Durham Research Online

Deposited in DRO:
08 March 2018

Version of attached file:
Accepted Version

Peer-review status of attached file:
Peer-reviewed

Citation for published item:

Further information on publisher’s website:
https://doi.org/10.1093/petrology/egy020

Publisher’s copyright statement:
© The Author(s) 2018. Published by Oxford University Press. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse, distribution, and reproduction in any medium, provided the original work is properly cited.

Additional information:

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a link is made to the metadata record in DRO
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the full DRO policy for further details.
Tracking volatile behaviour in sub-volcanic plumbing systems using apatite and glass:
insights into pre-eruptive processes at Campi Flegrei, Italy

Michael J. Stock\textsuperscript{1,2*}, Madeleine C.S. Humphreys\textsuperscript{3}, Victoria C. Smith\textsuperscript{4}, Roberto Isaia\textsuperscript{5}, Richard A. Brooker\textsuperscript{6}, David M. Pyle\textsuperscript{1}

\textsuperscript{1}Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, UK
\textsuperscript{2}Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK
\textsuperscript{3}Department of Earth Sciences, Durham University, Science Labs, Durham, DH1 3LE, UK
\textsuperscript{4}Research Laboratory for Archaeology and the History of Art, University of Oxford, South Parks Road, Oxford OX1 3QY, UK
\textsuperscript{5}Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Vesuviano, via Diocleziano 328, 80154 Napoli, Italy
\textsuperscript{6}School of Earth Sciences, University of Bristol, Queens Road, Bristol BS8 1RJ, UK
\textsuperscript{*E-mail: ms2368@cam.ac.uk

ABSTRACT

Volatile elements play an important role in many aspects of the physicochemical architecture of sub-volcanic plumbing systems, from the liquid line of descent to the dynamics of magma storage and eruption. However, it remains difficult to constrain the behaviour of magmatic volatiles on short timescales before eruption using established petrologic techniques (e.g. melt inclusions): specifically, in the final days to months of magma storage. This study presents a detailed model of pre-eruptive volatile behaviour in the Campi Flegrei system (Italy), through combined analyses of apatite crystals and glass. The deposits of eight eruptions were examined, covering the full spectrum of melt
compositions, eruptive styles and periods of activity at Campi Flegrei in the past 15 kyr.

Measured apatite compositions are compared with thermodynamic models that predict the evolution of the crystal compositions during different fractional crystallisation scenarios, including (i) volatile-undersaturated conditions, (ii) H$_2$O-saturated conditions, and (iii) under varying $P$-$T$ conditions. The compositions of clinopyroxene-hosted and biotite-hosted apatite inclusions are consistent with crystallisation under volatile-undersaturated conditions that persisted until late in magmatic evolution. Apatite microphenocrysts show significantly more compositional diversity, interpreted to reflect a mixed cargo of crystals derived from volatile-undersaturated melts at depth and melts which have undergone cooling and degassing in discrete shallow-crustal magma bodies. Apatite microphenocrysts from lavas show some re-equilibration during cooling at the surface. Clinopyroxene-hosted melt inclusions within the samples typically contain 2-4 wt% H$_2$O, indicating that they have been reset during temporary magma storage at 1-3 km depth, similar to the depth of sill emplacement during recent seismic crises at Campi Flegrei. Comparable apatite compositional trends are identified in each explosive eruption analysed, regardless of volume, composition or eruption timing. However, apatites from the different epochs of activity appear to indicate subtle changes in the H$_2$O content of the parental melt feeding the Campi Flegrei system over time. This study demonstrates the potential utility of integrated apatite and glass analysis for investigating pre-eruptive volatile behaviour in apatite-bearing magmas.

**Keywords:** Apatite; melt inclusions; Campi Flegrei; volatiles; thermodynamic modelling

**INTRODUCTION**

Magmatic volatiles (H$_2$O, CO$_2$, halogens and SO$_2$) are minor but important constituents of most silicate melts, and affect almost every aspect of magmatic evolution and eruption.
Volatiles influence mineral phase stability and the liquid line of descent (Grove et al., 2003, Zimmer et al., 2010), as well as melt density (Lange & Carmichael, 1990) and viscosity (Giordano et al., 2008), thus exerting a major control on the depths of magma storage and the crustal-scale structure of sub-volcanic systems (Annen et al., 2006). Volatile exsolution and expansion drives volcanic eruptions, and their pre-eruptive behaviour plays an important role in controlling the style and tempo of volcanism at the Earth’s surface (Cashman, 2004, Edmonds, 2008, Huppert & Woods, 2002, Roggensack et al., 1997).

Given the fundamental role of volatiles in controlling volcanic processes, quantification of their pre-eruptive concentrations remains a high priority for any investigation. A variety of petrologic methods have been used to decipher the volatile histories of past eruptions, giving access to distinct snapshots of melt volatile contents over variable pre-eruptive timescales. For example, melt inclusions capture a record of magmatic volatiles at the time of entrapment, and have been used widely to constrain volatile concentrations in different magmatic settings (e.g. Dunbar et al., 1989, Saal et al., 2002, Stefano et al., 2011, Wallace, 2005). However, recent studies have revealed the rapidity of H+ diffusion in common igneous phenocrysts under magmatic conditions, relative to the timescales of pre-eruptive magma storage (e.g. Ingrin & Blanchard, 2006, Reubi et al., 2013, Woods et al., 2000). Melt inclusion H2O contents may diffusively re-equilibrate through their host crystals within hours to weeks, limiting this volatile record to the very final stages of magma storage and/or ascent (e.g. Bucholz et al., 2013, Danyushevsky et al., 2002, Gaetani et al., 2012, Lloyd et al., 2013, Portnyagin et al., 2008, Preece et al., 2014, Reubi et al., 2013). It has also been shown that significant amounts of CO2 may migrate from the inclusion melt into shrinkage bubbles, leading to underestimates of pressure (Moore et al., 2015). Understanding volatile systematics during late-stage magma storage and the onset magma ascent is essential for identifying
eruption-triggering processes and understanding the ‘warning’ signs that would be observed at the Earth’s surface in the build-up to an eruption.

Apatite [Ca$_4$(PO$_4$)$_3$F,Cl,OH] is a common accessory mineral in volcanic, plutonic and ore-forming environments (Piccoli & Candela, 2002) and has received increasing attention as a potential magmatic volatile ‘probe’, due to its ability to incorporate all major magmatic volatiles into its crystal structure. Halogens and OH are essential structural constituents in apatite and are incorporated as part of a series of exchange equilibria (Candela, 1986, McCubbin et al., 2015). Sulphate and CO$_3^{2-}$ may also substitute into apatite as trace components (e.g. Dietterich & de Silva, 2010, Pan & Fleet, 2002, Riker et al., in press).

Recent work has focussed on deciphering the relationship between apatite F-Cl-OH compositions and their host melt volatile contents (e.g. Boyce & Hervig, 2009, Boyce et al., 2014, Candela, 1986, McCubbin et al., 2011, Patiño Douce & Roden, 2006, Piccoli & Candela, 1994, Stock et al., 2016). One advantage of apatite analysis is that phenocryst-hosted apatite inclusions can preserve a record of melt volatile compositions under conditions where melt inclusions may have re-equilibrated (Stock et al., 2016). Since volatile re-equilibration in mineral-hosted apatite inclusions requires simultaneous diffusion of F, Cl and/or OH, this process will be rate-limited by halogen diffusivity in the host phenocrysts, which is significantly slower than H$^+$ (Bucholz et al., 2013, Lloyd et al., 2013). In contrast, F-Cl-OH diffusion within apatite crystals is relatively rapid and microphenocrysts are therefore able to exchange volatiles with host liquids on geologically short timescales (i.e. microphenocryst rims may re-equilibrate in weeks to years at magmatic temperatures [$T$]; Brenan, 1993). Since these timescales of apatite microphenocryst re-equilibration are longer than timescales of magma ascent (i.e. hours to days), apatite microphenocrysts may preserve a record of pre-eruptive conditions even when matrix glasses degas at low pressure ([$P$]; Stock et al., 2016).
In this paper, we investigate apatite and glass compositions in juvenile samples from eight eruptions of the Campi Flegrei volcano (Italy), to determine magmatic volatile systematics and processes in the build-up to eruptions. Campi Flegrei was selected as the focus of this study because the melts are known to be apatite-bearing and volatile-rich (Arienzo et al., 2016, Arienzo et al., 2010, Cannatelli et al., 2007, D'Antonio et al., 1999). It has also recently shown signs of unrest (Chiodini et al., 2012, Moretti et al., 2017). Building on the work of Candela (1986) and Piccoli and Candela (1994) we develop thermodynamic models that predict the theoretical compositional evolution of apatite as a function of changing magma compositions during fractional crystallisation in the presence/absence of different fluid phases. Different populations of apatite inclusions (hosted in biotite and clinopyroxene) and microphenocrysts are identified based on their volatile compositions and, through comparison with our thermodynamic models, we use these to constrain the pattern of magmatic volatile behaviour in the sub-volcanic plumbing system at Campi Flegrei. Although melt inclusions have re-equilibrated during magma ascent, coupled interpretation of apatite and glass compositions provides additional constraints on the structure of the Campi Flegrei plumbing system and the composition of the magmatic fluid phase prior to eruption. Finally, we discuss apparent variations in apatite volatile contents that are linked to different periods of eruptive activity at Campi Flegrei, and suggest that the volatile contents of incoming parental magmas vary with time.

GEOLOGICAL SETTING

Campi Flegrei comprises a nested caldera system, defined by collapse scarps that formed during the Campanian Ignimbrite (~40 kyr; Giaccio et al., 2017) and Neapolitan Yellow Tuff (NYT, ~15 kyr; Deino et al., 2004) eruptions (Fig. 1). It is one of the most active volcanoes in Europe, having produced >60 eruptions in the past 15 kyr, from vents located within the NYT Caldera (Smith et al., 2011). These are divided into three ‘epochs’ that represent periods of
eruptive activity, separated by prolonged quiescence (Di Vito et al., 1999). Vents for these eruptions are located within the NYT caldera (Fig. 1; Di Vito et al., 1999, Isaia et al., 2009). Epoch 1 occurred from ~15 to 10.6 kyr and produced ~30 explosive eruptions, with a typical inter-eruptive interval of ~70 yrs (Di Vito et al., 1999, Smith et al., 2011). Six low-magnitude explosive eruptions occurred in Epoch 2, between ~9.6 and 9.1 kyr, at an average interval of ~65 yrs (Di Vito et al., 1999, Smith et al., 2011), followed by a long period (~4 kyr) of quiescence. Twenty-seven eruptions occurred within the short Epoch 3 time-period, between ~5.5 and 3.5 kyr (Smith et al., 2011), with an average eruptive interval of ~75 yrs (Di Vito et al., 1999). Most Epoch 3 eruptions were small, explosive events (typically producing 0.02-0.10 km³ of material, dense rock equivalent [DRE]; Smith et al., 2011). However, uniquely within the past 15 kyr, Epoch 3 also includes 4 effusive lava domes (Di Vito et al., 1999, Melluso et al., 1995). The most recent Campi Flegrei eruption was at Monte Nuovo in 1538 CE. This occurred after a >3 kyr dormant period (Piochi et al., 2005), substantially greater than the typical inter-eruption time interval, and is therefore not considered part of Epoch 3 (Smith et al., 2011).

**Chemical diversity of eruptive products in the past 15 kyr**

The most mafic (shoshonitic) melt inclusions identified in Campi Flegrei typify the mantle melts feeding the system (Mangiacapra et al., 2008, Vetere et al., 2011). Major and trace element studies of Campi Flegrei whole-rocks and glasses show an evolutionary trend from these mafic melts to evolved trachytes or phonolites, with the entire suite formed by fractional crystallisation of a single parental magma composition, punctuated by periodic recharge events (Civetta et al., 1991, D'Antonio et al., 1999, Di Renzo et al., 2011, Di Vito et al., 2011, Fourmentraux et al., 2012, Pappalardo et al., 1999, Smith et al., 2011, Villemant, 1988). Pre-NYT (>15 kyr) melts encompass only the most evolved end of the compositional spectrum (Pappalardo et al., 1999). Post-NYT (<15 kyr) magmas do not follow a continual
compositional trend between eruptions (i.e. from primitive to evolved), but the most primitive
matrix glasses and whole-rocks are derived from Epoch 1, with Epochs 2 and 3 largely
indistinguishable based on their major element compositions (D'Antonio et al., 1999, Smith et
al., 2011). Matrix glasses from Monte Nuovo are unlike previous eruptions, with notably
higher Na$_2$O concentrations (Smith et al., 2011).

In contrast, isotopic heterogeneity in Campi Flegrei products suggests that the magmas cannot
have formed through fractional crystallisation alone (D'Antonio et al., 2007, Di Renzo et al.,
2011, Pappalardo et al., 1999, Pappalardo et al., 2002). Isotopic compositions of <15 kyr
Campi Flegrei melts reflects mixing between three distinct end-members, defined by Di
Renzo et al. (2011) as: the ‘NYT component’ ($^{87}$Sr/$^{86}$Sr: 0.70750–53, $^{143}$Nd/$^{144}$Nd: ~0.51246,
$^{206}$Pb/$^{204}$Pb: ~19.04, $\delta^{11}$B: ~ -7.9‰), the ‘Minopoli 2 component’ ($^{87}$Sr/$^{86}$Sr: ~0.70860,
$^{143}$Nd/$^{144}$Nd: ~0.51236, $^{206}$Pb/$^{204}$Pb: ~18.90, $\delta^{11}$B: ~ -7.32‰), and the ‘Astroni 6 component’
($^{87}$Sr/$^{86}$Sr: ~0.70726, $^{143}$Nd/$^{144}$Nd: ~0.51250, $^{206}$Pb/$^{204}$Pb: ~19.08, $\delta^{11}$B: ~ -9.8‰). The isotopic
composition of Campi Flegrei magmas is defined in the deep crust, before significant crystal
fractionation, but the major and trace element compositions of these primitive liquids must be
closely similar to permit evolution along the same liquid line of descent (Pappalardo et al.,
2002). The prevalence of these isotopic components correlates with the different epochs of
activity: Epochs 1 and 2 show mixing between ‘NYT’ and ‘Minopoli 2’ components; Epoch 3
shows mixing between ‘NYT’, ‘Minopoli 2’ and ‘Astroni 6’ components; and the Monte
Nuovo eruption sampled near end-member ‘Astroni 6 component’ melts (Di Renzo et al.,
2011). Enriched $\delta^{11}$B in Epochs 1 and 2, reflect a more metasomatised mantle source caused
by a higher slab-derived fluid input (D'Antonio et al., 2007) and/or a lower subducted
sediment input into the mantle wedge (Di Renzo et al., 2011, Tonarini et al., 2004). Higher
$^{87}$Sr/$^{86}$Sr and lower $^{143}$Nd/$^{144}$Nd and $^{206}$Pb/$^{204}$Pb ratios demonstrate greater crustal assimilation
in Epochs 1 and 2 than in Epoch 3 and Monte Nuovo (D'Antonio et al., 2007, Di Renzo et al.,
However, the Campi Flegrei liquid line of descent and extent of Sr and Pb isotopic heterogeneity is only compatible with very minor assimilation (D'Antonio et al., 2007, Fowler et al., 2007).

Water contents of Campi Flegrei melt inclusions typically vary from ~1 to ~4 wt% and show no systematic relationship with the degree of magma differentiation (Arienzo et al., 2016, Mangiacapra et al., 2008, Stock et al., 2016). Campi Flegrei melt inclusions generally have very low CO₂ concentrations (<250 ppm), with a few analyses extending up to 400-500 ppm (Arienzo et al., 2016, Arienzo et al., 2010, Marianelli et al., 2006, Stock et al., 2016).

**SAMPLES AND METHODS**

**Eruptions studied**

The eruptions investigated cover the full range of melt compositions, eruption sizes and styles of activity from Campi Flegrei in the past 15 kyr (Table 1; see Smith et al., 2011 for full stratigraphy). Vent locations, average matrix glass compositions and absolute eruption ages for the samples analysed in this study are in given Figure 1 and Table 1. The Minopoli 1 tuff cone was sampled because it is a small, phono-tephritic to tephri-phonolitic explosive eruption, typical of the early-Epoch 1 eruptions that followed the NYT event (Smith et al., 2011). Scoria was also sampled from the slightly larger, slightly more evolved Pisani 1 eruption, which occurred in mid-late Epoch 1 (Smith et al., 2011). Deposits from more recent eruptions are typically more evolved. We sampled Astroni 1 from Epoch 3, which represents the first of seven small explosive eruptions from the Astroni vent between 4 and 4.4 kyr (Isaia et al., 2004, Smith et al., 2011). These deposits comprise phreatomagmatic surge beds interbedded with subordinate magmatic Strombolian pumice layers (Smith et al., 2011).

Pomici Principali (PP) was the largest eruption in the last 15 kyr, generating a Plinian column and pyroclastic density currents (Bevilacqua et al., 2016, Di Vito et al., 1999, Smith et al.,
These were sampled to investigate relationships between eruption magnitude and apatite volatile compositions. The Baia-Fondi di Baia (B-FdB) and Monte Nuovo eruptions were sampled because they produced highly evolved melts, from vents in the western NYT caldera. Baia-Fondi di Baia was the first eruption of Epoch 2 and was particularly explosive, due to magma-H$_2$O phreatomagmatic interaction, but it only expelled a relatively small volume of material (Pistolesi et al., 2017). The most evolved melts identified in Campi Flegrei were produced in the historic Monte Nuovo tuff cone eruption (Smith et al., 2011). The latitic Santa Maria delle Grazie (SMdG) lava, which is thought to be part of a shallow dyke that fed the SMdG scoria cone (Isaia et al., 2009), and the subsequent trachytic Accademia lava dome (Isaia et al., 2009, Melluso et al., 2012), were sampled to assess differences between apatite volatile compositions in these deposits and explosive units.

**Samples**

All samples were collected from proximal deposits (Fig. 1), either by Smith et al. (2011) or during fieldwork for this study in March 2013 and September 2014. Minopoli 1, PP, Pisani 1, B-FdB and Astroni 1 samples are CF13, CF6, CF25, CF88 and CF69 of Smith et al. (2011). The Astroni 1 sample was investigated by Stock et al. (2016). CF88 is from the initial fallout (Baia) phase of the B-FdB eruption (Pistolesi et al., 2017). The Monte Nuovo sample (CF195) is from the upper pyroclastic flow unit (Table 1; Unit II of Piochi et al., 2005). The SMdG (CF200) and Accademia (CF163) samples were collected from the centre of the NYT caldera.

All samples have the major phase assemblage: K-feldspar + plagioclase + clinopyroxene + biotite + apatite + magnetite. Samples also contain fluorite ± sulphides ± sodalite ± leucite, with precipitation of these accessory phases constrained to late in magmatic evolution by their absence as phenocryst-hosted inclusions in natural samples, and by experimental studies and
thermodynamic models (Arzilli et al., 2016, Fowler et al., 2007). Olivine is reported in mafic
samples from Campi Flegrei (Cannatelli et al., 2007) but was not observed in this study.
Crystal contents are typically <5-30% (from qualitative observations and Isaia et al., 2004,
Mastrolorenzo & Pappalardo, 2006, Piochi et al., 2005) but notably lower in B-FdB (<<1%;
Mastrolorenzo & Pappalardo, 2006). In Monte Nuovo, two pyroxene populations can be
identified in hand specimen: one black and one green, as in other eruptions at Campi Flegrei
and Vesuvius (Cioni et al., 1998, D'Antonio et al., 1999). As apatite and melt inclusions show
no systematic compositional difference between these pyroxene populations, they are not
separated in the following discussion.

**Analytical methods**

Clinopyroxene and biotite phenocrysts were hand-picked from the 250-500 µm size fraction
in samples from explosive eruptions and the Accademia lava dome. Heavy liquid and
magnetic separation techniques were used to extract apatite microphenocrysts from the 44-
250 µm size fraction. Crystals and matrix ash grains were mounted in epoxy, ground and
polished for analysis. Lava samples were prepared as polished thin sections. Samples were
examined using an FEI Quanta 650 FEG scanning electron microscope (SEM), operating with
a 20 kV, ~6-7 nA beam, in the Department of Earth Sciences, University of Oxford. Only
apatite inclusions away from cracks and fully enclosed within host phenocrysts were
analysed, to ensure that they were trapped during phenocrystal growth and were unable to
subsequently re-equilibrate with melt/fluids. Melt inclusions were only analysed if they did
not show visual evidence for post-entrapment crystallisation and were away from cracks in
their host phenocryst. Ash, lapilli fragments and lavas were also assessed by SEM to identify
microlite-free regions for analysis of the matrix glass compositions.
Mineral and glass major, trace and halogen element compositions were analysed using a JEOL 8600 electron microprobe at the Research Laboratory for Archaeology and the History of Art, University of Oxford. Samples were re-polished prior to electron probe microanalysis (EPMA), to remove any compositional modification induced by SEM electron-beam exposure (Stock et al., 2015), and subsequently carbon coated along with secondary standards, to avoid variable light element X-ray attenuation. Apatite was analysed using a defocussed (5 µm), 15 kV, 10 nA beam, with halogens were analysed first. Where possible, apatite crystals were analysed with the c-axis parallel to the plane of the mount. This routine limits the potential for time-dependent variability in halogen X-ray counts during analysis (Goldoff et al., 2012, Stock et al., 2015, Stormer et al., 1993), while maintaining reasonable precision for low-concentration elements (i.e. Cl). In glass, most elements were measured using a defocussed (10 µm), 15 kV, 6 nA beam to minimise Na₂O and SiO₂ migration (e.g. Humphreys et al., 2006); when in low-abundance, SO₂, P₂O₅ and Cl were measured in a second analysis using a 30 nA current. In both crystals and glass, count times were 20-30 s for major elements and 30-90 s for minor elements (120 s for Cl and SO₂ in apatite). Backgrounds were determined by counting for half of the on-peak count time on either side of the peak. Glass and apatite analytical totals were typically 95-99% and 96-102%, respectively. Data were filtered to remove analyses with totals <92%, and >101.5% in glass. Apatite totals >100% likely reflect minor electron-beam induced compositional modification (Stock et al., 2015) and totals significantly <100% likely result from the absence of trace elements (e.g. REEs) in the analytical routine. Apatite OH contents in EPMA data are calculated ‘by difference’, assuming stoichiometry. Typical analytical uncertainties are in Tables 2 and 3.

A subset of apatites and glasses was analysed for H, F and Cl using a Cameca ims-4f secondary ion mass spectrometer (SIMS) at the Edinburgh Ion Micro-Probe Facility, University of Edinburgh, using methods outlined in Stock et al. (2016). Samples were re-
polished prior to SIMS analysis to remove any surficial halogen modification induced during EPMA (Stock et al., 2015). In apatite, F, Cl and H$_2$O concentrations were derived from working curves of $^{19}$F/$^{44}$Ca vs. F, $^{35}$Cl/$^{44}$Ca vs. Cl and $^1$H/$^{44}$Ca vs. H$_2$O, populated by independently characterised apatite standards (Fig. S1). Glass H$_2$O concentrations were similarly derived from working curves of $^1$H/$^{30}$Si vs. H$_2$O populated by well-characterised rhyolitic glasses (Fig. S2). Working curves were created at the beginning of each day, analytical session or when beam conditions were changed. NIST SRM610 was used as a primary standard for glass F calibration, with $^{44}$Ca as the internal standard, based on EPMA of the same spot. SIMS backgrounds were monitored using anhydrous synthetic apatite or clinopyroxene crystals for apatite and glass, respectively. Working curves have a polynomial fit for H$_2$O in apatite and linear fit for all other elements, with $R^2$ typically >0.99. Typical analytical uncertainties are in Tables 2 and 3.

**APATITE AND GLASS COMPOSITIONS**

In total, >800 apatite and >250 glass analyses were acquired on samples from the eight Campi Flegrei eruptions (Table 1), using EPMA to identify broad compositional trends (full datasets in Tables S1, S2; http://www.petrology.oxfordjournals.org) and SIMS to measure a subset of crystals and glasses for H$_2$O and halogens with lower analytical uncertainties (Tables 2, 3).

All glass data in the text and Figures 2, 3 and 4a-d are presented normalised to 100% anhydrous. All apatite analyses were made close to the centre of the mineral grains. Glass compositions could not be obtained from lava deposits (Table 1), due to melt inclusion devitrification and groundmass crystallisation. Apatite inclusions from these eruptions were excluded as they were not isolated from the melt/fluids after entrapment: biotites are partially (in the case of SMdG) or fully (for Accademia) broken down and pyroxenes are heavily fractured, such that all apatite inclusions are touching major cracks or are incompletely enclosed by their host crystals. Baia-Fondi di Baia melt inclusions were too small (typically
<20 μm) to analyse by SIMS. Astroni 1 apatite data from Stock et al. (2016) were recalibrated using updated standard compositions, resulting in minor modification of absolute compositions but no change to the trends in this dataset. These were included with additional glass and apatite analyses from this eruption.

**Glass major element compositions**

Melt inclusions and matrix glasses analysed in this study cover a wide compositional range from trachy-basalts and basanites to phonolites and trachytes (Tables 2, S1), encompassing almost the entire compositional diversity reported in <15 kyr Campi Flegrei deposits (Figs 2,3). Clinopyroxene-hosted melt inclusion compositions differ between eruptions: Minopoli 1 melt inclusions are the most mafic (50.46 to 56.84 wt% SiO$_2$) and cover the largest compositional range; Pisani 1 and PP include the next most mafic melt inclusions, with SiO$_2$ as low as 54.18 wt%; and melt inclusions from other eruptions are typically phonolitic to trachytic (Fig. 2). The same overall trend is seen for the matrix glasses (Fig. 3), although in general, they are more evolved than melt inclusions from the same eruption, with higher SiO$_2$ (typically >53 wt%) and alkali element concentrations (Tables 2, S1).

For all elements measured, melt inclusion and matrix glass compositions plot on a single compositional trend, in agreement with literature data (Figs 2, 3). Glass SiO$_2$, Na$_2$O and K$_2$O concentrations typically increase with decreasing MgO, while CaO, FeO$_{t}$ and TiO$_2$ concentrations decrease (Figs 2, 3, Tables 2, S1). However, glass K$_2$O and SiO$_2$ concentrations decrease at low MgO contents (≤0.5 wt% MgO). Some low-MgO matrix glasses from Monte Nuovo and B-FdB are particularly K$_2$O-depleted and Na$_2$O-rich (Fig. 3). This is consistent with fractional crystallisation models, which indicate early fractionation of olivine, clinopyroxene and magnetite (Fowler et al., 2007) but show a major change in
compatibility for K₂O and Na₂O at ≈0.5 wt% MgO, after plagioclase, biotite and K-feldspar come onto the liquidus (Cannatelli, 2012, Fowler et al., 2007, Stock et al., 2016).

Glass volatile compositions

Campi Flegrei melt inclusions analysed in this study show that Cl generally increases as MgO decreases, consistent with previous analyses (Fig. 4a). Minopoli 1 melt inclusions have the lowest Cl concentrations (0.32 to 0.85 wt%), while melt inclusions from Pisani 1 and PP are intermediate (0.58 to 0.89 wt%). Melt inclusions from other eruptions have higher Cl concentrations, extending up to 1.17 wt% (Fig. 4a; Table S1). Matrix glass Cl contents are typically similar to melt inclusions; the most Cl-depleted matrix glasses (0.50-0.79 wt%) are from Minopoli 1 and Pisani 1, with the highest Cl concentrations in matrix glasses from Monte Nuovo and B-FdB reaching 1.20 wt% (Fig. 4b; Table S1). Some low MgO (<0.5 wt%) matrix glasses from Astroni 1 and B-FdB have low Cl contents (<0.6 wt%), in agreement with the greater variability in matrix glass Cl concentrations at low MgO previously reported in the literature (Fig. 4b).

Mafic (≥2 wt% MgO) melt inclusions from Campi Flegrei show scattered F contents, with concentrations up to 0.46 wt% F in Minopoli 1 (Fig. 4c). In more evolved melt inclusions (≤2 wt% MgO), F is typically higher in inclusions with lower MgO contents, from <0.1 wt% in Pisani 1 and PP to ~0.4 wt% in B-FdB (Fig. 4c; Table S1). Fluorine concentrations up to 0.61 wt% have been reported in very low MgO melt inclusions (Fourmentraux et al., 2012). In general, matrix glass F concentrations are approximately constant (~0.1-0.3 wt%; Fig. 4d). However, F is significantly enriched in low MgO (<0.5 wt%) matrix glasses from Monte Nuovo (typically 0.6-0.8 wt% F), with a single analysis reaching 1.26 wt%.

Melt inclusions analysed in this study typically contain ~2-4 wt% H₂O and show no correlation with MgO (Fig. 4e), consistent with other Campi Flegrei eruptions (Arienzo et al.)
Some inclusions have H₂O concentrations as low as 1.04 wt%, with the largest variability at low MgO concentrations (<1.5 wt%), where H₂O concentrations extend to >5 wt%, within the range previously reported for <15 kyr Campi Flegrei eruptions (up to 6.96 wt%; Cannatelli et al., 2007). Matrix glass H₂O contents are lower than in melt inclusions; mafic Minopoli 1 and Pisani 1 matrix glasses consistently have H₂O concentrations <0.4 wt%, whereas more evolved (<1 wt% MgO) PP, Astroni 1 and Monte Nuovo matrix glasses have more variable H₂O concentrations, extending to >1 wt% (Fig. 4f).

Apatite volatile compositions

Apatite inclusions

Clinopyroxene-hosted apatite inclusions have measured F concentrations from 1.86 to 2.92 wt%; Cl concentrations from 0.41 to 1.27 wt% and OH concentrations from 0.39 to 1.42 wt% (Tables 3, S2). This translates to X_Cl/X_OH ratios from 0.19 to 1.22, X_F/X_OH from 1.33 to 5.79 and X_F/X_Cl from 2.96 to 12.8 (where X_F, X_Cl and X_OH are the mole fractions of F, Cl and OH, respectively). Variations in the apatite volatile site can typically be described by a F-OH exchange, with an approximately constant Cl component (Fig. 5a). Baia-Fondi di Baia is an exception, where Cl in clinopyroxene-hosted apatite inclusions is notably depleted relative to inclusions in other eruptions. In general, clinopyroxene-hosted apatite inclusions show a positive correlation between X_Cl/X_OH and X_F/X_OH and approximately constant X_F/X_Cl (Figs 5b, c).

Biotite-hosted apatite inclusions have a more restricted compositional range than clinopyroxene-hosted inclusions, with F, Cl and OH ranging from 1.81 to 2.76 wt%, 0.54 to 1.17 wt% and 0.53 to 1.20 wt%, respectively (Tables 3, S2). This translates to X_Cl/X_OH ratios from 0.28 to 0.95, X_F/X_OH from 1.20 to 4.11 and X_F/X_Cl from 3.31 to 9.47. Biotite-hosted inclusions plot on the same compositional trends as clinopyroxene-hosted inclusions (Fig. 5d-
However, within an individual eruption, biotite-hosted inclusions are typically offset to more OH-rich compositions, with lower $X_{Cl}/X_{OH}$ and $X_{F}/X_{OH}$ ratios (Tables 3, S2).

**Apatite microphenocrysts**

Apatite microphenocrysts show more compositional diversity than inclusions (Figs 5-7), with a small minority of F concentrations measured by EPMA reaching 4.54 wt%. These high F contents are almost exclusively in lava samples (Table S2) but exceed the maximum stoichiometric limit of 3.76 wt% F (Pyle et al., 2002); likely reflecting electron beam-induced sample damage in near end-member fluorapatite (Goldoff et al., 2012, Stock et al., 2015, Stormer et al., 1993). The highest F concentrations measured by SIMS (3.80 wt%; Table 3) are stoichiometric within analytical uncertainty. In apatite microphenocrysts, the minimum F concentration is 1.67 wt%, Cl ranges 0.02 to 1.47 wt% and measured OH concentrations are <1.97 wt% (Tables 3, S2). This translates to overall $X_{Cl}/X_{OH}$, $X_{F}/X_{OH}$ and $X_{F}/X_{Cl}$ ratios from ~0 to 16.5, 0.86 to 781 and 2.85 to 374, respectively, with $X_{Cl}/X_{OH} \leq 2.27$ and $X_{F}/X_{OH} \leq 25.8$ in explosive eruptions. Most apatite microphenocrysts sit on the same compositional trends as the inclusions (Figs 6, 7) but typically extend to more OH-rich compositions with lower $X_{Cl}/X_{OH}$ and $X_{F}/X_{OH}$ ratios. Compositional differences between apatite inclusions and microphenocrysts along this main trend were used by Stock et al. (2016) to give temporal context to apatite data from Astroni 1. Two subsidiary sets of apatite microphenocrysts are observed in some explosive eruptions, both with lower Cl contents than the main trend (Figs 6, 7). One has low $X_{Cl}/X_{OH}$ ratios with $X_{F}/X_{OH}$ and $X_{F}/X_{Cl}$ ratios that extend to very high values (i.e. in Monte Nuovo, Astroni 1, B-FdB, Pisani 1, PP, Minopoli 1); the other has high $X_{Cl}/X_{OH}$ and $X_{F}/X_{OH}$ ratios (i.e. in Astroni 1, B-FdB, PP, Minopoli 1). Additionally, a small number of inclusions from Pisani 1 define a trend towards high $X_{F}/X_{OH}$ at similar $X_{Cl}/X_{OH}$ ratios to the main population (Figs 7d-f). Apatite microphenocrysts from lava deposits (Accademia and SMdG) are distinct; in ternary space they typically show an increasing F component at the
expense of Cl, trending first towards the F-Cl join and then curving towards the F apex, but in
tern binary space they are scattered with no discernible trend (Fig. 6g-l).

Differences between eruptions

The SIMS analyses are more precise than the EPMA data, so subtle differences in apatite
compositions between eruptions are more clearly resolved. Clinopyroxene- and biotite-hosted
apatite inclusions from Epoch 1 eruptions (Minopoli 1, PP and Pisani 1) are typically more
OH-rich than those from the more recent Astroni 1 (Epoch 3) and Monte Nuovo eruptions;
this translates to lower $X_{Cl}/X_{OH}$ and $X_{F}/X_{OH}$ and slightly lower $X_{F}/X_{Cl}$ ratios in apatite
inclusions from Epoch 1 than younger eruptions (Fig. 5). The main population of apatite
microphenocrysts from Astroni 1 are also typically more F-rich, with higher $X_{Cl}/X_{OH}$, $X_{F}/X_{OH}$
and $X_{F}/X_{Cl}$ ratios than those from Epoch 1 eruptions. Monte Nuovo microphenocrysts in this
population extend to higher $X_{Cl}/X_{OH}$, $X_{F}/X_{OH}$ and $X_{F}/X_{Cl}$ ratios than those from Epoch 1, but
cover the entire compositional diversity of the main microphenocryst population from other
eruptions (Figs 6, 7). Baia-Fondi di Baia inclusions (Epoch 2) are relatively $X_{Cl}/X_{OH}$ depleted;
B-FdB microphenocrysts are compositionally similar to Epoch 1 (i.e. comparable $X_{Cl}/X_{OH}$)
but follow a different evolutionary trajectory. There is more overlap between eruptions in the
lower-precision EPMA dataset but it is still clear that apatite inclusions and microphenocrysts
from younger eruptions (Astroni 1 and Monte Nuovo) extend to more F-rich compositions,
with higher $X_{Cl}/X_{OH}$, $X_{F}/X_{OH}$ and $X_{F}/X_{Cl}$ ratios, than those from Epoch 1 (Figs 5-7).

THERMODYNAMIC FRAMEWORK FOR APATITE VOLATILE

INTERPRETATION

The composition of the apatite volatile site is described by a series of exchange equilibria
between F, Cl and OH (e.g. Pan & Fleet, 2002), for example:
\[ X_{\text{Cl}}^\text{Ap} + X_{\text{OH}}^\text{m} \rightleftharpoons X_{\text{OH}}^\text{Ap} + X_{\text{Cl}}^\text{m} \]  
(eq. 1)

\[ K_{\text{Cl-OH}}^{\text{Ap/m}}(P,T) = \frac{a_{\text{Cl}}^\text{Ap}}{a_{\text{OH}}^\text{Ap}} \cdot \frac{a_{\text{OH}}^\text{m}}{a_{\text{Cl}}^\text{m}} \]  
(eq. 2)

where \( a \) is activity. The evolution of F, Cl and H2O concentrations in the melt (i.e., \( a_{\text{OH}}^\text{m} \) and so on) during fractional crystallisation depends on the nature of both crystal-melt partitioning and fluid-melt exchange. Therefore, we can predict how apatite compositions in equilibrium with the melt will evolve during different fractional crystallisation scenarios using appropriate experimental \( K_{\text{DoS}} \) from the literature.

We have developed a thermodynamic model, relating apatite compositional evolution to changes in the volatile contents of silicate melts during crystallisation in the presence or absence of different magmatic fluids, building on the work of Candela (1986), who treated halogens and H2O as perfectly incompatible during volatile-undersaturated crystallisation.

First, we calculate the evolution of F, Cl and H2O in the melt due to crystal \( \pm \) fluid fractionation. We then compute the volatile composition of apatite in equilibrium with the melt at each stage of the crystallisation model. We assume that the apatite solid solution is ideal and that the apatite-melt exchange coefficients are unaffected by the changing melt composition. The validity of these assumptions, definitions of terminology, and the values of key parameters, including mineral-melt and fluid-melt partition coefficients and the solubility of halogens and H2O in the silicate melt, are discussed in the Supplementary Information. Our approach can be applied generally to determine apatite compositions during fractional crystallisation. The effects of pressure and temperature variations on apatite compositions are also outlined below.
Apatite fractional crystallisation models

The initial melt Cl ($C_{Cl}^0$) and F ($C_F^0$) concentrations are set at 0.4 wt% and 0.2 wt%, respectively, based on the mafic melt inclusion compositions given in Tables 2 and S1. The initial melt H$_2$O concentration ($C_{H_2O}^0$) is set at 2.5 wt%, similar to the predicted Campi Flegrei melt H$_2$O concentration at apatite-in from Rhyolite-MELTS (Stock et al., 2016) and initial H$_2$O concentrations used for modelling by Fowler et al. (2007) and Cannatelli (2012).

During volatile-undersaturated crystallisation, the evolution of all volatile components in the melt is described by the Rayleigh equation:

$$C_i^m = C_i^0 \cdot \phi \overline{D}_{i/m}^{c/m} - 1$$  \hspace{1cm} (eq. 3)

where $C_i^m$ is the concentration of $i$ in the melt at a given melt fraction ($\phi$) and $\overline{D}_{i/m}^{c/m}$ is the bulk crystal-melt partition coefficient.

We simulate the onset of saturation with a H$_2$O-rich fluid by imposing pre-defined H$_2$O solubility limits ($C_{H_2O}^{sat}$), here taken as 7.5 wt% H$_2$O, which is appropriate for phonolite liquids at 200 MPa (Webster et al., 2014). Once this solubility limit is reached, the H$_2$O concentration in the melt is held constant to simulate isobaric fractionation (or can be linearly decreased to illustrate the effect of polybaric decompression). Further H$_2$O that exsolves due to continuing fractionation is assigned to a separate fluid phase, following Candela and Holland (1986), and we calculate the F and Cl concentration of that fluid phase using the fluid-melt partition coefficients (i.e. $D_F^{f/m}$ and $D_{Cl}^{f/m}$, respectively). This is iteratively extracted from the evolving melt by mass balance. We calculate mole fractions of Cl, F and total H$_2$O in the melt following Li and Hermann (2017) and use the H$_2$O speciation model of Zhang (1999) for a temperature of 1020 °C to calculate the mole fraction of OH in the melt. Finally, we calculate the mole fraction of F-apatite, Cl-apatite and OH-apatite in equilibrium with the
calculated melt composition, following Candela (1986), and thus apatite $X_{\text{Cl}}/X_{\text{OH}}$, $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$.

**Model outputs: apatite compositional evolution during fractional crystallisation**

During volatile-undersaturated crystallisation for a range of parameters (see Supplementary Information), apatite compositions typically show a decrease in both $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios, while $X_{\text{Cl}}/X_{\text{OH}}$ may increase or decrease depending on the exact values of the crystal-melt partition coefficients for F, Cl and OH (Fig. 8b-c). In contrast, H$_2$O-saturated crystallisation is characterised by a strong decrease in apatite $X_{\text{Cl}}/X_{\text{OH}}$ ratios per unit crystallisation, with increasing $X_{\text{F}}/X_{\text{Cl}}$ and variable $X_{\text{F}}/X_{\text{OH}}$ (Fig. 8e-f). This is because fluid-melt partition coefficients for Cl are typically much higher than for F (Webster et al., 2014, Borodulin et al., 2009). In ternary space, volatile-undersaturated trajectories are typified by apatite compositional evolution away from the F apex (Fig. 8a). Conversely, during H$_2$O-saturated crystallisation apatite compositions move towards the F-OH binary (Fig. 8d). Under polybaric H$_2$O-saturated conditions, where H$_2$O is lost from the melt during depressurisation, crystal compositions may then curve towards the F apex (Fig. 8d).

*The melt volatile composition*

Varying the initial melt $C_i^0$ translates the starting point of the model in apatite compositional space, and changes the relative magnitudes of the calculated variations in apatite volatile components per unit crystallisation. However, the slope or direction in binary or ternary space remains the same (Fig. 9a,b). In the general H$_2$O-saturated case, decreasing $C_{\text{sat}}^{\text{H}_2\text{O}}$ (e.g. at lower pressure or a different melt composition) reduces the extent of volatile-undersaturated crystallisation before second boiling, but does not affect the trajectory of apatite compositional-evolution after volatile-saturation is achieved (Fig. 9c,d). Our model does not deal with saturation of either fluorite, which is present only as a late-stage accessory mineral,
or brine. Fluorine and Cl act as incompatible elements during fractionation (i.e. higher halogen concentrations in low MgO in glass analyses; Fig. 4a-d), which suggests that brine exsolution is also not a major factor at Campi Flegrei. We would anticipate that formation of fluorite and/or brine would change the mineral-melt and/or fluid-melt volatile partition coefficients at the late stages of fractional crystallisation.

**Effect of pressure and temperature on apatite composition**

As apatite-melt halogen-OH exchange coefficients depend on pressure and temperature (Piccoli & Candela, 1994, Riker et al., in press), mineral compositions may vary, even at a constant melt composition (e.g. Eq. 2). This is not treated in the fractional crystallisation model detailed above but we illustrate the effects of cooling in Figure 10, using the experimental regression of Riker et al. (in press); this is qualitatively consistent with the earlier work of Piccoli and Candela (1994). Cooling drives apatite compositions to higher $X_{Cl}/X_{OH}$, $X_{F}/X_{OH}$ and $X_{F}/X_{Cl}$ ratios, reflecting an increasing preference for the smaller F anion at low temperatures. However, the slope (in binary space) of the cooling trend depends strongly on the Cl concentration of the liquid; at low melt Cl contents, apatite is driven towards high $X_{F}/X_{OH}$ only (Fig. 10). Pressure has little effect on apatite compositions at constant melt composition (Piccoli & Candela, 1994, Riker et al., in press), with depressurisation primarily allowing a slight increase in the apatite Cl component, which is reflected in a minor decrease in $X_{F}/X_{Cl}$ and increase in $X_{Cl}/X_{OH}$ ratios.

**DISCUSSION**

**Application of apatite thermodynamic model to Campi Flegrei**

The clear differences in model apatite trajectories between H$_2$O-saturated and volatile-undersaturated conditions (Fig. 8) suggest that apatites may hold significant clues to
understanding the late-stage variations in fluid systematics in magmatic-hydrothermal systems.

Texturally-constrained analyses give a temporal dimension to the apatite dataset (Figs 5-7) and analysis of Astroni 1 has shown that the $X_{\text{Halogen}}/X_{\text{OH}}$ ratios of crystals on the main compositional trend decrease during magmatic evolution (Stock et al., 2016). The same temporal trend is apparent in all eruptions analysed: apatite inclusions trapped in early-formed clinopyroxene phenocrysts (clinopyroxene-in = 1080 °C; Stock et al., 2016) extend to higher $X_{\text{Halogen}}/X_{\text{OH}}$ ratios than in late-formed biotite phenocrysts (biotite-in = 910 °C; Stock et al., 2016). Figure 6a-c shows that a good model fit can be achieved with our natural apatite analyses from Campi Flegrei using $K_{\text{Cl-OH}}^{\text{Ap/m}} = 25$, $K_{\text{F-OH}}^{\text{Ap/m}} = 75$ and $K_{\text{Cl-F}}^{\text{Ap/m}} = 0.22$, which are within the range identified experimentally (Riker et al., in press) and the effects of varying input parameters on the model fit is shown in Figures 8, 9, S3-S6. The model fit (Fig. 6a-c) represents ~70% crystallisation at volatile-undersaturated conditions, with constant crystal-melt partition coefficients $\bar{D}_{\text{Cl}}^{c/m} \approx 0.99$, $\bar{D}_{\text{F}}^{c/m} \approx 0.8$ and $\bar{D}_{\text{OH}}^{c/m} \approx 0.01$ (Figs 6a-c). These are realistic given the increase in glass halogen concentrations with decreasing MgO and the low modal abundance of apatite and biotite. The low $X_{\text{Cl}}/X_{\text{OH}}$ values identified in some apatite microphenocrysts can be partially reproduced by subsequent H$_2$O-saturated crystallisation, with $\bar{D}_{\text{Cl}}^{f/m} = 20$ and $\bar{D}_{\text{F}}^{f/m} = 0.7$ (Figs 6a-c), consistent with alkali melt-fluid halogen partitioning experiments under magmatic conditions (Borodulin et al., 2009, Signorelli & Carroll, 2000). However, our simple isobaric, isothermal H$_2$O-saturated crystallisation models cannot reproduce the range of $X_{\text{F}}/X_{\text{OH}}$ ratios observed in the natural low $X_{\text{Cl}}/X_{\text{OH}}$ subsidiary population (Fig. 8d-f). Decompression-induced degassing could account for some of this compositional variability but cooling, after theapatites have re-equilibrated under H$_2$O-saturated conditions, appears to be the primary mechanism to drive compositions to the very high $X_{\text{F}}/X_{\text{OH}}$ ratios observed in some eruptions (e.g. PP; Figs 7,10). The second, high $X_{\text{Cl}}/X_{\text{OH}}
and $X_F/X_{OH}$ subsidiary population (e.g. Minopoli 1) is consistent with re-equilibration of apatites during cooling of a less degassed melt (Fig. 10).

**Pre-eruptive volatile behaviour and the structure of the Campi Flegrei magmatic system**

Our models reproduce the main compositional trend in apatite inclusions and microphenocrysts through protracted volatile-undersaturated crystallisation (Figs 5-7). This suggests that the main zone of magma storage and crystallisation remained volatile-undersaturated until late in magmatic evolution (i.e. after the entrapment of biotite-hosted inclusions, see Stock *et al.*, 2016) prior to past eruptions at Campi Flegrei. Thermodynamic (Rhyolite-MELTS) fractional crystallisation models, combined with relevant phonolite solubility data, also show that H$_2$O would remain undersaturated in Campi Flegrei melts until after biotite-in (i.e. $\sim$910°C) at pressures $\geq$150 MPa (Carroll & Blank, 1997, Stock *et al.*, 2016, Webster *et al.*, 2014). Our conclusion that the system remained persistently volatile-undersaturated until a late stage is therefore consistent with independent estimates of Campi Flegrei magma storage conditions, which suggest a high-pressure zone of major melt storage and crystallisation (Fig. 11). Seismic tomography shows that the current region of major melt storage beneath Campi Flegrei is $\sim$1 km thick and at a depth of 7.5 km (Zollo *et al.*, 2008), which would equate to storage pressures of $\sim$170 to 190 MPa. This broadly agrees with phase equilibria models, which indicate that mineral and glass compositions produced in past Campi Flegrei eruptions were stable at pressures between 150 and 300 MPa (i.e. 6.6-13.3 km; Bohrson *et al.*, 2006, Cannatelli, 2012, Fowler *et al.*, 2007); and the volatile contents of melt inclusions from $<$15 kyrs Campi Flegrei eruptions (Fig. 11), which give saturation pressures up to 229 MPa ($\sim$10 km; Arienzo *et al.*, 2016 [using a crustal density of 2.3 g/cm$^3$ after Rosi & Sbrana, 1987]). In particular, magma storage depths inferred from melt inclusion volatile contents for the Agnano-Monte Spina (Arienzo *et al.*, 2010) and Nisida (Arienzo *et al.*, 2016) eruptions overlap at 6.5 to 9.4 km, which agrees very well with the current depth of major
magma storage (7.5 to 8.5 km; Zollo et al., 2008). This appears to demonstrate that melt storage and crystallisation before past eruptions occurred at very similar depths to today.

In addition to the main population of apatite inclusions and microphenocrysts, two subsidiary sets of lower-Cl microphenocrysts are present in some eruptions, as discussed above. Apatites with low $X_{Cl}/X_{OH}$ ratios and high $X_{F}/X_{OH}$ and $X_{F}/X_{Cl}$ ratios (i.e. in Monte Nuovo, Astroni 1, B-FdB, Pisani 1, PP, Minopoli 1; Figs 6, 7) are consistent with H$_2$O-saturated fractionation at high $D_{Cl}^{f/m}$, where Cl is efficiently extracted from the melt into the fluid phase, but with cooling following extensive fluid exsolution. This requires equilibrating first with low Cl concentrations in the melt due to degassing, so that any later thermal re-equilibration drives apatites to high $X_{F}/X_{OH}$ and $X_{F}/X_{Cl}$ only (Fig. 10). The second subsidiary set of apatites, with elevated $X_{Cl}/X_{OH}$ and/or $X_{F}/X_{OH}$ ratios (i.e. in Astroni 1, B-FdB, PP, Minopoli 1; Figs 6, 7), are consistent with equilibration during cooling of a melt that is not depleted in Cl (i.e. where Cl has not been extracted into an exsolving fluid; Fig. 10).

These compositions represent a small fraction of our dataset, but the analyses are from the cores of microphenocrysts, suggesting that they may have been fully equilibrated under different conditions. In contrast, microphenocrysts that plot on the main trend show no evidence of re-equilibration or overgrowth of new compositions, within the scale of our analyses (Stock et al., 2016 checked several grains for compositional zonation within >16 µm of the rim; although we anticipate that fine-scale zonation might be observable using higher-resolution methods). The rapid experimental diffusivities of halogens in apatite (Brenan, 1994) suggests that these few anomalous grains must therefore have been spatially separated within the magmatic system. The simplest interpretation of our data is that the low-$X_{Cl}/X_{OH}$ apatites represent mushy material left over after incomplete evacuation of magma from separate, shallower storage regions (Fig. 11). Small, melt-rich magma bodies at ~2-4 km
beneath the current Campi Flegrei have been imaged by seismic tomography (De Siena et al., 2010) and inferred from modelling of long-term ground deformation (Amoruso et al., 2014a), fumarolic gas emissions (Carlino et al., 2015) and heat flow measurements (Di Maio et al., 2015). These shallow magma bodies could derive from emplacement of sills between eruptions; recent seismic crises (1982-1984 and 2011-2013) have been attributed to sill intrusion at 2.75-5 km depth (Fig. 11; Amoruso et al., 2014b, D’Auria et al., 2015, Woo & Kilburn, 2010). Such small, shallow magma bodies would be saturated in volatiles and cooled by interaction with the country rock, allowing microphenocrysts to grow or re-equilibrate.

Apatite inclusions, trapped before the magmas were emplaced in the shallow crust, would be ‘armoured’ by their host phenocrysts, preventing re-equilibration and retaining their volatile-undersaturated signature. Inclusions that were incompletely enclosed by their host phenocrysts do show evidence of diffusional re-equilibration, manifest as depleted Cl contents relative to fully-enclosed inclusions (Stock, 2016). We suggest that magmas ascending from the deep storage region may interact with these shallow melt bodies during eruptions, assimilating some of the residual material and acquiring a mixed cargo of microphenocrysts (Fig. 11). Magmas derived from the deep storage region degassed H$_2$O during ascent, resulting in low matrix glass H$_2$O contents (Fig. 4f). Similar F and Cl contents in matrix glasses and melt inclusions (Fig. 4a-d) demonstrate that halogens were not significantly degassed, despite $D_{\text{Cl}}^{f/m} > 1$ (Signorelli & Carroll, 2000). Relatively undepleted matrix glass Cl concentrations are consistent with kinetically-induced vapour-melt disequilibrium during rapid ascent (Barclay et al., 1996, Shea et al., 2014, Webster et al., 1993).

The apatite microphenocrysts from Pisani 1 that branch away from the main population at moderate $X_{\text{Cl}}/X_{\text{OH}}$ are consistent with cooling (Fig. 10), but before any H$_2$O-saturated crystallisation has taken place. We suggest that these crystals formed in the main magma
storage region at depth, possibly in cooler regions of the reservoir (e.g. close to the walls) and were incorporated before eruption (Fig. 11).

The majority of apatite inclusions and microphenocrysts from B-FdB are compositionally distinct, with significantly lower Cl contents than other explosive eruptions (Figs 5, 7a-c). This could be explained if part of the B-FdB magma crystallised from a melt with a different initial volatile content (i.e. lower Cl, higher H₂O; Fig. 9a,b). Baia-Fondi di Baia occurred at the start of Epoch 2 after a long hiatus in activity (Smith et al., 2011), and may have assimilated some of the country rock surrounding its magma reservoir during this time. Large volumes of residue from the Campanian Ignimbrite magma chamber underlie the Campi Flegrei caldera (D'Antonio, 2011) and represent a potential assimilant. Melt inclusions from the Campanian Ignimbrite extend to high H₂O contents and Campanian Ignimbrite glasses are consistently Cl-deficient compared with eruptions in the past 15 kyrs (cf. Fig. 4a,b, Marianelli et al., 2006, Signorelli et al., 1999). Furthermore, B-FdB glasses are depleted Sr and Ba and enriched in Zr relative to other <15 kyrs eruptions (Smith et al., 2011), again suggesting possible contamination from older (>15 kyrs) Campi Flegrei eruptions, including the Campanian Ignimbrite (Tomlinson et al., 2012).

Apatite microphenocrysts from Accademia and SMdG lava samples are distinct from those in explosive deposits. They do not show the same dominant compositional trend of F-OH exchange with an approximately constant Cl, but rather define a trend with an increasing F component at the expense of Cl, curving first towards the F-Cl binary and then towards the F apex (Fig. 6g-l). This is analogous to modelled trend of apatite compositional evolution during cooling. However, in binary space, apatite microphenocrysts from lava deposits are scattered with no discernible trend. We interpret this as variable extents of diffusive re-equilibration in the lavas (Fig. 10). Although microphenocrysts sit on the same cooling trend, they have different starting points and have variably rehomogenised. Such extensive re-
equilibration of microphenocryst compositions is unique to lava samples and we interpret that it occurred during slow cooling of the host magma at/near the surface (Fig. 11).

Apatite inclusions in clinopyroxene and biotite record volatile-undersaturated crystallisation (see above) and we would therefore expect the H_2O contents of melt inclusions in the same phenocryst phases to correlate negatively with MgO, as H_2O behaves incompatibly during magmatic evolution. However, there is no correlation between clinopyroxene-hosted melt inclusion H_2O and MgO concentrations in any of the analysed eruptions, and most melt inclusions measured in this study contain ~2.0-3.8 wt% H_2O (Fig. 4e). This may indicate that melt inclusion H_2O contents have been reset after entrapment, reflecting the final (H_2O-saturated) equilibration pressure at shallow crustal levels. Rapid H^+ diffusion through common phenocrysts causes re-equilibration of melt inclusion H_2O concentrations on short timescales (potentially hours to weeks under magmatic conditions) in response to any change in external conditions (e.g. Ingrin & Blanchard, 2006, Reubi et al., 2013, Woods et al., 2000).

In contrast, re-equilibration of apatite inclusions would be inhibited by the need for coupled halogen diffusion to retain stoichiometry (Bucholz et al., 2013). Occasional volatile-rich melt inclusions in <15 kyr Campi Flegrei deposits attest to evolved melts at depth (i.e. ≥5 wt% H_2O in Fig. 4e).

Campi Flegrei melt inclusions consistently have very low CO_2 contents (e.g. Arienzo et al., 2010, Marianelli et al., 2006, Stock et al., 2016), so we used a polynomial regression through published 850-950 °C, CO_2-free phonolite and trachyte solubility data (Carroll & Blank, 1997, Di Matteo et al., 2004, Larsen & Gardner, 2004, Schmidt & Behrens, 2008, Webster et al., 2014) to estimate a saturation pressure of ~24-76 MPa for the degassed melt inclusions (2.0-3.8 wt% H_2O). This is equivalent to storage depths of ~1.1-3.4 km, which coincides with the depth of small, melt-rich magma bodies imaged beneath the current Campi Flegrei caldera (~2-4 km; De Siena et al., 2010). We infer that ascending magmas interacted with these
shallow melt bodies on eruption, stalling or slowing such that melt inclusions from the deep reservoir re-equilibrated (Fig. 11), and incorporating phenocrysts with degassed melt inclusions (along with apatite microphenocrysts) which were stored in this shallow crystal residue.

**Inter-eruption variability in pre-eruptive magma volatile contents**

Our data generally show the same qualitative trends in apatite inclusion and microphenocryst compositions in explosive eruptions, regardless of the erupted volume, melt composition or epoch of activity. The majority of apatite inclusions and microphenocrysts plot on a trend that is consistent with volatile-undersaturated fractionation. However, in different eruptions, this main apatite trend is offset depending on the epoch of activity, suggesting a temporal variation in melt volatile composition. This is particularly evident in SIMS data, which is more precise than EPMA. For example, apatite inclusions from Astroni 1 (Epoch 3) and the historical Monte Nuovo eruptions are typically F-rich and OH-depleted with higher $X_{\text{Halogen}}/X_{\text{OH}}$ ratios than those in Epoch 1 (Minopoli 1, PP, Pisani 1; Fig. 5). The same is true for microphenocrysts, except that microphenocrysts from Monte Nuovo cover the entire compositional range measured in other eruptions (Figs 6, 7). Epoch 2 (B-FdB) crystals have similar $X_{\text{Cl}}/X_{\text{OH}}$ ratios to those from Epoch 1 but cannot be compared directly given their distinct compositional trajectory (Fig. 7b,c).

Melt inclusion halogen contents are typically lower in Epoch 1 than in later explosive eruptions (Fig. 4a,c), consistent with the more primitive Epoch 1 major element glass compositions (Figs 2, 3). As $\overline{D}_F^{c/m} > \overline{D}_\text{Cl}^{c/m} > \overline{D}_{\text{H}_2\text{O}}^{c/m}$ during apatite crystallisation (Supplementary Information), we would anticipate melt H$_2$O contents to be proportionally lower for Epoch 1 magmas. Consequently, we would expect apatites forming from the more primitive Epoch 1 magmas to have higher $X_{\text{Halogen}}/X_{\text{OH}}$ than those forming from Epoch 3.
maggas, the opposite to what is observed (Fig. 5). This disparity can be explained by a systematic difference in the melt volatile composition at the point of initial apatite crystallization (i.e. apatite-in; \(C^0\)), changing apatite compositions without significantly affecting mineral phase stabilities or the trajectory of apatite compositional evolution. Specifically, the change to higher \(X_{\text{Halogen}}/X_{\text{OH}}\) in Astroni 1 (Epoch 3) and Monte Nuovo suggests a decrease in melt \(H_2O\) concentrations at apatite-in (\(C^0_{H_2O}\)) relative to Epoch 1 (Fig. 9a, b). At Campi Flegrei, Rhyolite-MELTS models demonstrate that \(C^0_{H_2O}\) depends on the \(H_2O\) content of the melt at the liquidus, and does not change significantly due to variations in pressure or oxygen fugacity (Stock et al., 2016). Variability in Campi Flegrei apatite compositions from different epochs is therefore likely to reflect temporal variations in the \(H_2O\) concentration of parental melts feeding the system; Epoch 1 parental melts have higher apparent \(H_2O\) contents than more recent eruptions. This agrees with isotopic evidence, which suggests that Epochs 1 and 2 were fed by the ‘Minopoli 2’ and ‘NYT’ end-members (i.e. a high slab derived fluid and/or low subducted sediment mantle wedge input) primitive melts, whereas Epoch 3 and Monte Nuovo melts include the ‘Astroni 6 end-member’ component (i.e. a reduced slab derived fluid and/or low subducted sediment mantle wedge input; D’Antonio et al., 2007, Di Renzo et al., 2011).

CONCLUSIONS

Apatite analysis represents a robust approach for assessing magmatic volatile behaviour that has many major advantages over established techniques (i.e. melt inclusion analysis). Apatite microphenocrysts remain in equilibrium with their host melts on geologically-short timescales but are unable to re-equilibrate on very short timescales during magma ascent. In contrast, apatite inclusions are isolated from the magma on entrapment and preserve a record of conditions earlier in crystallisation. In explosive Campi Flegrei eruptions, apatite inclusions

...
record persistent volatile-undersaturated conditions until late in the crystallisation history of
the evolving magma, interpreted to occur in a deep magma reservoir at ~7.5-8.5 km, which
corresponds with the current depth of major magma storage at Campi Flegrei. In addition to
this main volatile-undersaturated trend, apatite microphenocrysts also display subsidiary
trends, related to cooling and H₂O-saturated crystallisation. The compositional diversity of
apatite microphenocrysts is consistent with a mixed crystal cargo, attained as melts ascending
from depth interact with crystal residue in discreet shallow-crustal magma bodies.
Clinopyroxene-hosted melt inclusion H₂O contents from Campi Flegrei commonly record
saturation pressures equating to 1-3 km depth, due to incorporation of phenocrysts that have
been stored in the shallow crust and/or stalling of ascending magmas as they interact with
shallow crustal magma bodies. This corresponds with melt zones imaged seismically beneath
the current Campi Flegrei caldera and the depth of sill emplacement during recent seismic
crises. In lava deposits, apatite microphenocrysts diffusively re-equilibrated during cooling at
the surface. A systematic offset in volatile-undersaturated apatite compositions between
eruptions suggest that the H₂O content of parental melts feeding the system was higher in
Epoch 1 than in more recent times (i.e. Epoch 3 and Monte Nuovo). Although we have
focused on Campi Flegrei, our approach of comparing thermodynamic models of apatite
compositional evolution with empirical analyses can be applied widely to determine the
temporal evolution of pre-eruptive volatile behaviour in other volcanic systems, providing
new perspectives on sub-volcanic processes.

ACKNOWLEDGEMENTS

We thank Richard Hinton, Norman Charnley and Stuart Kearns for analytical assistance and
advice, Roel van Elsas for support in mineral separation, and Dan Harlov for generously
providing synthetic apatite standard materials. Jason Coumans wrote a MATLAB version of
the thermodynamic model which helped in defining the different crystallisation scenarios. The
paper was greatly improved by thorough, constructive reviews from Massimo D’Antonio, Richard Hervig and an anonymous reviewer, and we are grateful to Georg Zellmer for editorial handling. We thank Jenni Barclay and Lars Hansen for their comments on an early iteration of this work and Jim Webster, Jenny Riker and Jon Wade for their valuable feedback and discussion.

**FUNDING**

M.J.S. was supported by a NERC studentship (NE/K500811/01) and a Junior Research Fellowship from Christ’s College, Cambridge. M.C.S.H. was supported by a Royal Society University Research Fellowship. M.C.S.H., V.C.S. and R.B. acknowledge funding from a NERC grant (NE/K003852/1). SIMS analysis was funded by a NERC Edinburgh Ion Microprobe Facility grant (IMF519/0514).

**REFERENCES**


Arienzo, I., Moretti, R., Civetta, L., Orsi, G. & Papale, P. (2010). The feeding system of
Agnano–Monte Spina eruption (Campi Flegrei, Italy): dragging the past into present activity
and future scenarios. Chemical Geology 270, 135-147.

Arzilli, F., Piochi, M., Mormone, A., Agostini, C. & Carroll, M. R. (2016). Constraining pre-
eruptive magma conditions and unrest timescales during the Monte Nuovo eruption (1538 ad;
Campi Flegrei, Southern Italy): integrating textural and CSD results from experimental and

content and degassing history of an evolving peralkaline volcano. Journal of Volcanology and
Geothermal Research 74, 75-87.

episodic volcanism of Campi Flegrei caldera (Italy) with uncertainty quantification. Journal
of Geophysical Research: Solid Earth 121, 7821-7845.

Petrogenesis of the Campanian ignimbrite: implications for crystal-melt separation and open-
system processes from major and trace elements and Th isotopic data. Developments in
Volcanology 9, 249-288.

partitioning of tantalum, niobium, manganese, and fluorine between aqueous fluoride fluid
and granitic and alkaline melts. Doklady Earth Sciences 427, 868-873.


Boyce, J. W., Tomlinson, S. M., McCubbin, F. M., Greenwood, J. P. & Treiman, A. H.


rich basalt–trachyphonolite interaction in the lava domes of the Phlegrean Fields (Italy).


IntCal13 and Marine13 radiocarbon age calibration curves 0-50,000 years cal BP.

*Radiocarbon* 55, 1869-1887.


FIGURE CAPTIONS
**Figure 1.** Simplified geological map of the Campi Flegrei caldera showing major structural features, adapted from Vitale and Isaia (2014). The locations of sampling sites (black squares) and vents for each eruption analysed in this study (Table 1) are marked and labelled.

**Figure 2.** Clinopyroxene-hosted melt inclusion major element compositions from explosive Campi Flegrei eruptions. All data were measured by EPMA and are normalised to 100%. Data are distinguished by eruption (see legend). Grey points show a compilation of literature clinopyroxene- and olivine-hosted melt inclusion compositions in <15 kyr Campi Flegrei deposits, from Cannatelli *et al.* (2007), Mangiacapra *et al.* (2008), Arienzo *et al.* (2010), Arienzo *et al.* (2016) and Fourmentraux *et al.* (2012).
**Figure 3.** Matrix glass major element compositions from explosive Campi Flegrei eruptions.

All data were measured by EPMA and are normalised to 100%. Data are distinguished by eruption (see legend in Fig. 2). Grey points show literature matrix glass compositions in <15 kyr Campi Flegrei deposits, from Smith *et al.* (2011).
Figure 4. Halogens (a-d) and H$_2$O (e,f) versus MgO compositions in melt inclusions (a,c,e) and matrix glasses (b,d,f) from explosive Campi Flegrei eruptions. MgO and Cl were measured by EPMA (points with no outlines). F and H$_2$O were measured by SIMS (points...
with grey outlines). The red dashed lines show EPMA F detection limits of 0.09 wt%. Data in panels a-d are normalised to 100%. Data are distinguished by eruption (see legend in Fig. 2). Grey circles show literature melt inclusion and matrix glass compositions in <15 kyr Campi Flegrei deposits, from the same sources as Figures 2 and 3, respectively. The grey crosses show the compositions of Campanian Ignimbrite melt inclusions and matrix glasses, from Signorelli et al. (1999).

**Figure 5.** Volatile compositions of clinopyroxene- (a-c) and biotite-hosted (d-f) apatite inclusions from explosive Campi Flegrei eruptions. Data are presented both in ternary space (a,d) and on binary plots of $X_{Cl}/X_{OH}$ versus $X_{F}/X_{OH}$ (b,e) and $X_{Cl}/X_{OH}$ versus $X_{F}/X_{Cl}$ (c,f). Points with black outlines were measured by SIMS and points without outlines were measured by EPMA. Data are distinguished by eruption (see legend in Fig. 2). The coloured fields highlight EPMA and SIMS data from Epoch 1 (red), and Astroni 1 (Epoch 3) and the historic Monte Nuovo eruptions (blue).
Figure 6. Volatile compositions of apatite microphenocrysts from the historic Monte Nuovo (a-c) and Epoch 3 (d-l) eruptions of Campi Flegrei. Data are presented both in ternary space (a,d,g,j) and on binary plots of $X_{Cl}/X_{OH}$ versus $X_{F}/X_{OH}$ (b,e,h,k) and $X_{Cl}/X_{OH}$ versus $X_{F}/X_{Cl}$.
Inset in c shows an expansion of the area outlined by the black dashed box in the main panel. Points with black outlines were measured by SIMS and points without outlines were measured by EPMA. Non-stoichiometric analyses with F > 3.76 wt% (i.e. in lava deposits) are plotted as end-member fluorapatite, with non-stoichiometry likely due to F migration during EPMA (Goldoff et al., 2012, Stock et al., 2015, Stormer et al., 1993). Data are distinguished by eruption (see headings). Lines in a-c show the theoretical trajectory of apatite compositional evolution predicted by our thermodynamic model that best fits natural apatite compositions from Campi Flegrei. $C_{Cl}^0 = 0.4$ wt%, $C_F^0 = 0.2$ wt%, $C_{H_2O}^0 = 2.5$ wt%, $K_{Cl-F}^{ap-m} = 0.22$, $K_{Cl-OH}^{ap-m} = 25$, $K_{F-OH}^{ap-m} = 75$, $D_{Cl}^{c/m} = 0.99$, $D_{F}^{c/m} = 0.8$ and $D_{H_2O}^{c/m} = 0.01$. H$_2$O speciation is calculated after Zhang (1999) for temperature of 1020 °C. The black solid line shows modelled apatite compositional evolution during ~70% volatile-undersaturated crystallisation. The grey lines shows modelled apatite compositional evolution during subsequent H$_2$O-saturated crystallisation, with $D_{Cl}^{f/m} = 20$ and $D_{Cl}^{f/m} = 0.7$, after $C_{H_2O}^{m}$ concentration reaches $C_{H_2O}^{sat}$ at 7.5 wt%. The grey line types illustrate the difference between isobaric (0% H$_2$O loss; solid lines) H$_2$O-saturated crystallisation and polybaric H$_2$O-saturated crystallisation with 0.15 wt% (dashed lines) and 0.25 wt% (dotted lines) H$_2$O loss from the melt into the fluid phase per percent crystallisation.
Figure 7. Volatile compositions of apatite microphenocrysts from Epoch 2 (Baia-Fondi di Baia; a-c) and Epoch 1 (d-l) Campi Flegrei eruptions. Data are presented both in ternary space (a,d,g,j) and on binary plots of $X_{Cl}/X_{OH}$ versus $X_{F}/X_{OH}$ (b,e,h,k) and $X_{Cl}/X_{OH}$ versus $X_{F}/X_{Cl}$.
Insets in c, f, i and l show expansions of the areas outlined by the black dashed boxes in the main panels. Points with black outlines were measured by SIMS and points without outlines were measured by EPMA. Data are distinguished by eruption (see headings).

Figure 8. Theoreticalapatite compositional trajectories for different crystallisation scenarios (not specific to Campi Flegrei). Data are presented both in ternary (a,d) space and on binary plots of $X_{Cl}/X_{OH}$ versus $X_{F}/X_{OH}$ (b,e) and $X_{Cl}/X_{OH}$ versus $X_{F}/X_{Cl}$ (c,f). In all models, $C^0_{Cl}=0.4$ wt%, $C^0_{F}=0.2$ wt%, $C^0_{H2O}=2.9$ wt%, $K^{ap-m}_{Cl-F}=0.22$, $K^{ap-m}_{Cl-OH}=25$, $K^{ap-m}_{F-OH}=75$ and apatite crystallisation begins at the black point (see discussion of input parameters in text). H$_2$O speciation is calculated after Zhang (1999) for temperature of 1020 °C. (a-c) Apatite compositional evolution during volatile-undersaturated fractional crystallisation. Crystal compositions evolve in the arrow direction until 85% crystallisation. Curves show the effect of varying $\overline{D}_i^{c/m}$, where $\overline{D}_F^{c/m} > \overline{D}_Cl^{c/m} > \overline{D}_{H2O}^{c/m}$ and $1 > \overline{D}_i^{c/m} > 0$. Line colours distinguish models with different $\overline{D}_Cl^{c/m}$ values (see legend in c). Line types distinguishes models with...
\( \overline{D}_F^{c/m} = 0.99 \) (solid lines), \( \overline{D}_F^{c/m} = 0.5 \) (dashed lines) and \( \overline{D}_F^{c/m} = 0.14 \) (dotted lines). \( \overline{D}_{H_2O}^{c/m} \) is set at 0.003; varying \( \overline{D}_F^{c/m} \) affects crystal Xf/XOH and XCl/XOH evolution in the opposing sense to \( \overline{D}_F^{c/m} \) and \( \overline{D}_{Cl}^{c/m} \). (d-f) Apatite compositional evolution during H2O-saturated fractional crystallisation. The black arrow shows an arbitrary trajectory of apatite compositional evolution under volatile-undersaturated conditions (\( \overline{D}_F^{c/m} = 0.8, \overline{D}_{Cl}^{c/m} = 0.65, \overline{D}_{H_2O}^{c/m} = 0.001 \)), until 61% crystallisation. Water saturates at 61% crystallisation when \( C_{H_2O}^{m} = \) \( C_{H_2O}^{s} = 7.5 \) wt% (see Supplementary Information) and crystal compositions continue to evolve in the arrow direction to 85% crystallisation. Line colours distinguish H2O-saturated models with varying \( D_{Cl}^{F/m} \) within a realistic range (see legend in f). \( D_{Cl}^{F/m} = 4 \) equates to the lowest value measured for phonolitic systems at 150 MPa by Signorelli and Carroll (2000) and apatite trajectories at \( D_{Cl}^{F/m} > 50 \) are almost indistinguishable. \( D_{F}^{F/m} = 0.7 \) in all models (see Supplementary Information) and \( D_{Cl}^{F/m} \) values are unaltered after H2O-saturation. If fluid-melt Cl partitioning is non-Nernstian (Supplementary Information), apatite compositional evolution will not follow any single trajectory at set \( D_{Cl}^{F/m} \) but will cross between these lines towards higher \( D_{Cl}^{F/m} \). Line types illustrate the difference between isobaric (0% H2O loss; solid lines) H2O-saturated crystallisation and polybaric H2O-saturated crystallisation with 0.1 wt% (dashed lines) and 0.25 wt% H2O loss (dotted lines) per percent crystallisation.
Figure 9. The effect of varying input parameters in general (i.e. not specific to Campi Flegrei) thermodynamic models of apatite compositional evolution in $X_{Cl}/X_{OH}$ versus $X_{F}/X_{OH}$ (a,c) and $X_{Cl}/X_{OH}$ versus $X_{F}/X_{Cl}$ (b,d) binary space. $C_{H_{2}O}^{0}$, $D_{F}^{c/m}$, $D_{Cl}^{c/m}$, $D_{H_{2}O}^{c/m}$, $D_{F}^{f/m}$, $K_{Cl-F}^{ap-m}$, $K_{Cl-OH}^{ap-m}$, $K_{F-OH}^{ap-m}$ and H2O speciation are as in Fig. 8d-f. Apatite crystallisation begins at the black point and continues to 85% crystallisation in all models. (a,b) Trajectories of volatile-undersaturated apatite compositional evolution with varying $C_{H_{2}O}^{0}$. Line colours distinguish models with $C_{H_{2}O}^{0} = 3.0$ wt% (purple), $C_{H_{2}O}^{0} = 1.5$ wt% (green) and $C_{H_{2}O}^{0} = 0.5$ wt% (red).
Line types distinguish models with $C_{Cl}^0 = 0.4$ wt% (solid lines) and $C_{Cl}^0 = 0.25$ wt% (dashed lines). (c,d) Trajectories of apatite compositional evolution with varying $C_{H_2O}^{sat}$, $C_{Cl}^0$ and $C_{H_2O}^0$ are as in Figure 8 and $D_{Cl}^{f/m} = 20$. The black arrows show an arbitrary trajectory of 61% volatile-undersaturated crystallisation, as in Figure 8e,f. Line colours show H$_2$O-saturated crystallisation after 61%, 47% and 28% crystallisation, where $C_{H_2O}^{sat}$ is 7.5 wt% (purple), 5.5 wt% (green) and 4 wt% (red), respectively.

**Figure 10.** Effect of re-equilibration on apatite compositions during cooling, shown in binary $X_{Cl}/X_{OH}$ versus $X_{F}/X_{OH}$ space. The solid lines represent an arbitrary trend of apatite compositional evolution during volatile-undersaturated (as in Fig. 8b; black line) followed by isobaric H$_2$O-saturated (as in Fig. 8e; red line) fractional crystallisation. The dotted red line illustrates polybaric H$_2$O-saturated fractional crystallisation (as in Fig. 8e). The dashed arrows show modelled trajectories of re-equilibration during cooling from 1000 °C to 750 °C, starting from different points on the volatile-undersaturated (point A) and H$_2$O-saturated (points B-D) trend. In each cooling model, the melt composition is fixed and $K_D$ values are calculated from the $P$-independent regressions of Riker et al. (in press). Cooling of a volatile-
undersaturated system, where Cl is retained within the melt (i.e. starting at point A), will cause apatite re-equilibration towards elevated $X_{Cl}/X_{OH}$ and $X_F/X_{OH}$ ratios (black dashed arrow). Extraction of Cl from the melt into the fluid following H$_2$O-saturation (i.e. starting sequentially from point B to point D) increasingly prevents elevation of $X_{Cl}/X_{OH}$ and drives apatite compositions to high $X_F/X_{OH}$ ratios only (dashed grey lines). Re-equilibration of apatites that grew under volatile-undersaturated conditions to H$_2$O-saturated conditions could potentially result in intermediate compositions in the space between A-B and B-D.

**Figure 11.** Schematic diagram summarising volatile systematics in the Campi Flegrei sub-volcanic plumbing system, based on apatite and glass compositions. The representative graphs (right) illustrate how apatite compositional trends relate to different parts of the magmatic system (black lines show apatite trends that form at a particular depth, grey lines show trends that form at a greater depth but are bought up to shallower levels by ascending magmas). The grey bars (left) display relative estimates of Campi Flegrei magma storage depths, derived from independent constraints: ‘current unrest’ estimates are from recent
ground deformation (Amoruso et al., 2014b, D’Auria et al., 2015, Woo & Kilburn, 2010), fumarolic gas emissions (Carlino et al., 2015) and heat flow measurements (Di Maio et al., 2015); melt inclusion estimates are for <15 kyr eruptions and are from 1 – Fourmentraux et al. (2012), 2 – Vetere et al. (2011), 3 – Arienzo et al. (2016) and 4 – Arienzo et al. (2010); phase equilibria constraints are from Fowler et al. (2007), Bohrson et al. (2006) and Cannatelli (2012); seismic tomography data are from Zollo et al. (2008) and De Siena et al. (2010). Pressure estimates were converted to depths using a consistent crustal density of 2.3 kg/cm$^3$ after Rosi and Sbrana (1987). Not to scale.