenocrysts. The mode of the CI is dominated by alkali feldspar, with lesser plagioclase and sparse clinopyroxene, spinel, apatite, and biotite.

Plotted in Fig. 9a are observed and predicted (continuous curve) clinopyroxene compositions in the pyroxene quadrilateral. The agreement is good considering the computed trend assumes perfect fractional crystallization and hence leads to the maximum down-temperature extent of Fe-enrichment possible in CSF from an assumed single fixed starting composition. The high-MgO clinopyroxene phenocrysts from Webster *et al.* (2003) (crosses in Fig. 9a) are compositionally similar to clinopyroxene predicted at higher temperatures, highlighting the ability of the MELTS simulator to faithfully capture near-liquidus monoclinic pyroxene compositions.

In Fig. 9c, CI spinel phenocrysts are plotted along with computed trends depicted as continuous curves in FeO– TiO_2 –Fe₂O₃ normalized coordinates [spinel data from Civetta *et al.* (1997)]. The discontinuous nature of the predicted spinel compositions should be noted. The compositional discontinuity occurs at T_{inv} . Observed CI spinel phenocryst compositions correspond fairly well to the low-temperature leg of the computed spinel compositional trend.

Biotite is present as rare phenocrysts in the CI. Because so few experimental data are available to calibrate activity-composition along the annite-phlogopite binary solution, a quantitative comparison between observed and predicted biotite compositions is not meaningful. Interestingly, MELTS does predict the saturation of biotite (at $T \leq T_{inv}$); this is, in fact, consistent with petrographic observations.

Figure 9e illustrates the range of observed and predicted feldspar ternary compositions. Data from the CI (this study) are plotted as circles; triangles represent data from Civetta *et al.* (1997). Observed plagioclase compositions fall into one of three regions: a band from An₉₀ to An₇₀, a less frequent group around An₅₀, and finally a sodic group between \sim An₂₅ and An₃₀ with about 10 mol% dissolved KAlSi₃O₈ (see also Fig. 2b). For alkali feldspar, the observed Or content varies from Or₉₀ to Or₄₅

(see also Fig. 2a). It is clear that the closed-system model does not fully reproduce the range of observed feldspar compositions. We examine the likely explanation for this discrepancy in the next section on open-system processes.

In summary, for most phases, there is good correspondence between the identity and composition of predicted and observed phases assuming isobaric fractional crystallization of RPM at 0·15 GPa, oxygen fugacity along the QFM to QFM +1 buffer and an initial dissolved water content of 3 wt%. The major discrepancy relates to compositions of predicted and observed feldspar phenocrysts (Fig. 9e). This, combined with the poor correlation between observed and predicted CaO, may be indicative of the process of country rock assimilation. In the following section, additional MELTS calculations and a discussion of the possible role of assimilation in CI magma evolution are presented.

ROLE OF CRUSTAL ASSIMILATION

The discrepancy between predicted and observed plagioclase compositions motivates consideration of the role of wall-rock assimilation in the petrogenesis of the CI. As noted by examination of Figs 2b and 9e, there are distinct compositional populations of plagioclase in the CI. Observed plagioclase in the range An₂₅₋₅₅ is consistent with CSF predictions of RPM composition. In contrast, the observed calcic (An_{67-90}) plagioclase subpopulation appears anomalous. Civetta et al. (1997) argued that calcic plagioclase crystals represent xenocrysts derived from undigested country rock. We note that although some of the calcic plagioclase exhibits disequilibrium textures, in many cases, calcic plagioclase crystals are found in the same samples that have potash-rich alkali feldspar crystals (Or_{80-90}) . Based on the ternary feldspar crystalline solution model of Elkins & Grove (1990), such high An and Or feldspars represent equilibrium assemblages. We therefore posit that it is unlikely that feldspar pairs represent undigested crustal material, as this would require pairs to be present in the country rock and be incorporated into the same parcel of CI magma. Instead, our hypothesis is that the feldspar compositions reflect crystallization from a melt that was modified by assimilation of country rock, a suggestion supported by trace element and isotopic considerations (Civetta et al., 1997; Bohrson et al., 2006, and in preparation). We performed MELTS numerical simulations of open-system assimilation-fractionation (OSAF) to test the influence of assimilation on the liquid line of descent and on phenocryst compositions.

In the sections that follow, we first provide a regional summary of the composition of the crust beneath



Fig. 9. Calculated solid phase compositions for the best-case CSF and OSAF MELTS simulations. Crosses, melt inclusion data (Webster *et al.* 2003); triangles, data from Civetta *et al.* (1997); circles, data from this study; black squares, CSF MELTS results; dashed line, OSAF MELTS results (model parameters described in Fig. 4 and text). Representative temperatures are marked along the trends. (a) Clinopyroxene (CSF) (Morimoto, 1989, classification). (b) Clinopyroxene (OSAF) (Morimoto, 1989, classification). (c) Spinel (CSF). (d) Spinel (OSAF). (e) Feldspar (CSF). (f) Feldspar (OSAF). Representative tie-line connecting equilibrium feldspars is also shown.

Campania, with a focus on possible contaminants. We then summarize a sequence of MELTS isothermal assimilation calculations, to deduce the composition of assimilant that best solves the 'anomalous feldspar' problem. This assimilant composition is termed SFS (skarn plus foid-bearing syenite). We then present results from a numerical study of the systematics of isenthalpic assimilation of SFS in which the initial assimilant temperature and the mass ratio of SFS to pristine melt $(M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o})$ are varied and the equilibration temperature $(T_{\rm eq})$, mass of crystals generated by assimilative reaction, and the effects of assimilation in producing compositional gaps or changes in melt composition along the assimilation—fractionation liquid line of descent are determined. Finally, we present detailed results of an OSAF simulation based on the SFS assimilant composition. We show that this OSAF case goes a long

way in solving the 'anomalous feldspar' problem and does

Regional context

a good job of capturing the liquid line of descent.

Available data on the crustal structure beneath the Campi Flegrei region suggest a thickness of <25 km (Corrado & Rapolla, 1981; Ferrucci et al., 1989), and several lines of evidence suggest that the crust is lithologically heterogeneous. Borehole studies at Campi Flegrei and other volcanic edifices within Campania and environs indicate that the shallow crust (down to $\sim 4 \text{ km}$) is made up of Cretaceous-Oligocene flysch sequences and Mesozoic-Cenozoic carbonate-siliciclastic formations (Finetti & Morelli, 1974; Bernasconi et al., 1981; Sollevanti, 1983; Buonasorte et al., 1987; Bruno et al., 1998). Buried Quaternary calc-alkaline basalts and basaltic andesites have been recovered in the Campanian Plain region (Di Girolamo, 1978; Barbieri et al., 1979; Beccaluva et al., 1991). Crustal xenoliths have been identified in shoshonites erupted within the Campi Flegrei in the past 12 kyr (Pappalardo et al., 2002a), and in deposits from Vesuvius (Fulignati et al., 2000a,b). Of immediate interest are xenoliths within a proximal breccia unit of the CI-the so-called the Breccia Museo (Fulignati et al., 2004; Fedele et al., 2006; unit C of Rosi et al., 1996). These xenoliths include hydrothermally altered alkalisyenites enriched in chlorine and incompatible trace elements such as U, Zr, Th, and rare earth elements (REE). Modally, these altered svenites contain up to 80% K-rich alkali feldspar, as well as subordinate plagioclase, scapolite, amphibole, pyroxene, biotite, magnetite, titanite, apatite and sodalite, and rare U-, Zr- and REE-bearing phases (Fedele et al., 2006). The shoshonite-hosted xenoliths include a variety that may be derived from upper crustal Lower Miocene arenaceous rocks exposed in Campania and a vesicular type that may be derived from Hercynian basement (Pappalardo et al., 2002a). A notable feature of the Campi Flegrei xenoliths is that they are commonly hydrothermally altered. Xenoliths from eruptive products of Vesuvius have been interpreted as metasomatic products of reaction across magma bodycarbonate wall-rock interfaces and are made up of feldspathoid-bearing syenites such as leucite syenite, skarn, and cumulate clinopyroxenites (Fulignati et al., 1998; 2000a,b, 2001, 2004; Gilg et al., 2001).

Assimilation models: the ground rules

We performed >80 MELTS simulations to study the effects of assimilation on the liquid line of descent and on the composition, appearance order, and abundance of phenocrysts. Here, we highlight results most relevant to explaining the observed feldspar compositions. We also describe significant similarities and differences between the OSAF and CSF models. All MELTS OSAF calculations presented in this study were accomplished in the following manner. From the liquidus temperature to 1000°C, CSF was carried out. At 1000° C, assimilant was added to the melt. After thermal and chemical equilibration of the new system, any crystals that formed as a result of assimilation were removed. In isothermal assimilation the new system remains at 1000° C as it is connected to a heat bath; in isenthalpic assimilation, the new system has a unique equilibration temperature (T_{eq}), a value found as part of the calculation. Following OSAF, the melt was then allowed to evolve once again by CSF down to low melt fractions. It is important to note that when fractional crystallization is the sole specified magmatic process, heat is dissipated into the country rock but mass does not enter the magma from the country rock. During increments of assimilation, mass from the country rock does enter the magma and the process is carried out isenthalpically.

As a starting point in the modeling, we assume that intensive variable conditions used for the CSF case remain valid (RPM with 3 wt% water, QFM to QFM +1, and 0.15 GPa). Although fO_2 is bounded by the QFM and QFM +1 buffers in the CSF case, to simplify the discussion, all OSAF models plotted in the figures are constrained to follow the QFM +1 buffer. The consequence is that predicted FeO concentrations are all several percent low compared with observed data. As is demonstrated in Fig. 4f with the QFM and QFM +1 closed-system fractionation cases, we expect that the fit for FeO would improve in open-system models constrained to follow the QFM buffer.

We recognize at the outset that there are many possible assimilation scenarios, far too many to study independently. Variables potentially important include the quantity of country rock assimilated (i.e. mass ratio M_a^o/M_m^o), the initial assimilant temperature (T_a^o), the assimilant composition, and the temperature or temperature interval at which assimilant is added to pristine melt. In view of imperfect knowledge regarding these conditions, our modest goal is to put approximate bounds on the extent and composition of assimilant. We do this by considering the geological boundary conditions and determining the amount and composition of assimilant that, when added to pristine RPM, allows for better correspondence between predicted and observed phenocryst compositions and the liquid line of descent.

Isothermal vs isenthalpic assimilation: some details

A clear discussion of the thermodynamics of assimilation including informative examples has been presented by Ghiorso & Kelemen (1987) and is strongly recommended as a primer. We have studied the processes of both isothermal and isenthalpic OSAF to constrain assimilant amount, composition, and initial temperature. In isothermal assimilation, the initial temperature of assimilant is equal to the melt temperature at the time of assimilant addition. In the results given here this temperature equals 1000°C. Isothermal assimilation implies that the melt-country rock system is connected to a thermal bath during the reaction process. In isenthalpic assimilation, assimilant at temperature T_a^{o} is added to melt at T_m° . In all OSAF calculations presented here, assimilant is added en masse at $T_{\rm m} = 1000^{\circ}$ C. In isenthalpic assimilation, an energy balance is applied such that the overall enthalpy of melt plus assimilant is constant throughout the interaction; the temperature and composition of melt changes abruptly upon assimilant addition in response to the crystallization of solids induced by assimilant addition and subsequent reaction. It is important to study the magnitude of the changes in melt composition induced by OSAF and compare them with the changes that come about as a result of pseudoinvariant point behavior found at $T_{inv} \approx 883^{\circ}C$ for isobaric CSF. Does assimilation suppress this feature, heighten it, or modify it in some particular way?

In the first set of simulations, we studied isothermal assimilation to focus on the effect of assimilant bulk composition on the liquid line of descent, phase proportions and phase compositions. From an extensive analysis, only a small part of which is presented below, we find that the most probable assimilant is a mixture of plagioclasebearing skarn and hydrothermally altered foid-bearing syenite (SFS), and that the ratio of assimilant to melt is $M_a^o/M_m^o \approx 0.1$. We then study the systematics of isenthalpic assimilation based on SFS composition and explore the effects of initial assimilant temperature (T_a^0) and mass ratio M_a^o/M_m^o on immediately post-OSAF temperature (T_{eq}) , on the mass of crystals precipitated from the melt as a result of assimilation $(M_{\rm crv})$, and on the abrupt change in melt composition as a result of assimilation. Based on these results, we then explore the details of a particular case of OSAF and show that isenthalpic assimilation of SFS wallrock $(M_a^o/M_m^o=0.1)$ forces calcic plagioclase (An_{90-70}) to precipitate at higher temperature compared with the CSF case (compare Figs 7 and 12). The early precipitation of calcic plagioclase is consistent with presence of otherwise anomalous calcic plagioclase phenocrysts (see Figs 2b and 9f). The predicted liquid line of descent for isenthalpic OSAF compares favorably with observations.

Identification of assimilant composition

Isothermal assimilation of flysch

Electronic Appendix 3 (http://www.petrology.oxford journals.org) gives the bulk composition of the assimilants discussed in this section. Isothermal assimilation of flysch was modeled via addition of alkali feldspar (20% by mass; $Ab_{65}Or_{35}$) + plagioclase (60% by mass; An_{60}) + quartz (20% by mass) to melt at 1000°C. The amount of assimilant added is defined by the ratio $M_a^o/M_m^o = 0.1$. Although the predicted feldspar compositional range is improved relative to CSF (An₇₆₋₂₀; Or_{78-60}), the predicted SiO₂ concentration is as high as 73 wt%, significantly higher than any CI compositions. Pred icted vs observed trends on other MgO variation diagrams exhibit similar discrepancies. Simple partial melting of a flysch bulk composition is hence rejected as being especially significant to the CI.

Isothermal assimilation of carbonate

Isothermal assimilation of limestone was simulated by addition of CaO (solid) to melt at 1000°C in the amount $M_a^o/M_m^o = 0.05$. MELTS does not have a thermodynamic model for CO_2 solubility, so we attempted to simulate the salient features of limestone addition by addition of crystalline CaO. Because the solubility at low pressure of CO_2 is small in basaltic to phonolitic melts, we believe this procedure is justified, at least to first order. Similarly, assimilation of dolomite was modeled by addition of a mixture of crystalline CaO and MgO (75% CaO by mass), also with $M_{\rm o}^{\rm o}/M_{\rm m}^{\rm o} = 0.05$. The most critical observation related to assessment of these models is that predicted trends on MgO-oxide variation diagrams are not improved relative to CSF. For example, at low melt fraction SiO₂ is much lower and Na₂O is much greater than observed in the CI samples. In addition, assimilation of model limestone or a limestone-dolomite mixture does not improve the predicted trajectory of the liquid line of descent on the CaO-MgO variation diagram. Plagioclase ranges from An₇₇ to An₈₉ and alkali feldspar ranges from Or₈₄ to Or₉₀ for limestone assimilation; for limestone-dolomite mixture the analogous ranges are An₇₆₋₈₀ and Or₈₄₋₈₈. These ranges are similar to the most An-rich and Or-rich feldspars observed in the CI, but, significantly, do not extend to the least An- or Or-rich compositions observed. We therefore reject simple carbonate assimilation, at least for the assimilant amount and intensive parameters assumed here.

Assimilation of syenite

Isothermal ($T_{\rm m} = 1000^{\circ}$ C) assimilation of hydrothermally altered syenite ($M_{\rm a}^{\circ}/M_{\rm m}^{\circ} = 0.10$) corresponding to sample BL2 of Fedele *et al.* (2006) yields a calculated liquid line of descent similar to that for CSF. Significantly, the CaO–MgO variation diagram correspondence between observed and predicted does not improve significantly. However, an important improvement relative to CSF is that the ranges of predicted feldspar compositions are greater (An_{59–19} and Or_{77–57}) than those of closed-system fractionation. In detail, however, the predicted range of precipitated feldspar compositions does not span the entire observed range. So although assimilation of syenite does improve the correspondence between observation and prediction by expanding the range of plagioclase phenocryst compositions, the correspondence remains imperfect.

Assimilation of skarn plus foid-syenite

The best isothermal OSAF case results involve assimilation $(M_a^o/M_m^o=0.10)$ of a mixture of hydrothermally altered feldspathoid-syenite plus aluminous skarn (mixture of An₉₀ plagioclase and clinopyroxene; see Electronic Appendix 3, available at http://www.petrology.oxford journals.org). We refer to this 'best-case' composition as skarn-foid-syenite (SFS). Predicted solid and liquid phase compositions agree well with CI petrochemical data. Pred icted plagioclase compositions range from $\sim An_{82}$ to An_{30} and closely correspond to observations; substantially more of the observed range is reproduced in the OSAF case compared with closed-system fractionation. The range of pred icted alkali feldspar compositions (Or79-61) is greater than the CSF range, and therefore encompasses more of the observed range. The fits for the compositions of clinopyroxene and spinel are equally good for the CSF and the isothermal OSAF case. The CaO-MgO variation diagram only slightly improves compared with the CSF case.

Isenthalpic assimilation simulations

MELTS isothermal assimilation calculations discussed above were carried out to focus on the effects of assimilant bulk composition on the liquid line of descent and on the composition of phenocrysts precipitated during postassimilation closed-system fractionation. We may recall that for isothermal assimilation, the initial temperature of the assimilant is not a parameter of the problem. In reality, of course, T_{a}^{o} does play a role, as wall-rock must be heated and undergo partial fusion; the energy required to heat and react or partially fuse assimilant is extracted from ambient melt. The extraction of heat from ambient melt lowers its temperature and induces an increment of crystallization. These effects are absent in MELTS CSF and isothermal assimilation calculations. Hence to realize conditions that most closely approximate to natural ones, a final set of MELTS OSAF calculations was undertaken assuming that the interaction of country rock (SFS) and magma occurred isenthalpically. The arguments for treating assimilation as an isenthalpic process were first advanced by Bowen (1922, 1928) and have been discussed more recently by Taylor (1980), Ghiorso & Kelemen (1987), Spera & Bohrson (2001, 2002, 2004), and Bohrson & Spera (2001, 2002, 2003). In MELTS isenthalpic assimilation, a discontinuous change in both melt temperature and composition generally occurs especially when assimilant is added at a single temperature or over a small temperature interval. We studied the details of isenthalpic assimilation by systematic and independent variation of T_a^o and $M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o}$ utilizing SFS as the assimilant. In all cases, assimilant at temperature T_a^o was added to melt at 1000°C.

In the first set of MELTS fractional crystallization– isenthalpic assimilation simulations, T_a^o was constant and equal to 350°C and the amount of assimilant, expressed as

the ratio $M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o}$, where $M_{\rm m}^{\rm o}$ is the mass of pristine melt to which assimilant mass $M_{\rm a}^{\rm o}$ is added, was varied. Results are shown in Fig. 10a. As expected, the equilibration temperature, T_{eq} , monotonically but nonlinearly decreases as the mass of assimilant increases. For example, at $M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o} = 0.3$, $T_{\rm eq} \approx 900^{\circ}$ C, which corresponds to a 100° decrease from the melt temperature (1000°C) at which assimilant was added. Clearly, assimilation of cold wallrock induces considerable cooling. In Fig. 10b, the ratio of the mass of crystals precipitated in response to assimilation $(M_{\rm crvs}/M_{\rm m}^{\rm o})$ is shown. The dashed line in Fig. 10b of slope equal to unity means that for every 1kg of wall-rock assimilated, 1kg of crystals is precipitated from melt in response. Up to a mass ratio $M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o} \approx 0.2$, the mass of newly precipitated crystals is about equal to the mass of assimilant. As the ratio $M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o}$ increases, the effect of assimilation is to trigger an even greater response. For instance, at $M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o}=0.5$, the ratio of crystallized mass to original melt is ~ 1 . Finally, in Fig. 10c, the change in melt composition is shown for various oxides as a function of $M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o}$. Many interesting effects are noted by careful examination of Fig. 10c. The absolute difference in SiO_2 of melt before assimilation to just after thermal and chemical potential equilibrium is reached at T_{eq} , $\Delta wt\%$, is clearly non-monotonic. For example, when $M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o} = 0.3$, there is a difference of about 2 wt% in SiO₂; that is, assimilation increases the SiO₂ content of the melt from \sim 57.07 wt% to ~59.08 wt%. Interestingly, at $M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o}=0.5$, there is essentially no change in the silica content of the melt after equilibration is reached. This shows that assimilation is nonlinear and that simple extrapolation can be misleading. The antithetic behavior of K₂O and Na₂O and the marked asymptotic behavior of CaO as M_a^o/M_m^o increases should be noted. Generalizations are difficult to make because wall-rock is a 10-component system and the phase equilibria can be complicated.

In Fig. 11, the effect of assimilant initial temperature, T_{a}^{o} is studied at fixed mass ratio $M_a^o/M_m^o = 0.10$. In Fig. 11a, the equilibration temperature is plotted against T_a^{o} ; as expected, T_{eq} increases as T_a^o increases. With $T_a^o = 700^\circ C$, the final equilibration temperature is \approx 975°C, whereas when $T_a^{o} = 350^{\circ}$ C, T_{eq} is 960°C. This shows that, at least for relatively small assimilant mass (ratio M_a^o/M_m^o), the equilibration temperature is not exceedingly dependent upon the initial wall-rock temperature. At higher ratios, there is undoubtedly a stronger effect, although we have not studied it quantitatively. The ratio of crystals precipitated in response to added assimilant relative to the mass of pristine melt decreases as T_a^o increases, as noted in Fig. 11b. Finally, in Fig. 11c, the changes in melt composition as a function of T_a^o are shown. The increase or decrease in a specific oxide varies more regularly with T_a^o compared with M_a^o/M_m^o (compare Figs 10c and 11c), with CaO increasing and silica decreasing as the wall-rock



Fig. 10. Results of a systematic study of isenthalpic assimilation applied to CI evolution. In all cases, assimilant of mass M_a^o at initial temperature T_a^o (a typical upper crustal temperature of 350°C) is added to melt of mass M_m^o initially at 1000°C in a discrete batch. (a) Variation of mass ratio M_a^o/M_m^o with T_{eq} the post-assimilation equilibration temperature of the system. T_{eq} decreases as the mass of assimilant increases. The inflection point at $M_a^o/M_m^o = 0.3$ is due to enhanced crystallization and concomitant decrease in melt cooling in response to assimilation. (b) Variation of the mass of crystals (M_{crys}) precipitated in response to assimilation as a function of M_a^o . Up to $M_a^o/M_m^o \approx 0.25$, for every 1 kg of wall-rock assimilated an equivalent mass of phenocrysts precipitates. (c) Difference in wt% of labelled oxide as a result of assimilation. The starting composition is pristine melt at 1000°C and the end composition is the new melt composition at T_{eq} . For example, at $M_a^o/M_m^o = 0.3$, melt is enriched in SiO₂ by 2 wt%. Melt composition changes abruptly in response to assimilation; hence assimilation represents, in addition to pseudo-invariant behaviour, a mechanism for generation of a compositional gap.

temperature increases. It should be noted in particular that the effect of assimilation is to lower the CaO concentration in the melt and that this effect is most pronounced at low wall-rock initial temperature. In light of the mismatch between predicted and observed trend on the CaO–MgO variation diagram, this supports the idea of shallow-level assimilation where crustal temperatures are low.

Open-system assimilation and fractional crystallization

The isenthalpic assimilation-fractionation (OSAF) calculation that best describes observed CI data (SFS assimilant,



Fig. 11. Results of systematic study of isenthalpic assimilation applied to CI evolution. In all cases, $M_a^o/M_m^o=0$ ·l and assimilant is added in a single batch to melt at 1000°C. (See Fig. 10 caption for definitions.) (a) Variation of T_{eq} with T_a^o . (b) Variation of M_{crys} precipitated in response to assimilation with varying T_a^o . A low assimilant temperature promotes crystallization of a larger mass of crystals. (c) Difference in wt% of labelled oxide as a result of assimilation as a function of T_a^o . (Note the opposite behaviour of CaO and SiO₂) As T_a^o increases, the effect on melt composition decreases for all oxide components. Melt composition changes abruptly in response to assimilation especially at low T_a^o .

 $M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o}=0$ ·l) is detailed in this section. The calculation was accomplished in three parts. The first part, from the liquidus (l240°C) to l000°C, is closed-system fractional crystallization, identical to the CSF case discussed above (Fig. 4). When the melt temperature is 1000°C, cold ($T_{\rm a}^{\rm o}=350^{\circ}{\rm C}$) SFS country rock (mechanical mixture of skarn plus

foid-bearing syenite) is added to melt in the ratio $M_{\rm a}^{\rm o}/M_{\rm m}^{\rm o} = 0.10$. Once thermal and chemical equilibrium is attained following the isenthalpic assimilation 'event', melt, now of different composition, is allowed to evolve by closed-system crystal fractionation until low melt fraction conditions are attained. The phase equilibria and trajectory of



Fig. 12. Phase proportions as a function of magma temperature showing the results of OSAF MELTS simulations. Abbreviations are as in Fig. 7. Break at 1000–958:5°C represents isenthalpic addition of assimilant at an initial temperature of 350°C to magma initially at 1000°C. Cooling of magma and heating and reaction of country rock ends at an equilibration temperature $T_{eq} = 958$ °C. The ratio of mass crystallized to assimilant mass (M_{crys}/M_a^o) is 1.08 (see Fig. 10b). It should be noted that plagioclase saturates in OSAF at a higher temperature compared with CSF (see Fig. 7a).

the liquid line of descent for the open-system (OSAF) and closed-system (CSF) cases are portrayed in Fig. 4.

Assimilation of cold country rock lowers the melt temperature from 1000°C to 958°C and causes an increment of clinopyroxene, plagioclase and apatite to crystallize (Fig. 12). The mass of solids crystallized upon addition of assimilant is about equal to the mass of added SFS wallrock (i.e. $M_{\rm crv}/M_a^{\rm o} \approx 1$). A significant feature is that calcic plagioclase (Fig. 9f) precipitates at 958°C, about 80°C higher than in CSF in response to assimilation. The melt composition also changes discontinuously in response to assimilation, as noted by examination of the MgO-oxide variation diagrams of Figs 4 and 10c. Figure 12 shows that the pseudo-invariant temperature increases from 883°C to about 900°C. Significantly, the magnitude of the change in fraction of melt at T_{inv} is about equal to its value in CSF. Hence OSAF does not suppress invariant point behavior, a critical element of our theory for the origin of differentiated CI melt. Following the assimilation 'event', melt continues to evolve by closed-system crystal fractionation until the lowest melt fraction conditions are attained $(f_{\rm m} = 0.05)$. In Fig. 9b, d and f, the composition of clinopyroxene, spinel and feldspar phenocrysts predicted for OSAF are compared with observation. Comparison of Fig. 9e with Fig. 9f clearly shows how feldspar compositions in OSAF correspond better to observations compared with the predictions of feldspar compositions from the CSF case.

SUMMARY OF PHASE EQUILIBRIA CONSTRAINTS

Comparison of the phase equilibria calculations with petrochemical data on CI glass and pumice and observed mineral compositions indicates that fractional crystallization was the dominant process in the development of CI magma from a basaltic trachyandesite parent liquid. Observed arrays on MgO variation diagrams are best captured by isobaric (0.15 GPa or ~6 km depth) crystal fractionation with oxygen fugacity between QFM and QFM + 1 and an initial water content of 3 wt%. The assumed initial concentration of dissolved H₂O is consistent with values inferred from study of the high-MgO melt inclusions of Webster *et al.* (2003). Comparison between predicted and

observed phases is generally very good. The most striking inconsistency between predicted and observed relations is the presence of a population of calcic plagioclase crystals in the range An₆₇₋₉₀ in the CI (Figs 2b and 9e). Previous workers have claimed that these An-rich crystals are xenocrysts. Although we cannot preclude this interpretation, we suggest that crystallization of both An-rich plagioclase and Or-rich alkali feldspar took place as a result of the spatially heterogeneous assimilation of country rock at shallow to intermediate crustal depths (5-10 km). Detailed open-system assimilation-fractionation calculations support the notion that assimilation played a small, but non-negligible, role during the evolution of the CI. The calculations suggest that assimilant is a combination of wall-rock lithologies that are present in the crust in the Campanian region. Specifically, the models indicate involvement of a mixture of skarn and foid-bearing syenite, similar to syenite xenoliths found in the Campi Flegrei (Fulignati et al., 1998, 2000a,b, 2001, 2004; Gilg et al., 2001; Fedele et al., 2006) that may be associated with earlier stages of magmatism in the Campanian region [see De Vivo et al. (2001) for a compilation of the ages of the older magmatism at Campi Flegrei]. Assimilation improves the fit between predicted and observed feldspar compositions. The remaining discrepancy is the trajectory on the CaO-MgO variation diagram. It is at present unclear if this is the result of an inadequacy of the MELTS thermodynamic database, inappropriate selection of intensive variable constraints during OSAF, or a poor choice of the amount, initial temperature or composition of assimilant. Overall, we find the comparison between prediction and observation to be remarkably good.

An important aspect of the phase equilibration models (both CSF and OSAF) is pseudo-invariant behavior. That is, there exists a temperature, denoted T_{inv} , at which the crystallinity (fraction solid, f_s) changes from ≈ 0.5 to ≈ 0.9 . Although in a strict thermodynamic sense, the variance of the system is not zero, in practical terms a large amount of crystallization occurs in a small temperature interval no larger than a few degrees. The pseudo-invariant temperature is $\approx 883^{\circ}$ C for CSF and $\approx 900^{\circ}$ C for OSAF. Very marked changes in the physical characteristics of the melt and of the melt plus fluid mixture occur around T_{inv} . These are described in subsequent sections. It is significant that the existence of the pseudo-invariant point is a general feature of both closed- and open-system MELTS simulations for a variety of starting parental liquid compositions and oxygen buffers. Invariant point behavior is suppressed at higher pressure (e.g. P > 0.3 GPa) and for volatile-poor melts ($<1 \text{ wt\% H}_2\text{O}$), conditions (high pressure and dry melts) that are not relevant to the CI. Invariant point behavior provides a general mechanism to drive explosive Plinian air-fall and ash-flow eruptions. This eruption triggering mechanism does not require recharge.

MELT AND MAGMA PROPERTIES ALONG THE LIQUID LINE OF DESCENT

Figure 13 shows the dependence of magma and melt properties with temperature along the liquid line of descent for the CSF and OSAF system cases. It is clear that significant changes in properties of both melt and magma take place along the liquid line of descent especially near the invariant temperature, T_{inv} Figure 13a portrays the dissolved H₂O content of melt along the liquid line of descent for both CSF and OSAF. Melt saturates with respect to H₂O at 1127°C at ~4 wt% H₂O and continues to increase in melt as heat is extracted and crystals precipitate. For CSF at $T_{\rm inv}$ the H₂O content jumps from ~4.4 wt% to ~5 wt% and thereafter increases at the rate of $\sim 1 \text{ wt\% H}_2\text{O}$ per 50°C. In the OSAF case, there is a slight decrease in dissolved water at the temperature of assimilation (1000°C) because the assimilant is volatile-free. The jump at T_{inv} is less pronounced compared with CSF, although there is a similar pronounced increase in dissolved H₂O in the melt as crystallization proceeds.

Figure 13b portrays the shear viscosity of melt as a function of temperature along the liquid line of descent for CSF and OSAF. The viscosity is calculated using the algorithm of Shaw (1972). As temperature drops, the melt viscosity increases from about 2.5 Pas at the liquidus to 1950 Pas at $T_{\rm inv} \approx 883^{\circ}$ C for CSF and to 1600 Pas at $T_{\rm inv} \approx 900^{\circ}$ C for OSAF. Because isenthalpic assimilation leads to a discontinuity in melt composition between 1000°C and 958°C, the equilibrium melt viscosity varies discontinuously as well for OSAF. In both cases, melt viscosity increases with falling temperature in the range $T_{inv} < T < T_{liquidus}$ because the melt becomes increasingly more silica-rich and cooler. In contrast, at $T < T_{inv}$, melt viscosity drops precipitously as a result of an increase in Na2O and dissolved H2O despite decreasing temperature. The important point of Fig. 13b is that although the melt viscosity increases along the higher temperature part of the crystallization path, once sufficient heat has been lost from the system to wall-rock and T_{inv} is reached, melt viscosity decreases rather markedly. This has important ramifications for the efficiency of crystal-melt separation (see below).

Figure 13c shows the variation of melt and magma density as a function of temperature along the liquid line of descent. Magma is defined here as a homogeneous mixture of water-saturated melt plus bubbles of supercritical fluid. The density of the two-phase mixture of melt and fluid is computed according to

$$\frac{1}{\rho} = \frac{\phi_{\rm f}}{\rho_{\rm f}} + \frac{1 - \phi_{\rm f}}{\rho_{\rm m}} \tag{2}$$

where ρ , ρ_{f} , ρ_{m} , and ϕ_{f} represent the density of magma (treated as a two-phase melt plus fluid mixture),



Fig. 13. Variation of melt and magma physical properties along the liquid line of descent for CSF (QFM + 1) and OSAF models based on RPM starting melt composition for intensive parameters QFM + 1, 0.15 GPa, and 3 wt% initial H₂O. The slope changes at $T = 883^{\circ}$ C correspond to the simultaneous saturation of alkali feldspar and plagioclase at the pseudo-invariant point temperature, T_{inv} . The termination of each MELTS trend is labelled ($f_m = 0.05$). (a) T vs dissolved H₂O content. (b) T vs melt viscosity. (c) T vs density of liquid and two-phase (melt plus fluid) magma. (d) T vs volume fraction of exsolved supercritical fluid (H₂O). H₂O first saturates at 1127°C.

supercritical fluid and melt, respectively, and ϕ_f is the mass fraction of the fluid phase in the two-phase magmatic mixture. The density of both melt and magma decreases with falling temperature for both closed- and open-system cases. For both CSF and OSAF around T_{inv} , there is a steep drop in the melt density, primarily reflecting the effect of the melt becoming increasingly Na₂O and water rich. The decrease in melt density, similar to the effects of decreasing viscosity, enhances the proclivity for crystal–melt separation (see below). Also, the density of the magmatic mixture (melt plus fluid) decreases because the melt density decreases and also because the mass fraction of the fluid phase (ϕ_f) in the magma dramatically increases at T_{inv} .

In Fig. 13d variation in the volume (θ_f) fraction of supercritical fluid along the crystallization path is shown, again for both CSF and OSAF. It is important to recognize that at temperatures at and just below T_{inv} , more than 90 wt% of the original melt (RPM) has crystallized. The viscosity of a homogeneous multiphase mixture with ~90 wt% crystals is enormous (~10¹⁵ Pa s) and clearly not relevant to the products of the Campanian eruption, which have an average crystal content of ~3 vol.%. On the other hand, the explosive Campanian eruption, which produced an eruptive

column ~45 km in height (Carey & Sigurdsson, 1989), clearly did involve a very large volume fraction of supercritical fluid. The fluid volume fraction is accordingly computed based on the two-phase (melt + fluid) sub-system. The dramatic increase in the volume fraction of fluid in the CI magma, from about 10 vol.% at temperatures just above $T_{\rm inv}$ to >60 vol.% just below $T_{\rm inv}$ has important dynamical ramifications. Fluid volume fractions exceeding approximately 70% (Cashman et al., 2000; Petford, 2003) correspond to the volume fraction at which magma fragmentation occurs and are consistent with a pyroclastic Plinian eruption. In fact, one can reasonably argue that this dramatic increase in the fraction of supercritical fluid just below $T_{\rm inv}$ actually triggered the CI eruption. The idea is that once failure of the magma body walls occurs, the release of pressure from the isobaric condition will initiate further exsolution of fluid from melt, and upon ascent a positive feedback will come into play such that the magma viscosity continues to decrease. This, in turn, increases the rate of ascent and hence the rate of decompression, and generates even further fluid exsolution, thereby leading to positive feedback.

In summary, the physical properties of melt and magma evolve towards increasing magma dynamical instability along the liquid line of descent in both the CSF and OSAF cases. Changes in the composition, thermodynamic and transport properties of melt and magma are heightened dramatically at and just below T_{inv} and act as an eruption trigger for explosive eruption of pyroclastic material.

TIMESCALE AND PRE-ERUPTIVE DYNAMICS OF THE CI MAGMATIC SYSTEM

The phase equilibria model discussed above places important constraints on the evolution of the CI magmatic system. However, a phase equilibria model alone addresses neither the timescale for CI magma evolution nor the mechanics of how crystals, melt, and fluid become physically separated. According to the phase equilibria model, development of CI volatile saturated magma is the result of ~90% crystallization of a basaltic trachyandesitic parental melt. Hence, an explanation of the timescale and mechanics of crystal-melt-fluid separation is an essential ingredient of any hypothesis for CI petrogenesis. Was crystallization primarily in situ along the margins (sidewalls, top and bottom) of the parent CI magma body? What role does gravitative crystal settling and bubble flotation play? How vigorous might convection have been? What was the role of compositional convection? Was the 'boxfilling' mechanism quantitatively significant? Did compaction or gas-driven filter pressing play an important role?

The purpose of the following sections is to address these issues qualitatively and semi-quantitatively by scale analysis. We recognize that these issues are among the most controversial and uncertain topics in modern petrogenesis and a fully quantitative detailed treatment is beyond the scope of a single study. The goal is to outline reasonable possibilities for a clear physical picture of how the CI magma formed. We also indicate how the various hypotheses can be tested using additional geochemical information in future studies.

Timescale for CI generation by fractional crystallization

Here we develop a simple thermal model based on elementary scaling to provide upper and lower bounds on the time frame of development of evolved CI magma from a basaltic trachyandesitic parent composition driven by crystal fractionation. This scale is based on thermal considerations. That is, a certain amount of enthalpy must be removed from the starting melt in order to develop CI magma. Roughly, about 1 MJ/kg of heat must be removed in an isobaric closed-system process to pass from the liquid state at the liquidus temperature to the lowest melt fraction (Spera *et al.*, 2000). A timescale can be derived by making some simple assumptions regarding the rate of heat extraction (\bar{q}), the fraction of parental melt volume ($f_{\rm m}$) that

differentiates to form CI magma of volume $V_{\rm CI}$, and the fraction (α) of that volume that erupts to form the CI $(V_{\rm ECI})$. Typically α lies between unity and 0.1. By definition, $V_{\rm ECI} = \alpha f_{\rm m} V$. In the scale analysis we treat the volume of the magma body that undergoes crystallization as a simply connected region of volume V and surface area A. Area and volume are related according to $A = KV^{2/2}$ ³, where K is a dimensionless proportionality constant that depends on the shape of the magma reservoir. It is easy to show that for cubical, spherical and disk-like magma volumes of differing aspect ratio, the constant K varies between about 5 and 7. A timescale, $\tau_{\rm th}$, for fractionation is constructed by assuming that magma of volume V and density ρ loses heat at the rate \dot{q} and that the total amount of heat that needs to be removed is the difference in enthalpy of magma from the starting temperature, 1240°C, to the lowest melt fraction ($f_{\rm m} = 0.05$) temperature of 862°C. This enthalpy, ΔH , is computed from MELTS and represents the total decrease in specific enthalpy of magma during crystallization from the liquidus to the lowest fraction of remaining melt, $f_{\rm m}$, based on the starting volume of parental magma. With these assumptions, the timescale is calculated by simple heat balance as

$$\tau_{\rm th} = \frac{\rho \Delta \hat{H}}{K \dot{q}} \left(\frac{V_{\rm ECI}}{\alpha f_{\rm m}} \right)^{1/3}.$$
 (3)

Equation (3) may be written explicitly in terms of the time, *t*, since the start of fractionation according to

t

$$= au_{\rm th}H$$
 (4)

where

$$\bar{H} = \frac{\hat{H}_{\text{liq}} - \hat{H}(f_{\text{m}})}{\Delta \hat{H}}$$
(5)

is the dimensionless enthalpy. It should be noted that \bar{H} is a function of the melt fraction; \hat{H}_{liq} and $\hat{H}(f_{\text{m}})$ are respectively specific enthalpy at the liquidus and specific enthalpy as a function of f_{m} . \bar{H} is zero at the liquidus temperature and reaches a maximum at low temperature, at the lowest f_{m} .

Once the parameters in (3) are set, it is simple to relate the enthalpy content of the system, which comes from the phase equilibration calculation, to the absolute time after initiation of fractional crystallization using equation (4). The timescale, $\tau_{\rm th}$, is calculated for parameters chosen to provide upper and lower timescales as a function of the DRE eruptive volume ($V_{\rm ECI}$) of the CI. The parameters ρ , $\Delta \hat{H}$, K and $f_{\rm m}$ are sensibly constant and set equal to 2200 kg/m³, 1 MJ/kg, 5 and 0.05, respectively. Based on measured mean heat flux values for worldwide continental geothermal systems such as Long Valley, CA, USA, Yellowstone, USA and other systems (White, 1965; Smith & Shaw, 1975, 1979; Fournier *et al.*, 1976; Smith *et al.*, 1978; Cheng, 1979; Spera *et al.*, 1982; Carrigan, 1988), typical



Fig. 14. Eruptive volume vs upper and lower limits on thermal timescale, $\tau_{\rm th}$, for development of CI magma by crystal fractionation. Dashed line represents an estimated CI DRE eruptive volume of 200 km³ (Rolandi *et al.*, 2003). α represents the fraction of differentiated magma of CI composition that erupts to form the Campanian Ignimbrite. \dot{q} is the mean heat flux (\dot{q} =1–4 W/m²) out of the magma body that fractionated to give the CI derivative melt.

heat flux values lie in the range $\dot{q} \approx 0.6-10 \text{ W/m}^2$ (15–250 HFU, 1 HFU = 10^{-6} cal/cm² s). Observed gradients and fluid temperatures at geothermal boreholes Mofete and S. Vito in Campi Flegrei give present-day heat flows of $\approx 1-2.5 \text{ W/m}^2$ (AGIP, 1987; Rapolla *et al.*, 1989; Wohletz et al., 1999; de Lorenzo et al., 2001). Values in the past may have been slightly higher; we adopt as minimum and maximum bounds on heat flow 1 W/m² and 4 W/m², respectively. The fraction α , of differentiated magma that erupted to form the CI from a possibly larger subjacent volume of differentiated magma is difficult to estimate but probably lies in the range 0.5-1 (Crisp, 1984; White et al., 2006). Here we adopt maximal and minimal values of 0.8–0.4 for simplicity. In Fig. 14, the timescale $\tau_{\rm th}$ is shown as a function of the DRE eruptive volume of the CI (V_{ECI}) for the range of estimated parameters. Estimates for the DRE volume of the CI vary from $\sim 80 \text{ km}^3$ to $> 200 \text{ km}^3$. The timescale ranges from ~ 60 kyr to ~ 300 kyr for a CI volume of $V_{\rm ECI} = 200$ km³. Using a value for τ according to this simple thermal model allows one to attach an approximate absolute timescale for the fractionation process. In particular, one can establish a scale to estimate the age of crystals. Figure 15a shows such a scale with $\tau_{\rm th}$ equal to 200 kyr based on equations (3) - (5).

The implication of Fig. 15a is that each type of phenocryst has an age range. For example, if the hypothesis of CSF is correct, then the oldest clinopyroxene phenocrysts, some of which contain relatively MgO-rich MIs, ought to



Fig. 15. (a) Phase proportions as a function of magma temperature, showing a temporal crystallization history for the CI. Ages represent time before the CI eruption at 39-28 ka when specific minerals began crystallizing according to the best-fit CSF model. Melt temperature was buffered by pseudo-invariant point crystallization $(T_{\rm inv} = 883^{\circ}{\rm C})$ for ≈ 20 kyr. (b) Crystallization sequence and duration for CI crystals based on thermal model presented in the text.

be 140 kyr older than the oldest alkali feldspar crystals. Such timescale predictions are testable by isotopic studies on particular phenocryst populations based on composition and crystal size distributions. In Fig. 15b, the duration of particular phenocryst growth is shown. Again, it is clear that if an independent estimate could be made of the difference in age of different phenocrysts, then that information could be used to estimate the average rate of heat loss from the magma body that gave rise to the CI. The critical point to appreciate is that scale analysis combined with results from MELTS simulations for particular eruptions provide a framework for assessing timescale information gleaned from other types of studies.

Separation of crystals and melt

To generate trachytic CI melt from a basaltic trachyandesite parent, 90-95% wt% fractionation of solids is required (see Fig. 7a). Because the average crystallinity of CI samples is $\sim 3 \text{ vol.}\%$, it is clear that some mechanism must separate crystals from melt. Here we examine some possibilities and estimate their relevant timescales for comparison with the thermal timescale established in the previous section. The conclusion is that in situ marginal crystallization and crystal settling are the dominant mechanisms that act to separate evolved melt from crystallized solids. Other possible physical processes such as fluid-driven filter pressing and compaction at the base of a magma body may contribute but are considered of secondary significance. An excellent quantitative discussion of separation of crystals from melt to produce large-volume crystal-poor rhyolites has been given by Bachmann & Bergantz (2004). The compositions those workers considered (high-silica rhyolites) are 100-1000 times more viscous than both parental CI melt and CI magma itself, so their detailed conclusions may not apply. Nevertheless, the discussion in their paper is useful for making judgements regarding important mechanisms for systems of different bulk composition.

In situ crystallization

In situ crystallization relies on compositional convection driven by crystallization in a permeable mush region along the margins of the magma body (floor, roof, etc.) to separate crystals from melt (McBirney, 1980; Turner, 1980; Sparks et al., 1984; Spera et al., 1984, 1995; Lowell, 1985; Nilson et al., 1985; Trial & Spera, 1990; Marsh, 1996, 2002). The phase equilibria models clearly indicate that melt density decreases during the course of cooling and solidification as a result of the overwhelming effects of chemical buoyancy. The generation rate of evolved melt scales with the rate of crystallization, a function of the evolving temperature field. As enthalpy flows from the mush region to colder wall-rock, crystallization proceeds and buoyant melt develops within the mush. As a marginal mush zone grows in thickness, interstitial melt can percolate and accumulate upwards. The intensity of this flow depends on the local temperature field and rate of crystallization and on the thickness and characteristic length of the marginal multi-phase region. If circumstances are favorable, such as sloping boundaries and protective cupolas where back mixing can be avoided, 'box-filling' may occur. The volumetric rate of generation of evolved melt, V, may be roughly estimated using a simple porous mush model (Trial & Spera, 1990):

$$\dot{V} = \frac{K\Delta\rho g\delta L}{f_{\rm m}\mu}.$$
(6)

In equation (6) the parameters are the permeability, $K \approx 10^{-7}$ m², the intrinsic (chemical) density difference driving the

percolative flow, $\Delta \rho \approx 200 \text{ kg/m}^3$, the acceleration due to gravity, $g = 10 \text{ m/s}^2$, porosity $f_{\rm m} \approx 0.8$, melt viscosity, $\mu \approx 2000 \text{ Pa}$ s, mush layer thickness $\delta \approx 50 \text{ m}$ and mush layer extent, $L \approx 5 \text{ km}$. This gives a volume rate of evolved melt production of $\sim 10^{-3} \text{ km}^3/\text{yr}$ or a period of 200 kyr to generate the eruptive volume of the Campanian Ignimbrite ($V_{\rm ECI} \approx 200 \text{ km}^3$). We may recall that 200 kyr is the approximate timescale for heat extraction independently estimated based on heat flow losses.

Observational evidence supporting the in situ mechanism is found from study of juvenile pumice and cognate xenoliths found in a peculiar unit of the CI-the Breccia Museo (BM) (unit C of Rosi et al., 1996; see also Fulignati et al., 2004; Fedele et al., 2006). The BM is a coarse-grained proximal unit of the CI that contains porphyritic trachytic to phonolitic pumice fragments. We may recall that most pumice in the CI elsewhere is sparsely porphyritic with ≈ 3 vol.% phenocrysts. The BM crystal-rich pumice fragments contain ≈ 30 vol.% phenocrysts (alkali feldspar, plagioclase, clinopyroxene, biotite, apatite, and spinel). This highly porphyritic component of the BM unit of the CI was interpreted by Fulignati et al. (2004) as having formed in a marginal mushy crystallization zone as expected for in situ crystallization. We concur with this interpretation and conclude that in situ crystallization is a viable mechanism for separation of crystals from melt to produce differentiated CI melts. If marginal in situ crystallization was important, then a density-stratified region in the upper portions of the magma body from which the CI was erupted may have developed during a time frame of the order of 200 kyr.

Crystal settling

Another possible mechanism for separation of crystals from melt involves the process of crystal settling, which has been studied for over 80 years (Bowen, 1928; Shaw, 1965; Bartlett, 1969; Sparks et al., 1984; Marsh & Maxey, 1985; Martin & Nokes, 1989; Bachmann & Bergantz, 2004). In the simplest case, melt is stagnant and the problem is simply application of Stokes' settling, with allowance for the effects of crystallinity on settling rate (hindered settling). In the more complicated case, the effects of convective motion of melt, which can keep crystals suspended if sufficiently vigorous, must be taken into account. Crystal settling is maximized in the former case. Even in the case of vigorous convection, crystal settling remains possible because convective velocities must decrease to zero along the margins (sidewalls, roof and floor) of the magma body. In the sections below we first analyze crystal settling in a stagnant fluid. This is applicable to settling of crystals grown within a densitystratified magma perhaps near the roof or in an isolated cupola. Then we consider the more general case of the likelihood of crystal settling when convective motions driven by thermal or compositional buoyancy are significant.

The main conclusion is that in either case crystal settling is a viable process to produce trachytic CI melt on a timescale far shorter than the thermal timescale, τ_{th} , established in equation (3). In other words, the rate-limiting process is extraction of heat and not settling of crystals, which can easily keep up with heat extraction.

Simple crystal settling

Hindered settling velocities of monodisperse crystals of diameter d in a stagnant viscous crystal-melt suspension of melt fraction f_m and melt shear viscosity μ are calculated from

$$U_{\rm set} = \frac{g\Delta\rho d^2}{18\mu} \frac{f_{\rm m}^2}{[1 + (1 - f_{\rm m})^{1/3}]^{[5(1 - f_{\rm m})/3f_{\rm m}]}}$$
(7)

(Barnea & Mizrahi, 1973; Bachmann & Bergantz, 2004). In equation (7), $\Delta \rho$ represents the density difference between crystal and melt. The characteristic time for efficient crystal settling (τ_{set}) is given by

$$\tau_{\rm set} = L/U_{\rm set} \tag{8}$$

where *L* represents a characteristic magma body length scale. Based on mean crystal densities (calculated from the MELTS thermodynamic database) for spinel (4700 kg/m³), olivine (3200 kg/m³), clinopyroxene (3200 kg/m³), apatite (3060 kg/m³), biotite (2700 kg/m³), plagioclase (2600 kg/m³), and alkali feldspar (2500 kg/m³) and mean crystal diameters, characteristic crystal settling has been calculated using melt density and shear viscosity of 2250 kg/m³ and 1000 Pa s, respectively (Fig. 13b and c). Bubble rising times are also calculated assuming the fluid phase is pure H₂O at 0.15 GPa and 900°C.

For distance scale of L = 1 km, simple Stokes' phenocryst sinking times lie in the range $10^2 - 10^3$ years except for apatite. Because of its small size, apatite settling times are of the order of 10^4 years. The H₂O bubble rise time for a 1 mm diameter bubble is \sim 10 years. For hindered settling with the fraction of crystals, $f_s = 1 - f_m$, conservatively set equal to 0.5, these times increase by a factor of two. The straightforward conclusion is that Stokes' settling is very rapid compared with the thermal timescale and hence is an efficient mechanism of crystal-melt separation in stagnant regions such as in a density-stratified magma body cap. Similarly, exsolved H₂O-rich bubbles can rapidly accumulate roofward by flotation. Olivine settling rates are faster than those of the feldspars in CI melts. In addition, olivine is no longer a stable phase when feldspar becomes stable (Fig. 15b). Therefore we conclude that olivine crystals may have been removed from the CI magma before eruption.

Crystal settling with convection

Sedimentation in a convecting fluid has been theoretically and experimentally studied in the magmatic context by Martin & Nokes (1989) in considerable detail. They developed a simple analysis valid when the ratio of crystal settling speed (U_{set}) to the mid-height melt convective velocity (W), U_{set}/W , is $\ll 1$, when the crystal content is low and when re-entrainment of sedimented crystals along the magma body floor is neglected. The model posits that crystals behave as uniformly mixed passive tracers in the interior of convecting magma because U_{set}/W ≪1 but that at the base of the magma body, where convective motions vanish, crystals are free to settle at their Stokes' or hindered settling velocities. Based on estimates of melt mid-height convective vertical velocity (e.g. Spera et al., 1982; Martin & Nokes, 1989; Trial & Spera, 1990), it is easy to show that the condition $U_{\text{set}}/W \ll 1$ is satisfied for the magma body associated with the CI eruption. Quantitatively, the rate at which the volume fraction of solids (crystals) in the well-mixed interior, $d\theta_s/dt$, decreases with time is given by

$$\frac{\mathrm{d}\theta_{\mathrm{s}}}{\mathrm{d}t} = -\frac{U_{\mathrm{set}}}{L}\theta_{\mathrm{s}} \tag{9}$$

where θ_s is the volume fraction of crystals and *L* is the chamber height. Equation (9) may be integrated using the definition of the settling timescale from equation (8) to give

$$\theta_{\rm s} = \theta_0 \exp(-t/\tau_{\rm set}) \tag{10}$$

where θ_0 is the initial crystallinity in the well-mixed region. It is clear from equation (10) that the volume fraction of crystals decays exponentially and the *e*-folding timescale (the time needed for reduction of the crystallinity by a factor of $e \approx 2.7$) is identical to the Stokes' or hindered settling timescale. The surprising result of this model is that the settling timescale is independent of the vigor of convection and is identical to the timescale for removal of crystals from a stagnant melt. Although increasing the Rayleigh number does increase the mean convective velocity, higher velocity means a great mass flow through the momentum boundary layer region where crystals can be efficiently removed by Stokes' settling.

Koyaguchi *et al.* (1990) studied systems with a somewhat higher crystal fraction and concluded that the stagnant settling timescale is a minimum value because of re-entrainment effects associated with unsteadiness of the larger-scale convective flow. However, even allowing for an increase in the timescale by a factor of 10, it appears that crystal settling can still be quantitatively significant on the thermal timescale. The conclusion is that even if convection within the undifferentiated portion of the magma body is vigorous, crystals will be removed by settling on a timescale shorter than the thermal scale of $\tau_{\rm th} \approx 200$ ka.

Compaction

An additional mechanism for separation of crystals from melt is compaction within a basal mush zone leading to expulsion of the interstitial melt (e.g. McKenzie, 1984; Shirley, 1986). Recently, Bachmann & Bergantz (2004) have estimated the time required to segregate large volumes $(V \sim 500 \text{ km}^3)$ of crystal-poor rhyolite melt from parental silicic mush purely by compaction. The volumetric rate of compaction-driven melt expulsion (Trial & Spera, 1990; Bachmann & Bergantz, 2004) is

$$\dot{V} = \frac{(1-\theta)^2 (1-e^{-1}) K \Delta \rho g L^2}{\mu}$$
(11)

where θ represents the porosity of volume fraction of melt within the mushy floor layer. The idea is that melt filterpressed out by mush compaction would be compositionally evolved (differentiated). For parameters applicable to the genesis of the CI ($\theta \approx 0.5$, $K \approx 10^{-8} \text{ m}^2$, $\Delta \rho \approx 300 \text{ kg/m}^3$, $L \approx 3$ km, $\mu = 1000$ Pa s), the volumetric rate of expulsion is $\approx 1.5 \times 10^{-4} \text{ km}^3$ /year. At this rate, the time needed to form 200 km^3 of melt is ~150 kyr. If we consider that not all the differentiated melt was actually erupted (i.e. $\alpha < 1$), we conclude that melt expulsion by compaction was probably not the dominant mechanism of crystal-liquid separation although compaction may have contributed to the process. The crystal-melt separation processes of in situ (marginal) crystallization and crystal settling are apparently significantly faster than simple mush compaction.

Gas-driven filter pressing

A final mechanism considered for separation of melt from crystals is termed gas filter pressing, first proposed by Anderson et al. (1984) and recently discussed by Sisson & Bacon (1999) and Bachmann & Bergantz (2003). The physical basis of the mechanism involves an isochoric (constant volume) process. In particular, in a region undergoing crystallization and concomitant fluid exsolution, if the crystallizing region inflates slowly relative to fluid exsolution, fluid overpressure will develop. Sisson & Bacon (1999) suggested that the development of a pressure gradient leads to percolation of melt from regions of high crystallinity to regions of low crystallinity. There is evidence that this process may be important on a small scale (Bacon et al., 1986). However, recent calculations by Bachmann & Bergantz (2003) on the mechanics of this process suggest that it is rather inefficient in expelling large quantities of differentiated melt from a mush on a timescale compatible with the one inferred as relevant to the generation of evolved CI melt $(\tau_{\rm th} \sim 100-200 \, \rm kyr)$. Filter pressing could play a role in forming aplitic dikes and small volumes of crystal-poor evolved melt; generation of hundreds of cubic kilometers of crystal-poor trachytic melt on a 10⁵ years timescale is, however, deemed unlikely.

CONCLUSIONS

- (1) Comparison between results of phase equilibria models using MELTS (Ghiorso & Sack, 1995) and observed major element pumice or bulk-rock and mineral data provide constraints on the parental composition (including water content), pressure, and oxygen fugacity for the magma body associated with the Campanian Ignimbrite. The basaltic trachyandesitic parental melt composition is similar to that of clinopyroxene-hosted high-MgO melt inclusions (Webster *et al.*, 2003), when correction is made for reaction between melt and host clinopyroxene. Parental melt has ≈ 3 wt% water and evolved by isobaric fractionation at pressures near 0-15 GPa (equivalent to ≈ 6 km depth), between the QFM and QFM + 1 oxygen fugacity buffers.
- (2) Phase equilibria have been calculated along the liquid line of descent. At 0.15 GPa, olivine is the liquidus phase ($T_{\text{lig}} = 1235^{\circ}\text{C}$), followed by saturation of clinopyroxene (1162 $^{\circ}$ C), supercritical water (1127 $^{\circ}$ C), spinel (1078°C), and apatite (1018°C). At ≈ 883 °C, defined as a pseudo-invariant point, the magmatic system undergoes significant changes as biotite, alkali feldspar and plagioclase crystallize simultaneously and the fraction of melt changes at fixed temperature from ~ 0.5 to 0.1. Good agreement between calculated and observed melt and mineral compositions illustrates that the Campanian magmatic system evolved dominantly, solely, by closed-system but not fractional crystallization.
- (3) Observed plagioclase and alkali feldspar compositions outside the range predicted by the closed-system model provide evidence for open-system contamination. MELTS models of isobaric assimilationfractionation constrain wall-rock compositions and provide broad limits on the thermal and mass conditions of assimilation. Assimilation, modeled as an isenthalpic process, probably involved magma interaction with a small mass of upper crustal skarn and foid-bearing syenite, rocks known to make up part of the crust beneath Campania. Although assimilation affects the liquid line of descent, pseudo-invariant point behavior remains; multiple simultaneous phase saturation may be a general feature of open or closed crustal magmatic systems that are relatively water-rich and evolve at low pressure.
- (4) Viscosity, density, dissolved water concentration of melt and magma and the fluid phase volume fraction in magma (both open and closed systems) typically change smoothly as a function of temperature. However, at the pseudo-invariant point, all properties change dramatically. It is important to emphasize that these thermodynamic and transport properties

change essentially isothermally $(T = T_{inv})$ as enthalpy is removed from the system by heat transfer. Viscosity and density decrease whereas dissolved water and volume fraction supercritical H₂O in magma increase. The rather dramatic decrease in viscosity (from 1700 Pa s to ~200 Pa s), coupled with a change in volume fraction of water from ~0.1 to 0.8 and a significant decrease of magma density, acts as a dynamical eruptive trigger.

- (5) Scale analysis allows calculation of a thermal timescale for evolution of the magmatic system, given rates of heat loss constrained by geothermal observations, the liquidus to lowest melt fraction enthalpy difference, and the volume of the system. Reasonable values yield a timescale of evolution of ~200 kyr, meaning that the Campanian magma body probably evolved from mafic to trachytic composition over this time. Similar analysis applied to individual crystal phases provides estimates of durations of crystallization and therefore potential age ranges for discrete crystal populations.
- (6) Thermal timescale information also allows predictions to be made about possible mechanisms of crystal-melt separation, clearly required by the contrast between the predicted amount of crystallization (~90-95% to generate trachytic compositions) and observed modal proportions of crystals (average 3% in Campanian pumice). In situ crystallization and crystal settling, with or without convection, are both mechanisms that can efficiently separate crystals and melt over a timescale of 200 kyr.
- (7) The approach of comparing predictions of multicomponent-multiphase equilibria models subject to differing boundary conditions (closed or open) with geochemical data on liquids (glass), melt inclusions, pumice and phenocrysts for specific eruptions has much to recommend it. At the very least, certain parameters such as pressure or oxygen fugacity can be narrowly constrained. Furthermore, development of straightforward open or closed thermodynamic models allows construction of a framework for studying possible deviations from local equilibrium conditions. The models provide physical and chemical data that can be used to make predictions about thermal timescales, mechanisms of formation (e.g. viable mechanisms of crystal-melt separation) and eruptive dynamics. The ability to test such predictions using additional physical, kinetic, dynamical, remote sensing, geophysical and geochemical data available for magmatic systems has great potential for improved understanding of how magma bodies evolve and erupt. In particular, large eruptions such as the Campanian produce global climatic effects (net cooling) that are maximized by very high volumetric discharge ultimately triggered by phase equilibria.

SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal* of *Petrology* online.

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