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Tracking Volatile Behaviour in Sub-volcanic Plumbing Systems Using Apatite and Glass: Insights into Pre-eruptive Processes at Campi Flegrei, Italy

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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 petrological 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 crystallization scenarios, including (1) volatile-undersaturated conditions, (2) H2O-saturated conditions and (3) varying P–T conditions. The compositions of clinopyroxene-hosted and biotite-hosted apatite inclusions are consistent with crystallization under volatile-undersaturated conditions that persisted until late in magmatic evolution. Apatite microphenocrysts show some re-equilibration during cooling at the surface. Clinopyroxene-hosted melt inclusions within the samples typically contain 2–4 wt % H2O, 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 H2O 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.

Key words: apatite; melt inclusions; Campi Flegrei; volatiles; thermodynamic modelling
INTRODUCTION

Magmatic volatiles (H₂O, CO₂, halogens and SO₂) 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 the pre-eruptive behaviour of volatiles plays an important role in controlling the style and tempo of volcanism at the Earth’s surface (Ruggensack et al., 1997; Huppert & Woods, 2002; Cashman, 2004; Edmonds, 2008).

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 petrological 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; Wallace, 2005; Stefano et al., 2011). However, recent studies have revealed the rapidity of H⁺ diffusion in common igneous phenocrysts under magmatic conditions, relative to the timescales of magmatic volatile transport (Woods et al., 2000; Ingrin & Blanchard, 2006; Reubi et al., 2013). 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. Danyushevsky et al., 2002; Portnyagin et al., 2008; Gaetani et al., 2012; Bucholz et al., 2013; Lloyd et al., 2013; Reubi et al., 2013; Preece et al., 2014). 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 of 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 [Ca₅(PO₄)₃F, CI, 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’, owing 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 CO₃²⁻ may also substitute into apatite as trace components (e.g. Pan & Fleet, 2002; Dietterich & de Silva, 2010; Riker et al., 2018). Recent work has focused on deciphering the relationship between apatite F–Cl–OH compositions and their host melt volatile contents (e.g. Candela, 1986; Piccoli & Candela, 1994; Patiño Douce & Roden, 2006; Boyce & Hervig, 2009; McCubbin et al., 2011; Boyce et al., 2014; 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 in which melt inclusions may have re-equilibrated (Stock et al., 2016). Because 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 that of 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 their host liquids on geologically short timescales [i.e. microphenocryst rims may re-equilibrate in weeks to years at magmatic temperatures (7): Brennan, 1993]. Because 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 study, 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 its melts are known to beapatite-bearing and volatile-rich (D’antonio et al., 1999; Cannatelli et al., 2007; Arienzo et al., 2010, 2016). It has also recently shown signs of unrest (Chiordini et al., 2012; Moretti et al., 2017). Building on the work of Candela (1986) and Piccoli & Candela (1994) we develop thermodynamic models that predict the theoretical compositional evolution of apatite as a function of changing magma compositions during fractional crystallization in the presence or 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 the 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 ka; Giaccio et al., 2017) and Neapolitan Yellow Tuff (NYT, ~15 ka; 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 ka and produced ~30 explosive eruptions, with a typical inter-eruptive interval of ~70 years (Di Vito et al., 1999; Smith et al., 2011). Six low-magnitude explosive eruptions occurred in Epoch 2, between ~9.6 and 9.1 ka, at an average interval of ~65 years (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 ka (Smith et al., 2011), with an average eruptive interval of ~75 years (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 four effusive lava domes (Melluso et al., 1995; Di Vito et al., 1999). 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 crystallization of a single parental magma composition, punctuated by periodic recharge events (Villemant,
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; for full stratigraphy see Smith et al., 2011). Vent locations, average matrix glass compositions and absolute eruption ages for the samples analysed in this study are given in Fig. 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 ka (Isaia et al., 2004; Smith et al., 2011). These deposits comprise phreatomagmatic surge beds interbedded with subordinate Strombolian pumice layers (Smith et al., 2011). Pomici Principali (PP) was the largest eruption in the last 15 ky, generating a Plinian column and pyroclastic density currents (Di Vito et al., 1999; Smith et al., 2011; Bevilacqua et al., 2016). 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, owing to magma–H2O phreatomagmatic interaction, but it expelled only a relatively small volume of material (Pistolesi et al., 2017). The most evolved melts identified in Campi Flegrei were produced in the historical 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.
Table 1: Summary of eruption deposits analysed, including age estimate, deposit characteristics (i.e. eruption style), erupted volume (i.e. magnitude estimate), average matrix glass composition, vent location and sampling location

| Epoch | Eruption       | Sample number | Age (cal. years BP) | Deposit type | Erupted volume (km³) | Average matrix glass composition | Vent location* | Sampling location |
|-------|----------------|---------------|--------------------|--------------|----------------------|----------------------------------|----------------|------------------|
|       | Monte Nuovo    | CF195         | 1538 CE*           | Pyroclastic  | ~0.03*               | Phonolite                        | 423095         | 4520870          |                  |
| Epoch 3| Astroni 1      | CF69          | 4155–4357*         | Ash fall     | ~0.06*               | Phonolite                        | 427999         | 4522122          |                  |
|       | Santa Maria    | CF163         | 4205–4507*         | Shallow feeder| <0.01*              | Trachyte§                        | 427551         | 4519262          |                  |
|       | delle Grazie  | CF200         | 4393–4507*         | Dome         | <0.01*               | Latte†                           | 427625         | 4519806          |                  |
|       | Baia–Fondi     | CF88          | 9525–9705*         | Pumice fall  | 0.01–0.04*           | Trachyte                         | 421855         | 4517930          |                  |
| Epoch 1| Pisani 1       | CF25          | 10516–12107*       | Scoria fall  | 0.1–0.3*             | Tephri-phonolite-trachy-andesite | 428260         | 4523970          | 430237*          | 4525994*          |
|       | Pomici         | CF6           | 11907–12107*       | Plinian fall | 0.43–1.28*           | Tephri-phonolite-phonolite       | 428698         | 4522284          | 433890*          | 4522346*          |
|       | Principali     | CF13          | 11907–12725*       | Scoria fall  | <0.1*                | Tephri-phonolite-phonolite       | 432400         | 4522670          | 432805*          | 4522632*          |
|       | Minopoli       |               |                    |              |                      |                                  |                |                  |                  |

Erupted volumes are given as dense rock equivalent. Where exposure permitted, samples were collected vertically through volcaniclastic units and included both lapilli- and ash-sized material. The Pomici Principali sample represents only the B3 Plinian phase of the eruption and the Baia–Fondi di Baia sample comprises only the basal Baia fallout units. Samples from the deposits of these eruptions show only limited diversity in glass compositions (Smith et al., 2011) and the analysed samples are therefore assumed representative of the bulk erupted material.

*Data from Smith et al. (2011). All ages of Smith et al. (2011) have been recalibrated using IntCal13 (Reimer et al., 2013).
†Data from Pistolesi et al. (2017).
‡Data from Bevilacqua et al. (2016).
§Whole-rock composition from Melluso et al. (2012).
¶Whole-rock composition from Isaia et al. (2009).

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 several samples, and by experimental studies and thermodynamic models (Fowler et al., 2007; Azzillì et al., 2016). 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; Piochi et al., 2005; Mastrolorenzo & Pappalardo, 2006) but are 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 extractapatite 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. Onlyapatite inclusions away from cracks and fully enclosed within host phenocrysts were analysed, to ensure that they were trapped during phenocryst growth and were unable to subsequently re-equilibrate with melt or fluids. Melt inclusions were analysed only if they did not show visual evidence for post-entrapment crystallization and were located 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 defocused (5 μm), 15 kV, 10 nA beam, with halogens 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 (Stormer et al., 1993; Goldoff et al., 2012; Stock et al., 2015), while maintaining reasonable precision for low-concentration elements (i.e. Cl). In glass, most elements were measured using a defocused (10 μm), 15 kV, 6 nA beam to minimize 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% probably reflect minor electron-beam induced compositional modification (Stock et al., 2015) and totals significantly <100% probably result from the absence of trace elements [e.g. rare earth elements (REEs)] in the analytical routine. Apatite OH contents in EPMA data were calculated ‘by difference’, assuming stoichiometry. Typical analytical uncertainties are reported in Tables 2 and 3.

A subset of apatites and glasses was analysed by secondary ion mass spectrometry (SIMS) for H, F and Cl using a Cameca ims-4f system at the Edinburgh Ion Micro-Probe Facility, University of Edinburgh, using the methods outlined by 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 H2O concentrations were derived from working curves of 1H/44Ca vs H2O, 35Cl/44Ca vs Cl and 1H/44Ca vs H2O, populated by independent characterised apatite standards (Supplementary Data Fig. S1; supplementary data are available for downloading at http://www.petrology.oxfordjournals.org). Glass H2O concentrations were similarly derived from working curves of 1H/30Si vs H2O populated by well-characterised rhyolitic glasses (Supplementary Data 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 44Ca 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 H2O in apatite and linear fit for all other elements, with R2 typically >0.99. Typical analytical uncertainties are reported 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 are given in Supplementary Data Tables S1 and S2) and SIMS to measure a subset of crystals and glasses for H2O and halogens with lower analytical uncertainties (Tables 2 and 3). All glass data in the text and Figs 2, 3 and 4a–d are plotted normalized 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), owing to melt inclusion devitrification and groundmass crystallization. Apatite inclusions from these eruptions were excluded as they were not isolated from melt or 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 trachybasals and basanites to phonolites and trachytes (Table 2; Supplementary Data Table S1), encompassing almost the entire compositional diversity reported in <15 ka Campi Flegrei deposits (Figs 2 and 3). Clinopyroxene-hosted melt inclusion compositions differ between eruptions: Minopoli 1 melt inclusions are the most mafic (50.46–56.84 wt % SiO2) and cover the largest compositional range; Pisani 1 and PP include the next most mafic melt inclusions, with SiO2 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 SiO2 (typically >53 wt %) and alkali element concentrations (Table 2; Supplementary Data Table S1). For all elements measured, melt inclusion and matrix glass compositions plot on a single compositional trend, in agreement with literature data (Figs 2 and 3). Glass SiO2, Na2O and K2O concentrations typically increase with decreasing MgO, whereas CaO, FeOt (all Fe as FeO) and TiO2 concentrations decrease (Figs 2 and 3; Table 2; Supplementary Data Table S1). However, glass K2O and SiO2 concentrations decrease at low MgO contents (≤0.5 wt % MgO). Some low-MgO matrix glasses from Monte Nuovo and B–FdB are particularly K2O-
Table 2: Major and volatile element analyses of representative Campi Flegrei glasses

| Eruption:       | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo |
|-----------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Analysis #:     | CF195_cp  | CF195_cp  | CF195_cp  | CF195_cp  | CF195_cp  | CF195_cp  | CF195_cp  | CF195_cp  | CF195_cp  | CF195_cp  | CF195_cp  | CF195_cp  | CF195_cp  |
|                 | x113_m6   | x84_m1    | x86_m2    | x86_m3    | x110_m1   | x113_m7   | x113_m7   | x113_m7   | x112_m1   | x112_m2   | x123_m3   | x123_m3   | x137_m5   |
| Type:           | mi        | mi        | mi        | mi        | mi        | mi        | mi        | mi        | mi        | mi        | mi        | mi        | mi        |
| SiO₂            | 57.87     | 57.35     | 57.81     | 56.19     | 58.05     | 57.63     | 58.35     | 58.26     | 59.68     | 58.71     |           |           |           |
| Na₂O            | 4.45      | 4.04      | 4.11      | 3.94      | 5.04      | 4.65      | 4.20      | 4.08      | 5.03      | 4.42      |           |           |           |
| MgO             | 0.55      | 0.77      | 0.75      | 0.74      | 0.76      | 0.79      | 0.87      | 0.81      | 0.51      | 0.70      |           |           |           |
| Al₂O₃           | 18.17     | 17.70     | 17.26     | 16.54     | 18.02     | 18.03     | 18.12     | 19.67     | 17.11     |           |           |           |           |
| K₂O             | 4.40      | 4.67      | 4.97      | 4.87      | 4.91      | 4.94      | 4.94      | 4.82      | 3.65      | 4.42      |           |           |           |
| CaO             | 2.22      | 2.59      | 2.56      | 2.48      | 2.72      | 2.26      | 2.81      | 2.33      | 2.24      |           |           |           |           |
| TiO₂            | 0.43      | 0.48      | 0.42      | 0.46      | 0.40      | 0.42      | 0.50      | 0.53      | 0.49      |           |           |           |           |
| MnO             | 0.09      | 0.09      | 0.11      | 0.15      | 0.10      | 0.10      | 0.12      | 0.12      | 0.11      |           |           |           |           |
| FeOt            | 3.11      | 3.62      | 3.46      | 3.30      | 3.90      | 3.36      | 3.83      | 3.66      | 3.57      |           |           |           |           |
| P₂O₅            | 0.08      | 0.15      | 0.13      | 0.14      | 0.08      | 0.12      | 0.13      | 0.10      | 0.11      |           |           |           |           |
| Cl               | 0.95      | 0.66      | 0.73      | 0.64      | 0.85      | 0.86      | 0.67      | 0.94      | 0.77      |           |           |           |           |
| F                | 0.25      | 0.22      | 0.23      | 0.22      | 0.28      | 0.25      | 0.22      | 0.23      | 0.28      |           |           |           |           |
| H₂O             | 2.82      | 3.48      | 2.84      | 5.56      | 3.47      | 2.45      | 2.44      | 1.04      | 2.28      | 2.54      |           |           |           |
| Total           | 100.47    | 99.93     | 99.96     | 99.01     | 99.12     | 100.67    | 99.31     | 100.01    | 99.87     |           |           |           |           |

(continued)
| Eruption: | Analysis #: | Type: | mg | mg | mg | mg | mi | mi | mi | mi | mi | mi | mi | mi |
|----------|-------------|-------|----|----|----|----|----|----|----|----|----|----|----|----|
| Pisani | CF13_cpx | SiO₂ | 58.94 | 56.79 | 58.68 | 58.39 | 52.97 | 55.86 | 55.81 | 52.47 | 57.52 | 55.12 |
| Pisani | CF25_cpx | Na₂O | 4.26 | 2.87 | 4.52 | 4.95 | 3.53 | 3.36 | 3.46 | 3.55 | 3.57 | 3.55 |
| Pisani | CF25_cpx | MgO | 0.48 | 0.52 | 0.59 | 0.34 | 1.34 | 1.00 | 1.17 | 1.05 | 0.97 | 1.07 |
| Pisani | CF25_cpx | Al₂O₃ | 18.19 | 18.09 | 18.01 | 16.03 | 17.97 | 17.53 | 17.89 | 17.60 | 18.25 | 18.01 |
| Pisani | CF25_cpx | K₂O | 8.66 | 8.09 | 8.67 | 6.70 | 8.20 | 8.14 | 7.88 | 7.70 | 7.98 | 7.99 |
| Pisani | CF25_cpx | CaO | 2.10 | 2.41 | 2.49 | 2.34 | 3.43 | 3.57 | 3.58 | 3.65 | 3.57 | 3.58 |
| Pisani | CF25_cpx | TiO₂ | 0.40 | 0.48 | 0.45 | 0.54 | 0.62 | 0.59 | 0.63 | 0.64 | 0.58 | 0.56 |
| Pisani | CF25_cpx | MnO | 0.18 | 0.14 | 0.20 | 0.26 | 0.20 | 0.21 | 0.10 | 0.13 | 0.22 | 0.22 |
| Pisani | CF25_cpx | FeOt | 3.06 | 3.37 | 3.35 | 4.28 | 4.70 | 4.76 | 4.91 | 5.00 | 5.23 | 5.07 |
| Pisani | CF25_cpx | P₂O₅ | 0.09 | 0.10 | 0.13 | 0.05 | 0.45 | 0.24 | 0.25 | 0.28 | 0.18 | 0.21 |
| Pisani | CF25_cpx | Cl | 0.86 | 0.85 | 0.92 | 0.15 | 0.69 | 0.70 | 0.78 | 0.71 | 0.77 | 0.83 |
| Pisani | CF25_cpx | F | 0.09 | 0.26 | 0.29 | 0.23 | 0.19 | 0.19 | 0.21 | 0.23 | 0.24 | 0.23 |
| Pisani | CF25_cpx | H₂O | 6.63 | 0.93 | 0.10 | 0.77 | 2.17 | 2.23 | 2.37 | 2.30 | 2.12 | 2.32 |
| Pisani | CF25_cpx | Total | 97.83 | 94.98 | 99.23 | 99.92 | 96.17 | 98.39 | 99.04 | 95.35 | 101.22 | 98.75 |
| Minopoli | CF13_cpx | SiO₂ | 56.27 | 56.27 | 55.42 | 54.66 | 57.09 | 56.58 | 56.59 | 57.57 | 57.05 | 56.34 |
| Minopoli | CF13_cpx | Na₂O | 3.34 | 3.34 | 3.08 | 3.17 | 4.06 | 3.70 | 3.83 | 3.39 | 3.24 | 3.95 |
| Minopoli | CF13_cpx | MgO | 3.53 | 3.81 | 2.98 | 1.95 | 1.59 | 0.93 | 0.84 | 0.54 | 0.72 | 0.54 |
| Minopoli | CF13_cpx | Al₂O₃ | 18.72 | 17.82 | 17.90 | 18.21 | 18.24 | 18.19 | 18.24 | 18.15 | 18.11 | 18.15 |
| Minopoli | CF13_cpx | K₂O | 8.13 | 8.13 | 7.11 | 7.27 | 9.28 | 9.22 | 9.18 | 9.08 | 8.84 | 9.10 |
| Minopoli | CF13_cpx | CaO | 4.27 | 4.27 | 5.52 | 5.35 | 3.16 | 3.18 | 2.95 | 3.17 | 3.14 | 3.06 |
| Minopoli | CF13_cpx | TiO₂ | 0.65 | 0.65 | 0.75 | 0.69 | 0.41 | 0.45 | 0.47 | 0.41 | 0.46 | 0.55 |
| Minopoli | CF13_cpx | MnO | 0.09 | 0.09 | 0.13 | 0.06 | 0.09 | 0.16 | 0.17 | 0.04 | 0.14 | 0.14 |
| Minopoli | CF13_cpx | FeOt | 5.41 | 5.41 | 6.21 | 6.09 | 3.92 | 3.92 | 3.94 | 3.82 | 3.93 | 3.90 |
| Minopoli | CF13_cpx | P₂O₅ | 0.42 | 0.42 | 0.50 | 0.49 | 0.14 | 0.14 | 0.17 | 0.12 | 0.12 | 0.11 |
| Minopoli | CF13_cpx | Cl | 0.76 | 0.76 | 0.56 | 0.73 | 0.01 | 0.03 | 0.03 | 0.07 | 0.12 | 0.76 |
| Minopoli | CF13_cpx | F | 0.22 | 0.20 | 0.03 | 0.27 | 0.23 | 0.22 | 0.25 | 0.22 | 0.28 | 0.24 |
| Minopoli | CF13_cpx | H₂O | 0.14 | 0.14 | 0.05 | 0.33 | 1.26 | 3.84 | 2.52 | 1.98 | 3.35 | 2.35 |
| Minopoli | CF13_cpx | Total | 99.06 | 99.04 | 99.63 | 99.26 | 99.21 | 101.16 | 99.47 | 99.82 | 100.05 | 99.30 |

F and H₂O were measured by SIMS; all other elements were measured by EPMA. Analysis type refers to textural association: mi, melt inclusion; mg, matrix glass. Concentrations are in wt %, RP is representative absolute precision with 1SD based on counting statistics for F and elements measured by EPMA, and a 95% confidence interval based on regression of calibration standards for H₂O.
### Table 3: Major and volatile element analyses of representative Campi Flegrei apatite inclusions and microphenocrysts

| Eruption:       | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo | Monte Nuovo |
|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Crystal #:      | CFmap2_C    | CFmap2_C    | CFmap2_C    | CFmap2_C    | CFmap2_C    | CFmap2_C    | CFmap2_C    | CFmap2_C    | CFmap2_C    |
| Type:           | mpc         | mpc         | mpc         | mpc         | mpc         | mpc         | mpc         | mpc         | mpc         |
| P2O5            | 38.94       | 40.47       | 41.32       | 40.99       | 41.39       | 41.06       | 40.36       | 41.36       | 41.29       |
| SiO2            | 6.08        | 1.32        | 0.61        | 0.54        | 0.41        | 0.43        | 0.60        | 0.67        | 0.67        |
| CaO             | 53.20       | 52.93       | 53.68       | 54.32       | 53.37       | 54.19       | 53.78       | 54.67       | 53.85       |
| SO2             | 0.25        | 0.17        | 0.56        | 0.23        | 0.27        | 0.42        | 0.13        | 0.18        | 0.39        |
| F               | 2.28        | 2.02        | 2.47        | 2.36        | 2.50        | 2.08        | 2.94        | 3.30        | 2.12        |
| Cl              | 1.05        | 0.94        | 0.98        | 1.04        | 1.04        | 0.94        | 0.54        | 0.12        | 0.98        |
| OH              | 1.02        | 1.23        | 0.48        | 0.70        | 0.55        | 0.94        | 0.49        | 0.17        | 0.62        |
| O=O=F, Cl, OH   | 1.89        | 1.64        | 1.52        | 1.64        | 1.52        | 1.64        | 1.52        | 1.64        | 1.52        |
| Total           | 97.77       | 97.44       | 98.61       | 98.62       | 97.87       | 98.61       | 97.55       | 98.91       | 98.44       |

(continued)
Table 3: Continued

| Eruption: | Crystal #: | Crystal #: | Crystal #: | Crystal #: | Crystal #: | Crystal #: | Crystal #: | Crystal #: | Crystal #: | Crystal #: | Crystal #: | Crystal #: |
|-----------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Type:     |            |            |            |            |            |            |            |            |            |            |            |            |
|           |            |            |            |            |            |            |            |            |            |            |            |            |
| P_{2}O_{5} | 41.07      | 41.60      | 41.18      | 41.09      | 41.14      | 41.32      | 41.55      | 40.85      | 40.13      | 41.64      | 40.60      | 41.56      | 41.53      |
| SiO_{2}   | 0.64       | 0.61       | 0.61       | 0.57       | 0.59       | 0.89       | 0.60       | 0.53       | 0.59       | 0.47       | 0.59       | 0.58       |
| CaO       | 53.78      | 53.97      | 53.86      | 53.94      | 53.92      | 53.92      | 53.94      | 53.92      | 53.92      | 53.92      | 53.92      | 53.92      |
| SO_{2}    | 0.24       | 0.34       | 0.38       | 0.38       | 0.38       | 0.38       | 0.38       | 0.38       | 0.38       | 0.38       | 0.38       | 0.38       |
| F         | 2.34       | 2.40       | 2.40       | 2.40       | 2.40       | 2.40       | 2.40       | 2.40       | 2.40       | 2.40       | 2.40       | 2.40       |
| Cl        | 0.66       | 0.59       | 0.65       | 0.55       | 0.66       | 0.65       | 0.57       | 0.59       | 0.59       | 0.59       | 0.59       | 0.59       |
| OH        | 1.46       | 1.49       | 1.56       | 1.53       | 1.49       | 1.56       | 1.49       | 1.56       | 1.56       | 1.56       | 1.56       | 1.56       |
| Total     | 98.29      | 98.89      | 98.85      | 98.88      | 98.92      | 98.86      | 98.98      | 99.03      | 99.10      | 99.10      | 99.10      | 99.10      |

(continued)
Table 3: Continued

| Eruption: | Accademia | Maria delle Grazie | Santa Maria delle Grazie |
|-----------|-----------|--------------------|-------------------------|
| Crystal #: | CFmap2_C  | F163_10 mpc | CFmap2_C  | F163_10 mpc |
| Type: P2O5 | 4.015 | 41.61 | 40.40 | 39.79 | 39.79 | 40.02 | 38.69 | 40.03 | 39.94 | 39.93 | 40.03 |
| SiO2 | 0.40 | 0.59 | 0.50 | 0.65 | 0.54 | 0.40 | 0.65 | 0.40 | 1.00 | 1.00 | 0.97 |
| CaO | 5.385 | 5.295 | 5.14 | 5.09 | 5.14 | 5.42 | 5.36 | 5.64 | 5.36 | 5.36 | 5.36 |
| SO2 | 0.89 | 0.95 | 0.90 | 0.89 | 0.97 | 0.87 | 0.97 | 0.88 | 0.87 | 0.86 | 0.91 |
| F | 2.00 | 2.50 | 2.77 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Cl | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 |
| OH | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 | 0.61 |
| Total | 98.20 | 99.99 | 99.99 | 99.99 | 99.99 | 99.99 | 99.99 | 99.99 | 99.99 | 99.99 | 99.99 |

(continued)
### Table 3: Continued

| Eruption: | Crystal #: | Type: |
|-----------|------------|-------|
| **P₀₁** | CFmap1_cpx | mpc |
| **SiO₂** | CFmap1_cpx | mpc |
| **CaO** | CFmap1_cpx | mpc |
| **SO₂** | CFmap1_cpx | mpc |
| **F** | CFmap1_cpx | mpc |
| **Cl** | CFmap1_cpx | mpc |
| **OH** | CFmap1_cpx | mpc |
| **O₁F₁Cl₁OH** | CFmap1_cpx | mpc |
| **Total** | CFmap1_cpx | mpc |
| **P₀₂** | CFmap2_cpx | mpc |
| **SiO₂** | CFmap2_cpx | mpc |
| **CaO** | CFmap2_cpx | mpc |
| **SO₂** | CFmap2_cpx | mpc |
| **F** | CFmap2_cpx | mpc |
| **Cl** | CFmap2_cpx | mpc |
| **OH** | CFmap2_cpx | mpc |
| **O₁F₁Cl₁OH** | CFmap2_cpx | mpc |
| **Total** | CFmap2_cpx | mpc |
| **P₀₃** | CFmap3_cpx | mpc |
| **SiO₂** | CFmap3_cpx | mpc |
| **CaO** | CFmap3_cpx | mpc |
| **SO₂** | CFmap3_cpx | mpc |
| **F** | CFmap3_cpx | mpc |
| **Cl** | CFmap3_cpx | mpc |
| **OH** | CFmap3_cpx | mpc |
| **O₁F₁Cl₁OH** | CFmap3_cpx | mpc |
| **Total** | CFmap3_cpx | mpc |
| **P₀₄** | CFmap4_cpx | mpc |
| **SiO₂** | CFmap4_cpx | mpc |
| **CaO** | CFmap4_cpx | mpc |
| **SO₂** | CFmap4_cpx | mpc |
| **F** | CFmap4_cpx | mpc |
| **Cl** | CFmap4_cpx | mpc |
| **OH** | CFmap4_cpx | mpc |
| **O₁F₁Cl₁OH** | CFmap4_cpx | mpc |
| **Total** | CFmap4_cpx | mpc |

*(Continued)*
Table 3: Continued

Eruption: Minopoli 1 Minopoli 1 Minopoli 1 Minopoli 1 Minopoli 1 Minopoli 1 Minopoli 1 Minopoli 1 Minopoli 1 Minopoli 1
Crystal #: CFmap1_C CFmap1_C CFmap1_C CFmap1_C CFmap1_C CFmap1_C CFmap1_C CFmap1_C CFmap1_C CFmap1_C
Type: mpc mpc mpc mpc mpc mpc mpc mpc mpc mpc

| Element | CFmap1_C | CFmap1_C | CFmap1_C | CFmap1_C | CFmap1_C | CFmap1_C | CFmap1_C | CFmap1_C | CFmap1_C | CFmap1_C |
|---------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| P2O5    | 39.50    | 40.81    | 40.04    | 41.03    | 40.78    | 40.13    | 40.70    | 41.37    | 41.39    | 42.39    |
| SiO2    | 0.84     | 0.51     | 1.20     | 0.42     | 0.63     | 1.00     | 0.45     | 0.41     | 0.50     | 0.06     |
| CaO     | 54.03    | 53.92    | 53.26    | 54.06    | 53.77    | 52.90    | 53.86    | 53.81    | 54.92    | 54.64    |
| SO2     | 0.74     | 0.59     | 0.17     | 0.44     | 0.33     | 0.19     | 0.31     | 0.42     | 0.47     | 0.00     |
| Cl      | 0.05     | 0.05     | 0.90     | 0.81     | 0.93     | 0.94     | 0.88     | 0.86     | 0.41     | 0.12     |
| OH      | 1.35     | 1.01     | 1.10     | 0.98     | 0.24     | 1.04     | 0.97     | 0.88     | 1.29     | 0.51     |
| O=F, Cl, OH | 1.59 | 1.54 | 1.54 | 1.41 | 1.53 | 1.58 | 1.50 | 1.43 | 1.42 | 1.46 |
| Total   | 97.16    | 98.23    | 97.07    | 98.16    | 98.01    | 98.70    | 97.67    | 98.28    | 99.27    | 99.10    |

Halogen and OH were measured by SIMS; all other elements were measured by EPMA. Crystal type refers to textural association:

- cpx, clinopyroxene-hosted inclusion
- bt, biotite-hosted inclusion
- mpc, microphenocryst

Concentrations are in wt %. RP is representative absolute precision with 1SD based on counting statistics for elements measured by EPMA, and a 95% confidence interval based on regression of calibration standards for elements measured by SIMS.

Fig. 2. Clinopyroxene-hosted melt inclusion major element compositions from explosive Campi Flegrei eruptions. Data were measured by EPMA and are normalized 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 ka Campi Flegrei deposits from Cannatelli et al. (2007), Mangiacapra et al. (2008), Arienzo et al. (2010, 2016) and Fourmentraux et al. (2012).
depleted and Na$_2$O-rich (Fig. 3). This is consistent with fractional crystallization models, which indicate early fractionation of olivine, clinopyroxene and magnetite (Fowler et al., 2007) but show a major change in compatibility for K$_2$O and Na$_2$O at ~0.5 wt % MgO, after plagioclase, biotite and K-feldspar come onto the liquidus (Fowler et al., 2007; Cannatelli, 2012; 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 (0.32–0.85 wt %), whereas melt inclusions from Pisani 1 and PP are intermediate (0.58–0.89 wt %). Melt inclusions from other eruptions have higher Cl concentrations, extending up to 1.17 wt % (Fig. 4a; Supplementary Data 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; Supplementary Data 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; Supplementary Data 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 % H$_2$O and show no correlation between H$_2$O and MgO (Fig. 4e), consistent with other Campi Flegrei eruptions (Arienzo et al., 2016). Some inclusions have H$_2$O concentrations as low as 1.04 wt %, with the largest variability at low MgO concentrations (<1.5 wt %), where measured H$_2$O 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 H$_2$O contents are lower than in melt inclusions; mafic Minopoli 1 and Pisani 1 matrix glasses consistently have H$_2$O concentrations <0.4 wt %, whereas more evolved (<1 wt % MgO) PP, Astroni 1 and Monte Nuovo matrix glasses...
have more variable H$_2$O 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 % (Table 3; Supplementary Data Table S2). This translates to $X_F/X_{Cl}$ ratios from 0.19 to 1.22, $X_Cl/X_{OH}$ from 1.33 to 5.79 and $X_F/X_{OH}$ 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 an 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 $X_F/X_{Cl}$ (Fig. 5b and 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 (Table 3; Supplementary Data Table S2). This translates to $X_F/X_{OH}$ ratios from 0.28 to 0.95, $X_Cl/X_{OH}$ from 1.20 to 4.11 and $X_F/X_{Cl}$ from 3.31 to 9.47. Biotite-hosted apatite inclusions
hosted inclusions plot on the same compositional trends as clinopyroxene-hosted inclusions (Fig. 5d–f). 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 (Table 3; Supplementary Data Table 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 (Supplementary Data Table S2) but exceed the maximum stoichiometric limit of 3.76 wt % F (Pyle et al., 2002), probably reflecting electron beam-induced sample damage in near end-member fluorapatite (Stormer et al., 1993; Goldoff et al., 2012; Stock et al., 2015). 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 from 0.02 to 1.47 wt % and measured OH concentrations are <1.97 wt % (Table 3; Supplementary Data Table 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 plot on the same compositional trends as the inclusions (Figs 6 and 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 and 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 (Fig. 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 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
Fig. 6. Volatile compositions of apatite microphenocrysts from the historical 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 $X_{Cl}/X_{OH}$ vs $X_{F}/X_{OH}$ (b, e, h, k) and $X_{Cl}/X_{OH}$ vs $X_{F}/X_{Cl}$ (c, f, i, l). 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 probably the result of $F$ migration during EPMA (Stormer et al., 1993; Goldoff et al., 2012; Stock et al., 2015). 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, $C_F^0 = 0.4$ wt %, $C_O^0 = 0.2$ wt %, $C_{H_2O}^0 = 2.5$ wt %, $K_{Cl-F}^{ap-m} = 0.22$, $K_{Cl-OH}^{ap-m} = 25$, $K_{OH-F}^{ap-m} = 75$, $D_{F}^{Cl^{-}^{m}} = 0.99$, $D_{Cl^{-}}^{F^{m}} = 0.8$, and $D_{H_2O}^{Cl^{-}} = 0.01$. $H_2O$ speciation is calculated after Zhang (1999) for a temperature of 1020 $^\circ$C. The black continuous line shows modelled apatite compositional evolution during ~70% volatile-under saturated crystallization. The grey lines show modelled apatite compositional evolution during subsequent $H_2O$-saturated crystallization, with $D_{Cl^{-}}^{H_2O^{-}} = 20$ and $D_{Cl^{-}}^{H_2O^{-}} = 0.7$, after $C_{H_2O}^{sat}$ reaches $C_{H_2O}^{sat}$ at 7.5 wt %. The grey line types illustrate the difference between isobaric (0% $H_2O$ loss; continuous lines) $H_2O$-saturated crystallization and polybaric $H_2O$-saturated crystallization with 0.15 wt % (dashed lines) and 0.25 wt % (dotted lines) $H_2O$ loss from the melt into the fluid phase per 1% crystallization.
Fig. 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 $\text{X}_\text{Cl}/\text{X}_\text{OH}$ vs $\text{X}_\text{F}/\text{X}_\text{OH}$ (b, e, h, k) and $\text{X}_\text{Cl}/\text{X}_\text{OH}$ vs $\text{X}_\text{F}/\text{X}_\text{Cl}$ (c, f, i, l). 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).
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 $X_{Cl}/X_{Cl}$ ratios in apatite inclusions from Epoch 1 than in those from younger eruptions (Fig. 5). The main population of apatite microphenocrysts from Astroni 1 is also typically more F-rich, with higher $X_{Cl}/X_{OH}$, $X_{F}/X_{OH}$ and $X_{Cl}/X_{Cl}$ 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 $X_{Cl}/X_{Cl}$ ratios, than those from Epoch 1, but cover the entire compositional diversity of the main microphenocryst population from other eruptions (Figs 6 and 7). Baia–Fondi di Baia inclusions (Epoch 2) are relatively $X_{Cl}/X_{OH}$ depleted; B–FdB microphenocrysts are compositionally similar to those of 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 $X_{Cl}/X_{Cl}$ 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,

$$X_{Cl}^{Ap} + X_{OH}^{m} = X_{Cl}^{Ap} + X_{Cl}^{m}$$

where $X$ denotes mole fraction in the apatite (Ap) and melt (m) phases. Exchange coefficients ($K$) for these equilibria are defined as

$$K_{Cl-OH(m)} = \frac{a_{Cl}^{Ap} a_{OH}^{m}}{a_{Cl}^{m} a_{OH}^{Ap}}$$

where $a$ is activity. The evolution of F, Cl and H$_2$O concentrations in the melt (i.e. $a_{Cl}^{m}$ and so on) during fractional crystallization 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 crystallization scenarios using appropriate experimental $K$ values from the literature.

We have developed a thermodynamic model, relating apatite compositional evolution to changes in the volatile contents of silicate melts during crystallization in the presence or absence of different magmatic fluids, building on the work of Candela (1986), who treated halogens and H$_2$O as perfectly incompatible during volatile-undersaturated crystallization. First, we calculate the evolution of F, Cl and H$_2$O in the melt owing to crystal ± fluid fractionation. We then compute the volatile composition of apatite in equilibrium with the melt at each stage of the crystallization 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 H$_2$O in the silicate melt, are discussed in the Supplementary Data. Our approach can be applied generally to determine apatite compositions during fractional crystallization. The effects of pressure and temperature variations on apatite compositions are also outlined below.

**Apatite fractional crystallization 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 Table 2 and Supplementary Data Table S1. The initial melt H$_2$O concentration ($C_{H2O}^{0}$) 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 crystallization, the evolution of all volatile components in the melt is described by the Rayleigh equation:

$$C_{i}^{m} = C_{i}^{0} \cdot \varphi^{O_{Cl}^{m} - 1}$$

where $C_{i}^{m}$ is the concentration of $i$ in the melt at a given melt fraction ($\varphi$) and $D_{i}^{C_{Cl}^{m}}$ is the bulk crystal–melt partition coefficient.

We simulate the onset of saturation with an H$_2$O-rich fluid by imposing a pre-defined H$_2$O solubility limit ($C_{H2O}^{sat}$), 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 owing to continuing fractionation is assigned to a separate fluid phase, following Candela & Holland (1986), and we calculate the F and Cl concentration of that fluid phase using the fluid–melt partition coefficients (i.e. $D_{F}^{C_{Cl}^{m}}$ and $D_{Cl}^{C_{Cl}^{m}}$, respectively). This fluid 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 & 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 $X_{Cl}/X_{OH}$, $X_{F}/X_{OH}$ and $X_{Cl}/X_{Cl}$. 

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Volatile-undersaturated - varying $D_{\text{Cl}}^{\text{Cl/m}}$

(a) $D_{\text{Cl}}^{\text{Cl/m}} = 0.14$

(b) $D_{\text{Cl}}^{\text{Cl/m}} = 0.90$

(c) $D_{\text{Cl}}^{\text{Cl/m}} = 0.75$

(d) $D_{\text{Cl}}^{\text{Cl/m}} = 0.50$

(e) $D_{\text{Cl}}^{\text{Cl/m}} = 0.25$

(f) $D_{\text{Cl}}^{\text{Cl/m}} = 0.03$

H$_2$O-saturated - varying $D_{\text{Cl}}^{\text{Cl/m}}$

(a) $D_{\text{Cl}}^{\text{Cl/m}} = 50$

(b) $D_{\text{Cl}}^{\text{Cl/m}} = 20$

(c) $D_{\text{Cl}}^{\text{Cl/m}} = 10$

(d) $D_{\text{Cl}}^{\text{Cl/m}} = 4$

Fig. 8. Theoretical apatite compositional trajectories for different crystallization scenarios (not specific to Campi Flegrei). Data are presented both in ternary (a, d) space and on binary plots of $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\phi}/X_{\text{OH}}$ (b, e) and $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\phi}/X_{\phi}$ (c, f). In all models, $C_0^\text{Cl} = 0.4$ wt %, $C_0^\text{F} = 0.2$ wt %, $C_0^\text{OH} = 2.9$ wt %, $K_{\text{Cl,F}}^{\text{ap,m}} = 0.22$, $K_{\text{Cl,OH}}^{\text{ap,m}} = 25$, $K_{\text{F,OH}}^{\text{ap,m}} = 75$, and apatite crystallization begins at the black point (see discussion of input parameters in the text). H$_2$O speciation is calculated after Zhang (1999) for a temperature of $1020^\circ \text{C}$. (a–c) Apatite compositional evolution during volatile-undersaturated fractional crystallization. Crystal compositions evolve in the arrow direction until 85% crystallization. Curves show the effect of varying $D_{\text{Cl}}^{\text{Cl/m}}$, where $D_{\text{F}}^{\text{Cl/m}} > D_{\text{Cl}}^{\text{Cl/m}} > D_{\text{Cl,OH}}^{\text{Cl/m}}$ and $1 > D_{\phi}^{\text{Cl/m}} > 0$. Line colours distinguish models with different $D_{\text{Cl}}^{\text{Cl/m}}$ values (see legend in (c)). Line types distinguish models with $D_{\text{Cl}}^{\text{Cl/m}} = 0.99$ (continuous lines), $D_{\text{Cl}}^{\text{Cl/m}} = 0.5$ (dashed lines) and $D_{\text{Cl}}^{\text{Cl/m}} = 0.14$ (dotted lines). $D_{\text{Cl,OH}}^{\text{Cl/m}}$ is set at 0.003; varying $D_{\text{Cl,OH}}^{\text{Cl/m}}$ affects crystal $X_{\text{Cl}}/X_{\phi}$ and $X_{\text{Cl}}/X_{\text{OH}}$ evolution in the opposing sense to $D_{\text{F}}^{\text{Cl/m}}$ and $D_{\text{Cl}}^{\text{Cl/m}}$. (d–f) Apatite compositional evolution during H$_2$O-saturated fractional crystallization. The black arrow shows an arbitrary trajectory of apatite compositional evolution under volatile-undersaturated conditions ($D_{\text{F}}^{\text{Cl/m}} = 0.8$, $D_{\text{Cl}}^{\text{Cl/m}} = 0.65$, $D_{\text{Cl,OH}}^{\text{Cl/m}} = 0.001$), until 61% crystallization. Water saturates at 61% crystallization when $c_{\text{H}_2\text{O}} = C_{\text{H}_2\text{O}}^{\text{Cl}} = 7.5$ wt % (see Supplementary Data) and crystal compositions continue to evolve in the arrow direction to 85% crystallization. Line colours distinguish H$_2$O-saturated models with varying $D_{\text{Cl}}^{\text{Cl/m}}$ within a realistic range (see legend in (f)). $D_{\text{Cl}}^{\text{Cl/m}} = 4$ equates to the lowest value measured for phonolitic systems at 150 MPa by Signorelli & Carroll (2000) and apatite trajectories at $D_{\text{Cl}}^{\text{Cl/m}} > 50$ are almost indistinguishable, $D_{\text{Cl}}^{\text{Cl/m}} = 0.7$ in all models (see Supplementary Data) and $D_{\text{Cl}}^{\text{Cl/m}}$ values are unaltered after H$_2$O-saturation. If fluid-melt Cl partitioning is non-Nernstian (Supplementary Data), apatite compositional evolution will not follow any single trajectory at set $D_{\text{Cl}}^{\text{Cl/m}}$ but will cross between these lines towards higher $D_{\text{Cl}}^{\text{Cl/m}}$. Line types illustrate the difference between isobaric (0% H$_2$O loss; continuous lines) H$_2$O-saturated crystallization and polybaric H$_2$O-saturated crystallization with 0.1 wt % (dotted lines) and 0.25 wt % (dotted lines) H$_2$O loss per 1% crystallization.

Model outputs: apatite compositional evolution during fractional crystallization

During volatile-undersaturated crystallization for a range of parameters (see Supplementary Data), apatite compositions typically show a decrease in both $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\phi}/X_{\phi}$ ratios, whereas $X_{\text{Cl}}/X_{\text{OH}}$ may increase or decrease depending on the exact values of the crystal-melt partition coefficients for F, Cl and OH (Fig. 8b and c). In contrast, H$_2$O-saturated crystallization is characterized by a strong decrease in apatite $X_{\text{Cl}}/X_{\text{OH}}$ ratios per unit crystallization, with increasing $X_{\phi}/X_{\phi}$ and variable $X_{\text{Cl}}/X_{\text{OH}}$ (Fig. 8e and f). This is because fluid-melt partition coefficients for Cl are typically much higher than for F (Borodulin et al., 2009; Webster et al., 2014). 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 crystallization apatite compositions move...
towards the F–OH binary (Fig. 8d). Under polybaric H₂O-saturated conditions, where H₂O is lost from the melt during depressurization, crystal compositions may then curve towards the F apex (Fig. 8d).

The melt volatile composition
Varying the initial melt volatile concentrations (C₀) 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 crystallization. However, the slope or direction in binary or ternary space remains the same (Fig. 9a and b). In the general H₂O-saturated case, decreasing C₀ (e.g. at lower pressure or a different melt composition) reduces the extent of volatile-undersaturated crystallization before second boiling, but does not affect the trajectory of apatite compositional evolution after volatile-undersaturation is achieved (Fig. 9c and 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 crystallization.

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., 2018), mineral compositions may vary, even at a constant melt composition [e.g. equation (2)].
decrease in the apatite Cl component, which is reflected in a minor composition (Piccoli & Candela, 1994; Riker has little effect on apatite compositions at constant melt work of Piccoli & Candela (1994). Cooling drives apatite (2018); this is qualitatively consistent with the earlier tween H\textsubscript{2}O-saturated and volatile-undersaturated The clear differences in model apatite trajectories be- tween H\textsubscript{2}O-saturated and volatile-undersaturated conditions (Fig. 8) suggest that apatite 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 \(X\textsubscript{halogen}/X\textsubscript{OH}\) 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 \(X\textsubscript{halogen}/X\textsubscript{OH}\) 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 \(K\textsubscript{Ap/m}^{\text{cl–OH}} = 25, K\textsubscript{Ap/m}^{\text{F–OH}} = 75\) and \(K\textsubscript{Ap/m}^{\text{Cl–F}} = 0.22\), which are within the range identified experimentally (Riker et al., 2018) and the effects of varying input parameters on the model fit are shown in Figs 8 and 9, and Supplementary Data Figs S3–S6. The model fit (Fig. 6a–c) represents ~70% crystallization at volatile-undersaturated conditions, with constant crystal–melt partition coefficients \(D\textsubscript{F}/C\textsubscript{1} = 0.99, D\textsubscript{Cl}/C\textsubscript{1} = 0.8\) and \(D\textsubscript{OH}/C\textsubscript{1} = 0.01\) (Fig. 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 \(X\textsubscript{Cl}/X\textsubscript{OH}\) values identified in some apatite microphenocrysts can be partially reproduced by subsequent H\textsubscript{2}O-saturated crystallization, with \(D\textsubscript{Cl}/C\textsubscript{2} = 20\) and \(D\textsubscript{OH}/C\textsubscript{2} = 0.7\) (Fig. 6a–c), consistent with alkali melt–fluid halogen partitioning experiments under magmatic conditions (Signorelli & Carroll, 2000; Borodulin et al., 2009). However, our simple isobaric, isothermal H\textsubscript{2}O-saturated crystallization models cannot reproduce the range of \(X\textsubscript{Cl}/X\textsubscript{OH}\) ratios observed in the natural low \(X\textsubscript{Cl}/X\textsubscript{OH}\) subsidiary population (Fig. 8d–f). Decompression-induced degassing could account for some of this compositional variability but cooling, after the apatites have re-equilibrated under H\textsubscript{2}O-saturated conditions, appears to be the primary mechanism to drive compositions to the very high \(X\textsubscript{Cl}/X\textsubscript{OH}\) ratios observed in some eruptions (e.g. PP; Figs 7 and 10). The second, high \(X\textsubscript{Cl}/X\textsubscript{OH}\) and \(X\textsubscript{Cl}/X\textsubscript{OH}\) subsidiary population (e.g. Minopoli 1) is consistent with re-equilibration of apatites during cooling of a less degassed melt (Fig. 10).

**DISCUSSION**

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

The clear differences in model apatite trajectories between H\textsubscript{2}O-saturated and volatile-undersaturated conditions (Fig. 8) suggest that apatite 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 \(X\textsubscript{halogen}/X\textsubscript{OH}\) 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 \(X\textsubscript{halogen}/X\textsubscript{OH}\) 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 \(K\textsubscript{Ap/m}^{\text{cl–OH}} = 25, K\textsubscript{Ap/m}^{\text{F–OH}} = 75\) and \(K\textsubscript{Ap/m}^{\text{Cl–F}} = 0.22\), which are within the range identified experimentally (Riker et al., 2018) and the effects of varying input parameters on the model fit are shown in Figs 8 and 9, and Supplementary Data Figs S3–S6. The model fit (Fig. 6a–c) represents ~70% crystallization at volatile-undersaturated conditions, with constant crystal–melt partition coefficients \(D\textsubscript{F}/C\textsubscript{1} = 0.99, D\textsubscript{Cl}/C\textsubscript{1} = 0.8\) and \(D\textsubscript{OH}/C\textsubscript{1} = 0.01\) (Fig. 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 \(X\textsubscript{Cl}/X\textsubscript{OH}\) values identified in some apatite microphenocrysts can be partially reproduced by subsequent H\textsubscript{2}O-saturated crystallization, with \(D\textsubscript{Cl}/C\textsubscript{2} = 20\) and \(D\textsubscript{OH}/C\textsubscript{2} = 0.7\) (Fig. 6a–c), consistent with alkali melt–fluid halogen partitioning experiments under magmatic conditions (Signorelli & Carroll, 2000; Borodulin et al., 2009). However, our simple isobaric, isothermal H\textsubscript{2}O-saturated crystallization models cannot reproduce the range of \(X\textsubscript{Cl}/X\textsubscript{OH}\) ratios observed in the natural low \(X\textsubscript{Cl}/X\textsubscript{OH}\) subsidiary population (Fig. 8d–f). Decompression-induced degassing could account for some of this compositional variability but cooling, after the apatites have re-equilibrated under H\textsubscript{2}O-saturated conditions, appears to be the primary mechanism to drive compositions to the very high \(X\textsubscript{Cl}/X\textsubscript{OH}\) ratios observed in some eruptions (e.g. PP; Figs 7 and 10). The second, high \(X\textsubscript{Cl}/X\textsubscript{OH}\) and \(X\textsubscript{Cl}/X\textsubscript{OH}\) 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 pro- tracted volatile-undersaturated crystallization (Figs 5–7). This suggests that the main zone of magma storage and crystallization remained volatile-undersaturated until late in magmatic evolution (i.e. after the entrap- ment of biotite-hosted inclusions; see Stock et al., 2016) prior to past eruptions at Campi Flegrei. Thermodynamic (Rhyolite-MELTS) fractional crystallization 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. $/$C24 910 $/$C14 C) at pressures $/$H11407 150 MPa (Carroll & Blank, 1997; Webster et al., 2014; Stock et al., 2016). 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 crystallization (Fig. 11).

Seismic tomography shows that the current region of major melt storage beneath Campi Flegrei is $/$C24 1k m thick and at a depth of $/$C15k m (Zollo et al., 2008), which would equate to storage pressures of $/$C24 170–190 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 k m; Bohrson et al., 2006; Fowler et al., 2007; Cannatelli, 2012), and the volatile contents of melt inclusions from <15 ka Campi Flegrei eruptions (Fig. 11), which give saturation pressures up to 229 MPa (–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 6.5–9.4 km, which agrees very well with the current depth of major magma storage (7.5–8.5 km; Zollo et al., 2008). This appears to demonstrate that melt storage and crystallization 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 and 7) are consistent with H$_2$O-saturated fractionation at high $D_{Cl}$, 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 owing to degassing, so that any later thermal re-equilibration drives apatites to high $X_{Cl}/X_{OH}$ 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 and 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 subsidiary 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 halogenes in apatite (Brenan, 1993) suggest 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-XCl/XOH 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; Woo & Kilburn, 2010; Amoruso et al., 2014b; D’Auria et al., 2015). 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 allowing them to retain 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 H2O during ascent, resulting in low matrix glass H2O contents (Fig. 4f). Similar F and Cl contents in matrix glasses and melt inclusions (Fig. 4a–d) demonstrate that halogenes were not significantly degassed, despite DCli,m > 1 (Signorelli & Carroll, 2000). Relatively undepleted matrix glass Cl concentrations are consistent with kinetically induced vapour-melt disequilibrium during rapid ascent (Webster et al., 1993; Barclay et al., 1996; Shea et al., 2014).

The apatite microphenocrysts from Pisani 1 that branch away from the main population at moderate XCl/XOH are consistent with cooling (Fig. 10), but before any H2O-saturated crystallization 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 and 7a–c). This could be explained if part of the B–FdB magma crystallized from a melt with a different initial volatile content (i.e. lower Cl, higher H2O; Fig. 9a and b). The B-FdB eruption 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 Campian Iginimbrite magma chamber underlie the Campi Flegrei caldera (D’Antonio, 2011) and represent a potential assimilant. Melt inclusions from the Campian Iginimbrite extend to high H2O contents and Campian Iginimbrite glasses are consistently Cl-deficient compared with eruptions in the past 15 kyr (see Fig. 4a and b; Signorelli et al., 1999; Marianelli et al., 2006). Furthermore, B–FdB glasses are depleted in Sr and Ba and enriched in Zr relative to other <15 ka eruptions (Smith et al., 2011), again suggesting possible contamination from older (>15 ka) Campi Flegrei eruptions, including the Campian Iginimbrite (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 the 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 plot on the same cooling trend, they have different starting points and have variably rehomogenized. 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 or near the surface (Fig. 11).

Apatite inclusions in clinopyroxene and biotite record volatile-undersaturated crystallization (see above) and we would therefore expect the H2O contents of melt inclusions in the same phenocryst phases to correlate negatively with MgO, as H2O behaves incompatibly during magmatic evolution. However, there is no correlation between clinopyroxene-hosted melt inclusion H2O and MgO concentrations in any of the analysed eruptions, and most melt inclusions measured in this study contain ~2.0–3.8 wt % H2O (Fig. 4e). This may indicate that melt inclusion H2O contents have been reset after entrapment, reflecting the final (H2O-saturated)
equilibrium 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. Woods et al., 2000; Ingrin & Blanchard, 2006; Reubi et al., 2013). In contrast, re-equilibrium 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 $\sim$15 ka Campi Flegrei deposits attest to evolved melts at depth (i.e. $\geq$5 wt % $H_2O$ in Fig. 4e).

Campi Flegrei melt inclusions consistently have very low CO$_2$ contents (e.g. Marianelli et al., 2006; Arienzo et al., 2010; Stock et al., 2016), so we used a polynomial regression through published 850–950 $^\circ$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 $\sim$24–76 MPa for the degassed melt inclusions (2.0–3.8 wt % $H_2O$). This is equivalent to storage depths of $\sim$1.1–3.4 km, which coincide with the depth of small, melt-rich magma bodies imaged beneath the current Campi Flegrei caldera ($\sim$2–4 km; De Siena et al., 2010). We infer that ascending magmas interacted with these shallow melt bodies during 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 are more precise than the EPMA data. For example, apatite inclusions from Astroni 1 (Epoch 3) and the historical Monte Nuovo eruptions are typically F-rich and OH-depleted with higher $X_{Halogen}/X_{OH}$ 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 and 7). Epoch 2 (B-FdB) crystals have similar $X_{OH}/X_{OH}$ ratios to those from Epoch 1 but cannot be compared directly given their distinct compositional trajectory (Fig. 7b and c).

Melt inclusion halogen contents are typically lower in Epoch 1 than in later explosive eruptions (Fig. 4a and c), consistent with the more primitive Epoch 1 major element glass compositions (Figs 2 and 3). As $D_{F}^{m} > D_{Cl}^{m} > D_{H_2O}^{m}$ during apatite crystallization (see Supplementary Data), we would anticipate melt $H_2O$ 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 $X_{Halogen}/X_{OH}$ than those forming from Epoch 3 magmas, 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; $C_i$), changing apatite compositions without significantly affecting mineral phase stabilities or the trajectory of apatite compositional evolution. Specifically, the change to higher $X_{Halogen}/X_{OH}$ in Astroni 1 (Epoch 3) and Monte Nuovo suggests a decrease in melt $H_2O$ concentrations at apatite-in ($C_i$) relative to Epoch 1 (Fig. 9a and b). At Campi Flegrei, Rhyolite-MELTS models demonstrate that $C_i$ depends on the $H_2O$ content of the melt at the liquidus, and does not change significantly as a result of 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 (e.g. melt inclusion analysis). Apatite microphenocrysts remain in equilibrium with their host melts on geological 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 crystallization. In explosive Campi Flegrei eruptions, apatite inclusions record persistent volatile-undersaturated conditions until late in the crystallization history of the evolving magma, interpreted to occur in a deep magma reservoir at $\sim$5–8 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 $H_2O$-saturated crystallization. The compositional diversity of
The interaction between eruptions suggests that the H$_2$O 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.

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SUPPLEMENTARY DATA

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

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