

The volatile history of past volcanic eruptions

by

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“When we speak of the igneous rocks of our own times, we mean that small portion which happens in violent eruptions to be forced up by elastic fluids to the surface of the earth. We merely allude to the sand, scoriae, and lava, which cool in the open air; but we cannot obtain access to that which is congealed under the pressure of many hundred, or many thousand atmospheres.”

- Charles Lyell (1830)

ABSTRACT

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Volatile elements play an important role in almost every aspect of sub-volcanic systems, from the generation and storage of magma, to the timing and style of volcanic activity. Currently, the most common method for assessing pre-eruptive magmatic volatile contents is through analysis of trapped melt inclusions. However, the reliability of this record is uncertain, necessitating development of new, independent petrologic methods for determining the pre-eruptive volatile contents of past eruptions. This thesis combines physical and chemical models with empirical analyses to develop the use of apatite as a magmatic volatile ‘probe’.

The first research chapter investigates well-documented difficulties in electron microprobe analysis of apatite volatile concentrations. These are found to be caused by electron-beam induced heating and electric field generation. In determining these effects, it is possible to identify optimal operating procedures for apatite analysis. The next chapter explores the theoretical evolution of apatite volatile compositions as a function of magmatic evolution, building on previous work to develop thermodynamic models that relate crystal compositions to fluid systematics during fractional crystallisation. These provide a qualitative framework for interpreting apatite compositions in natural volcanic systems.

The remainder of the thesis is dedicated to identifying new insights that can be gained from the use of apatite as a magmatic volatile ‘probe’; this method is applied to constrain pre-eruptive processes at Campi Flegrei, Italy. Texturally-constrained apatite analyses are used to create a time-series of magmatic volatile evolution in the build-up to eruption. This reveals that volatile saturation occurred late in magmatic evolution, and represents a potential eruption trigger. Apatites from different eruptions show a long-term temporal variability in the H₂O contents of primitive melts feeding Campi Flegrei, which correlates with different epochs of activity. Melt inclusions from all eruptions have re-equilibrated post-entrapment. This study demonstrates the potential utility of apatite for investigating pre-eruptive volatile behaviour in apatite-saturated magmas.

EXTENDED ABSTRACT

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Volatile elements play an important role in almost every aspect of sub-volcanic systems, from the generation and storage of magma, to the timing and style of volcanic activity. Currently, the most common method for assessing pre-eruptive magmatic volatile contents is through analysis of trapped melt inclusions. However, the reliability of this record is uncertain, necessitating development of new, independent petrologic methods for determining the pre-eruptive volatile contents of past eruptions. Due to its ubiquity and ability to incorporate all major magmatic volatiles, analysis of apatite has the potential to help decipher magmatic volatile histories. The principle aims of this thesis are to develop the use of apatite as an alternative magmatic volatile ‘probe’, and to utilise it to gain new insights into pre-eruptive processes in the Campi Flegrei system, Italy. These are achieved using physical and thermodynamic models, in combination with empirical analysis of natural apatites and hydrous glasses.

Chapter 3 is a stand-alone analytical study that investigates the causes and mechanisms of well-documented but poorly understood temporal variability in halogen X-ray count rates, observed during electron microprobe analysis of apatite. This effect frequently results in erroneous volatile concentration measurements in apatite, limiting its use for determining magmatic processes. I tackle this directly by creating secondary ion mass spectrometry depth profiles of points on apatite crystals previously subject to electron-beam exposure. Through comparison with statistical models of electron-matter interactions and X-ray diffraction data, the observed count rate variability is shown to be an intrinsic crystallographic response to the thermal and electric fields induced within samples by the incident electron-beam. During irradiation of fluorapatite, halogens migrate towards the sample surface, likely through interstitial sites in the crystal structure. At the surface, they experience less X-ray attenuation, corresponding with an increase in count rates. With prolonged irradiation, crystals begin to undergo thermally-driven

breakdown and halogen loss, causing a long-term decline in count rates. Results show that increased beam currents amplify both the thermal and electric fields, inducing faster halogen migration. Furthermore, halogen migration is both highly anisotropic and composition dependant. The interstitial sites that facilitate surface enrichment are aligned along the crystal *c*-axis, and migration is only possible in the *a*-axis direction under ‘extreme’ electron-beam operating conditions (i.e. high beam currents). Similarly, halogen incorporation off of mirror planes in the crystal structure in near end-member chlorapatites alters the geometry of the interstitial sites, inhibiting volatile migration. This study suggests that after irradiation has stopped, the occupation of interstitial sites would be unstable and halogens may relax back to their original positions on long timescales or with sample heating.

Chapter 4 builds on previous work to develop thermodynamic models that predict the theoretical compositional evolution of apatite during volatile-undersaturated fractional crystallisation and during magmatic evolution in the presence of different fluid phases. The models take a two-step approach, first calculating changes in the concentrations of F, Cl and H₂O in the silicate melt as a function of the degree of crystallisation, then computing the volatile composition of apatite in equilibrium with the melt at each stage. Model input parameters and assumptions are discussed, and outputs are presented on binary plots of volatile ratios that permit examination of trends in the exchange reactions that contribute to filling the apatite volatile site. Simulations are run using a range of potential input parameters relevant to the Campi Flegrei system, to explore the compositional space that can be accessed by fractional crystallisation in each fluid scenario. Results show that certain trajectories of apatite volatile evolution can only be achieved by crystallisation in the presence of particular magmatic fluids. In combination with simulations of apatite compositional evolution in response to changes in pressure and temperature, these new models can be compared with natural volcanic apatite analyses to qualitatively assess magmatic fluid systematics at the time of crystallisation or crystal-melt re-equilibration.

The remainder of the thesis is dedicated to identifying new insights that can be gained from the novel use of apatite as a magmatic volatile ‘probe’. This is achieved by applying the analytical and theoretical advancements from Chapters 3 and 4 to constrain pre-eruptive processes at Campi Flegrei. Models of magma chamber evolution commonly assume relatively slow, incremental assembly under volatile-saturated conditions, with eruptions triggered by an injection of new volatile-rich melt or overpressure generated

through protracted crystallisation. Chapter 5 tests this model, using texturally-constrained apatite and glass analyses to create a time-series of magmatic volatile evolution in the build-up to the Astroni 1 eruption of Campi Flegrei. Data show that, far from incremental development of a volatile-saturated system, the magma chamber remained persistently volatile-undersaturated over long time periods in the build-up to eruption. Furthermore, volatile saturation and final pre-eruptive ‘priming’ of magmatic systems may only occur on very short timescales, on the order of days to a few years before eruption. This late-stage volatile saturation likely acted to trigger the Astroni 1 eruption. This result implies that the interval between eruptions at Campi Flegrei depends directly on recharge rate and the timescale of upper crustal storage. The findings of this study have importance for monitoring of Campi Flegrei and other hazardous systems, suggesting that ground-deformation and seismic evidence for long-term magma chamber assembly may not represent legitimate precursory activity. Rather, pre-eruptive activity may be characterised by the attainment of volatile saturation.

The final chapter of this thesis compares the compositions of apatites and glasses from eight different eruptions of Campi Flegrei, to identify temporal trends in pre-eruptive processes and volatile concentrations. Compositional trends in apatite microphenocrysts suggest a three-stage model of pre- or syn-eruptive magmatic fluid evolution for Campi Flegrei eruptions. In the first stage, magmas undergo protracted volatile-undersaturated crystallisation at depth (~7-7.5 km), as identified in Chapter 5. Before eruption, they saturate in a supercritical hydrosaline fluid phase. They then ascend to shallow crustal levels (~2-3 km) and apatites record low pressure, vapour-saturated conditions. Melt inclusion H₂O contents record only shallow crustal, volatile-saturated conditions and have likely re-equilibrated on ascent. Thus, using apatite to independently check its reliability, this study corroborates the fickleness of the melt inclusion volatile record. In addition to constraints on pre-eruptive fluid evolution, apatite microphenocrysts record a systematic difference in the pre-eruptive volatile budgets of different eruptions. This correlates with different epochs of activity and suggests that there is long-term variability in the volatile concentrations of primitive melts feeding the Campi Flegrei system in the past 15 kyr. Comparison between the pre-eruptive H₂O contents of different eruptions suggests that volatiles may exert a control on the style of volcanic activity at Campi Flegrei, with explosive mafic eruptions fed by the most volatile-rich magmas and evolved lava dome-forming melts containing relatively low pre-eruptive H₂O concentrations.

To Mum,
for always believing it was possible.

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Chapter 1

Introduction

This thesis aims to investigate and compare the pre-eruptive volatile histories of past volcanic eruptions on different temporal scales: first in the build-up to a single eruption, then over the long-term development of a volcanic system. The motivation for this is a wide range of theoretical, experimental and natural observations that suggest a fundamental link between magmatic volatile budgets and the behaviour of silicate melts in the Earth's crust. Existing studies rely heavily on analysis of erupted glasses (i.e. melt inclusions) to monitor dissolved volatile concentrations in sub-volcanic systems. However, the reliability of this approach is increasingly uncertain and data presented herein confirm that its applicability may be limited. A major focus of this work is therefore to develop the analytical techniques and theoretical understanding required to use igneous apatite crystals as an alternative magmatic volatile 'probe'.

1.1. Background

Magmatic volatiles are those species that exist dissolved within silicate melts under upper crustal pressures and temperatures, but exsolve on ascent to form a free gas or fluid phase. The most abundant volatile species in arc magmas are H₂O and CO₂, followed by SO₂ and halogen-group elements (Aiuppa *et al.*, 2009a; Symonds *et al.*, 1994; Wallace, 2005). Although these represent only a relatively minor compositional constituent of most terrestrial melts (generally <<10 wt%; e.g. Edmonds, 2008), they are disproportionately

important in volcanology. The exsolution and expansion of volatiles provides the impetus for volcanic eruptions, and their pre-eruptive behaviours and concentrations therefore play an important role in controlling the style and tempo of volcanism at the Earth's surface (Edmonds, 2008; Huppert and Woods, 2002; Roggensack *et al.*, 1997). Furthermore, volatile degassing represents a major global-scale impact of volcanic eruptions (Pyle and Mather, 2009), and sub-volcanic fluid separation controls the formation and distribution of many igneous ore deposits (e.g. Blundy *et al.*, 2015; Wilkinson, 2013).

Volatile elements are important in almost every aspect of the physiochemical architecture of magmatic plumbing systems. They affect the viscosity and density of silicate melts (Giordano *et al.*, 2008; Lange, 1994; Ochs and Lange, 1999), thus exerting a major control on the depth of magma storage (Annen *et al.*, 2006) and the crustal-scale structure of sub-volcanic systems (Christopher *et al.*, 2015; Wallace *et al.*, 1995). Furthermore, volatile concentrations may influence mineral phase stability during magmatic evolution (Gaetani, 1993; Pichavant *et al.*, 2002). Large-scale variability in volatile budgets has a fundamental impact on the liquid line of descent of evolving magmas, giving rise to the broadest-scale subdivision of igneous rocks on Earth: the alkali and tholeiitic series (Grove *et al.*, 2003; Zimmer *et al.*, 2010).

During magma ascent towards the surface, efficient open-system volatile exsolution promotes effusive volcanic activity and formation of lava domes, whereas viscous inhibition of gas escape can result in development of magma chamber overpressure and explosive eruptions (Cashman, 2004). The capacity for gas escape is a function of magma ascent velocity, bubble rise speed and coalescence, and the permeability of the surrounding country rock (Cashman and Sparks, 2013; Roggensack *et al.*, 1997). However, in many cases, eruption style also correlates with the pre-eruptive

concentration of dissolved volatile species in the melt phase (Cannatelli *et al.*, in press; De Vivo *et al.*, 2005; Raia *et al.*, 2000), due to the potential for greater oversaturation and fluid phase expansion during the rapid ascent of volatile-enriched melts (Edmonds *et al.*, 2014; Métrich and Wallace, 2008).

Volcanic eruptions are a major global hazard, causing large-scale humanitarian, economic and environmental damage. Given the fundamental role of volatiles in controlling volcanic processes, quantification of pre-eruptive volatile concentrations and fluxes is a primary volcanological objective. This may be achieved in two distinct ways: first, through measuring the composition and flux of exsolved volcanic gasses emitted at the Earth's surface, using satellite (e.g. Bluth *et al.*, 1994; Lopez *et al.*, 2013) or ground-based (e.g. Aiuppa *et al.*, 2009b; Aiuppa *et al.*, 2007; Symonds *et al.*, 1994) techniques. This is complicated by the necessity for deconvolution of volcanic and meteoric fluxes (Edmonds, 2008), and may be dangerous (Symonds *et al.*, 1994). Additionally, emissions can only be measured in active, degassing systems and thus cannot be used to assess pre-eruptive conditions in extinct or dormant volcanoes. These dormant systems are numerically significant, given that only ~575 of the >1545 Holocene eruptions occurred during historic times (Siebert *et al.*, 2011; Simkin and Siebert, 2015), and many of these were not monitored in the build-up to eruption. The second approach uses petrologic analysis of rocks and minerals to interpret the volatile histories of past eruptions (e.g. Boyce and Hervig, 2009; Edmonds *et al.*, 2014; Humphreys *et al.*, 2009; Lowenstern, 1995; Scott *et al.*, 2015). This is the focus of this thesis.

1.1.1. Established petrologic methods for assessing pre-eruptive volatile contents

A number of petrologic methods have been employed to assess the pre-eruptive concentrations of dissolved magmatic volatile species (Blundy and Cashman, 2008;

Wallace, 2005). Each of these has strengths and weaknesses, permitting or inhibiting their suitability for answering different geologic questions. In general, progress has followed technical developments (particularly in Secondary Ion Mass Spectrometry [SIMS] and Fourier Transform Infrared Spectroscopy [FTIR]) or the expansion of experimental datasets (Wallace, 2005). Existing petrologic methods for magmatic volatile assessment are briefly outlined below.

1.1.1.1. Phase equilibria studies

Studies have successfully assessed magmatic volatile contents (principally H₂O) through comparison between natural phase assemblages and experimental run products, produced at different starting compositions and pressure/temperature conditions (Fig. 1.1; Barclay *et al.*, 1996; Costa *et al.*, 2004; Rutherford *et al.*, 1985; Rutherford and Devine, 1988; Spulber and Rutherford, 1983). Both mineral compositions and phase proportions can be used to constrain crystallisation conditions (e.g. Blundy and Cashman, 2001). However, significant experimental campaigns are required to cover the range of parameter space necessary to constrain magma storage conditions (Fig. 1.1) and long experimental run times are often needed to attain equilibrium assemblages (i.e. weeks; Costa *et al.*, 2004). This approach is only capable of constraining magma volatile concentrations at the time of eruption (i.e. no temporal constraint) and typically assumes that the observed phase assemblage is in equilibrium with the bulk melt (Blundy and Cashman, 2008). Even where phase compositions and proportions converge, stability fields may be large, inducing uncertainty in pre-eruptive volatile estimates (e.g. Costa *et al.*, 2004).

A related approach uses compositional variability in equilibrium mineral-melt pairs to determine natural magmatic H₂O concentrations at the time of crystallisation (Putirka, 2008). Feldspar compositions are particularly susceptible to changing volatile concentrations, and a number of quantitative feldspar-melt hygrometers have been

developed through extrapolation of experimental datasets (Lange *et al.*, 2009; Mollo *et al.*, 2015; Waters and Lange, 2015). The necessary equilibrium mineral-melt pairs are not always available in natural samples, and disequilibrium is often not apparent (Humphreys *et al.*, in press). Feldspar-melt hygrometry is further limited by the compositional range of the current calibration dataset (Mollo *et al.*, 2015), and frequent low-temperature feldspar saturation (e.g. Fowler *et al.*, 2007) inhibits volatile determination early in crystallisation.

1.1.1.2. Fluid inclusions

Trapped inclusions of magmatic fluid within crystals can be used to determine the nature and composition of exsolved magmatic volatile phase(s) (Hansteen and Klügel, 2008; Roedder, 1992). These do not directly record the dissolved volatile component in the melt phase, and volatile-saturation at the time of entrapment is implicit. Fluid inclusions are

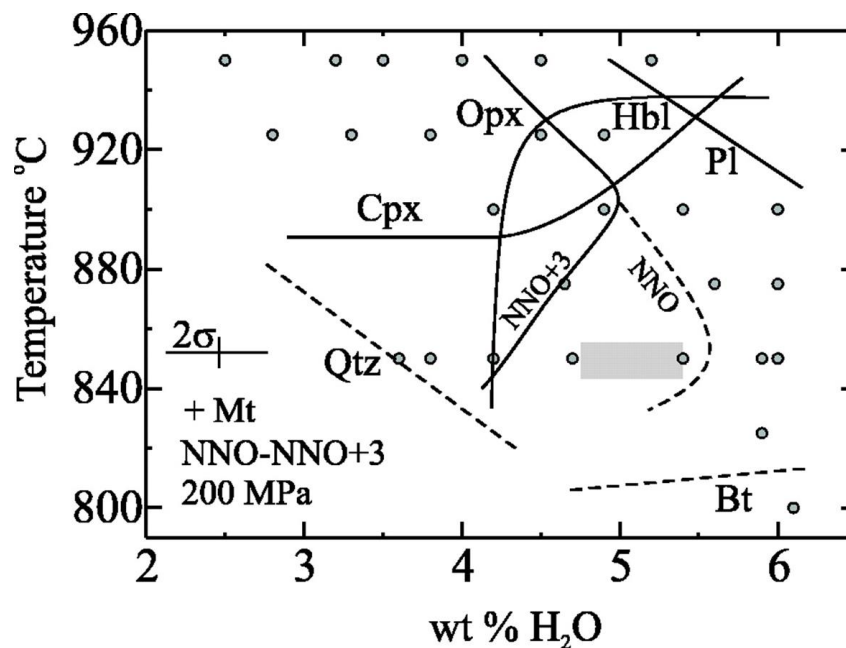


Figure 1.1 | Experimentally-derived phase relations in Volcán San Pedro, Chile (Costa *et al.*, 2004). Phase stabilities are shown in H₂O concentration versus temperature space, at 200 MPa, using a dacitic starting composition. Points show the range of experimental run conditions. Solid lines are defined stability fields, dashed lines are poorly-constrained phase boundaries. Cpx, clinopyroxene; Opx, orthopyroxene; Qtz, quartz; Hbl, hornblende; Pl, plagioclase; Bt, Biotite.

commonly used to decipher low-temperature processes in ore-forming environments (Heinrich *et al.*, 1999; Rusk *et al.*, 2004; Ulrich *et al.*, 1999) but have been applied in mantle (Andersen and Neumann, 2001; Roedder, 1965) and high-temperature volcanic environments (particularly where Cl or CO₂ is saturated; Roedder, 1992). The temporal evolution of the fluid phase may be assessed through analysis of inclusion trails (Heinrich *et al.*, 1999). However, interpretation is complicated by the occurrence of secondary inclusions (not trapped during crystallisation), the presence of multiple volatile-bearing components within inclusions, and potential for post-entrapment alteration of inclusion compositions during ascent (Hansteen and Klügel, 2008).

1.1.1.3. Hydrous glasses

Analysis of erupted volcanic glass is by far the most common method for assessing pre-eruptive concentrations of dissolved magmatic volatiles. Early studies undertook bulk analysis of lavas that were quenched either as subaerial obsidians (Dunbar and Kyle, 1992; Newman *et al.*, 1988) or submarine lavas (Byers *et al.*, 1985; Dixon *et al.*, 1991). Although this rapid quenching reduces the risk of post-entrapment volatile-loss, these glasses may hydrate at the Earth's surface (Friedman and Long, 1976) and inevitably underwent syn-eruptive degassing on ascent, limiting the usefulness of this technique for assessing pre-eruptive conditions (Bucholz *et al.*, 2013; Dixon and Stolper, 1995).

Melt inclusions are pockets of silicate melt that were trapped within crystals as they grew at depth (Fig. 1.2). As magmas ascend, their host crystals act as pressure vessels, potentially permitting inclusions to preserve pre-eruptive volatile concentrations (Lowenstern, 1995; Lowenstern, 2003). If inclusions are quenched on eruption, they can be analysed to determine magmatic volatile concentrations at the time of their host precipitation, overcoming the limitations of erupted lava analysis (e.g. Bégué *et al.*, 2015; Plank *et al.*, 2013; Raia *et al.*, 2000). This technique has been applied widely to determine

pre-eruptive volatile concentrations and magmatic processes in a variety of geologic settings, including arcs (e.g. Blundy *et al.*, 2010; Humphreys *et al.*, 2009; Portnyagin *et al.*, 2007; Sisson and Layne, 1993; Wallace, 2005), spreading centres (e.g. Saal *et al.*, 2002; Sobolev and Chaussidon, 1996; Wanless and Shaw, 2012) and hot spots (e.g. Koleszar *et al.*, 2009; Neave *et al.*, 2014; Sides *et al.*, 2014; Stefano *et al.*, 2011). Temporal information has been attained through analysis of inclusions within crystals that precipitated at different times during magmatic evolution (e.g. Blundy and Cashman, 2005; Roggensack, 2001).

Yet, as melt inclusions are increasingly applied to petrologic and volcanological problems, so their limitations have become apparent. A fundamental assumption is that the trapped liquids became isolated from the bulk melt during host precipitation.

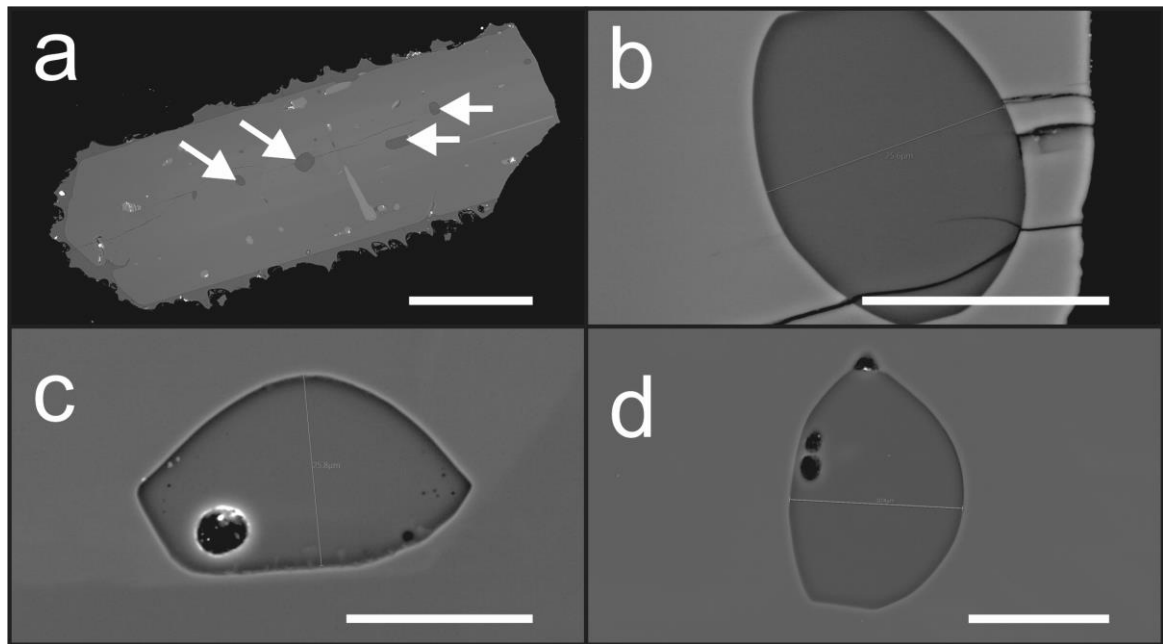


Figure 1.2 | Clinopyroxene-hosted melt inclusions from Campi Flegrei. a, Multiple melt inclusions (white arrows) within a clinopyroxene host crystal. **b,** Melt inclusion close to cracks in the host phenocryst, which may provide conduits for volatile leakage. **c,** Partially devitrified melt inclusion. **d,** Melt inclusion containing vapour bubbles, which may have formed during ascent. Scale bars are 250 μm in **a** and 25 μm in **b**, **c** and **d**.

However, this may not be the case during complex magmatic pressure-temperature-composition evolution, where crystal resorption and re-precipitation can form melt inclusion networks and permit re-connection with the bulk melt after initial entrapment (e.g. Faure and Schiano, 2005). If liquids are trapped, volatile elements in particular may still re-equilibrate with the bulk melt. This can occur through cracks in their host crystal (Fig. 1.2b) that commonly form due to dilatational stresses on ascent (Tait, 1992), or through diffusional re-equilibration (Lowenstern, 1995). The latter process is of particular importance because experimental studies have recently identified that H diffusion is very fast (relative to geological timescales) in many common host phenocrysts (Ingrin and Blanchard, 2006). In pyroxene, for example, melt inclusion H₂O concentrations can re-equilibrate within hours under magmatic conditions (Ingrin *et al.*, 1995; Woods *et al.*, 2000). Even in a closed system, the volatile composition of melt inclusion glasses may be altered by syn- or post-eruptive devitrification (Fig. 1.2c; Danyushevsky *et al.*, 2000; Danyushevsky *et al.*, 2002) or bubble growth (Fig. 1.2d; Moore *et al.*, 2015; Wallace *et al.*, 2015).

1.1.2. Assessing pre-eruptive volatile contents using mineral analysis

In light of the limitations of melt inclusions, petrologists are in need of new methods to assess pre-eruptive magmatic volatile concentrations. Direct analysis of mineral volatile compositions represents a promising alternative, which avoids problems such as post-entrapment volatile loss through cracks, devitrification and syn-eruptive bubble growth. This method can be subdivided into analysis of hydrous minerals, which have a dedicated volatile site in their crystal structure, and nominally anhydrous minerals, which incorporate volatiles as trace components.

1.1.2.1. Nominally anhydrous minerals

Pre-eruptive magmatic volatile concentrations have been assessed through analysis of minerals such as quartz, feldspars, pyroxene and olivine, which can incorporate small amounts of H₂O (hundreds of ppm) in their crystal structure (Edmonds *et al.*, in press; Johnson, 2006). Quantification of magmatic volatile contents from nominally anhydrous mineral analyses requires knowledge of mineral-melt partition coefficients (Aubaud *et al.*, 2004), which are often poorly constrained (Kohn and Grant, 2006) and may be complicated by incorporation of H₂O through complex coupled substitution mechanisms (Kohn *et al.*, 2005). Changes in magma volatile compositions can be assessed through measurement of volatile zoning profiles (e.g. Edmonds *et al.*, 2014) but mineral compositions may be overprinted by post-crystallisation diffusional re-equilibration with their host melts (Ferriss *et al.*, 2015). Furthermore, despite recent advances in analysis and sample preparation, the measurement of such small volatile abundances is still challenging. The method implicitly necessitates measurement of very low H₂O concentrations and analytical uncertainties may therefore be higher than in other petrologic methods for assessing magmatic volatile contents (Edmonds *et al.*, 2014).

1.1.2.2. Hydrous minerals

The most common hydrous minerals in terrestrial magmas are amphiboles, micas and apatite. Amphibole-group minerals incorporate halogens and other volatiles (OH and Li) into their crystal structure (Giesting and Filiberto, 2014) and have therefore been used previously to elucidate pre-eruptive magmatic volatile evolution (Humphreys *et al.*, 2009; Rowe *et al.*, 2008; Zhang *et al.*, 2012). However, the thermodynamics of amphibole-melt volatile exchange are a complex function of the crystal major element composition (Giesting and Filiberto, 2014), which in turn varies in response to changes in pressure and

temperature (Holland and Blundy, 1994; Johnson and Rutherford, 1989; Ridolfi *et al.*, 2010). Combined with limited experimental data regarding mineral-melt volatile exchange, this limits the application of amphiboles as magmatic volatile ‘probes’ (Giesting and Filiberto, 2014). Biotite similarly incorporates halogens (and OH) as integral structural constituents, but partitioning is affected by temperature (Icenhower and London, 1995) and crystal major element composition (Icenhower and London, 1997). Although attempts have been made to assess magmatic volatile contents through interpretation of biotite compositions (Coulson *et al.*, 2001; Zhang *et al.*, 2012), this is critically inhibited by the strong crystal-chemical control on volatile partitioning (Icenhower and London, 1997). Häuÿne has recently been used to determine magmatic SO₃ budgets (Cooper *et al.*, 2015) but given its scarcity, it is not considered further as a mineral volatile ‘probe’. In contrast with other hydrous minerals, apatite-melt F-Cl-OH partitioning is not significantly affected by crystal major element chemistry (Pan and Fleet, 2002) and it therefore shows great potential as magmatic volatile ‘probe’.

1.2. Apatite

Apatite is a common accessory mineral in igneous rocks and is present in many different volcanic and ore-forming systems (e.g. D'Antonio *et al.*, 1999b; Harlov *et al.*, 2002; Juster *et al.*, 1989; McConnell, 1973; Piccoli and Candela, 2002; Streck and Dilles, 1998). This is principally due to its high saturation temperature, poor solubility in naturally occurring melts and fluids, and the general incompatibility of phosphorous in other rock-forming minerals (Piccoli and Candela, 2002). In addition to its igneous occurrence, apatite forms in metamorphic (Cruft, 1966; Nash, 1984; Spear and Pyle, 2002) and sedimentary (Ruttenberg and Berner, 1993; Shemesh, 1990) environments, as well as in biological hard tissues (McConnell, 2012; Wopenka and Pasteris, 2005).

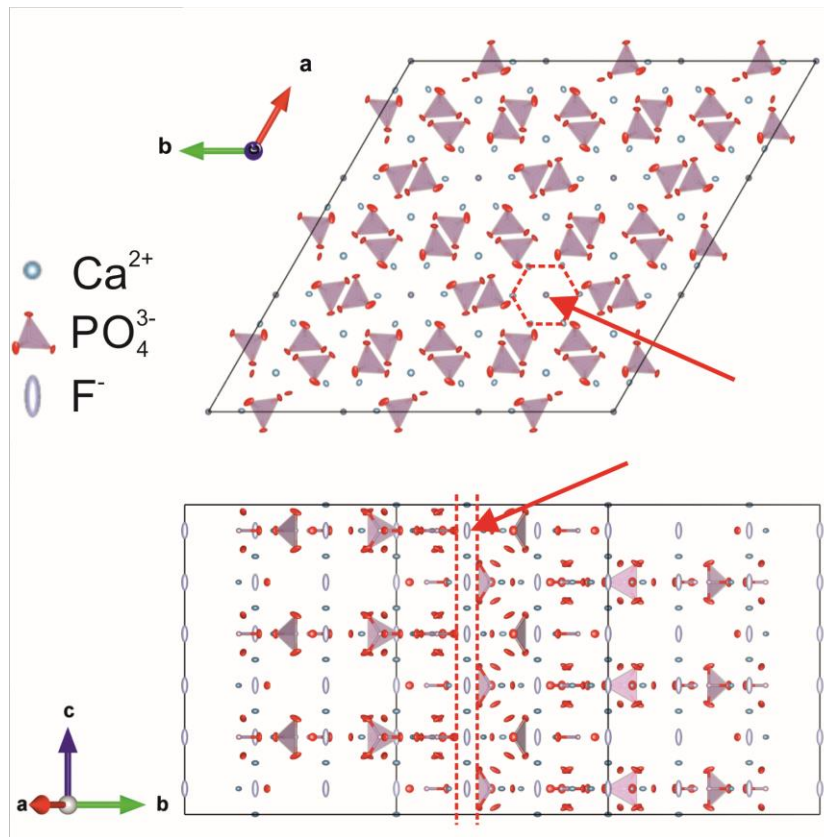


Figure 1.3 | The apatite crystal structure, measured by R.D. Johnson (Dept. Physics, Oxford). Single crystal XRD data showing the Durango fluorapatite crystal lattice at room temperature, parallel (top) and perpendicular (bottom) to c -axis. Atoms are shown as displacement ellipsoids with 90% probability. See legend for symbols. Planes show the outline of PO_4 tetrahedra. The arrows highlight the structural position of F atoms within the volatile channel site (Z site; red dashed lines).

Igneous apatites have the general formula $\text{Ca}_5(\text{PO}_4)_3\text{Z}$, where Z is typically F^- (fluorapatite), Cl^- (chlorapatite) or OH^- (hydroxylapatite; Elliott, 1994; Mackie and Young, 1974). However, the apatite structure is capable of significant deformation, permitting a wide range of mono- and poly-valent anionic and cationic substitutions (Pan and Fleet, 2002). This makes apatite something of a ‘dustbin mineral’ in igneous systems, significantly influencing the trace element budgets of silicate melts, in particular for Sr, U, Th and the rare earth elements (Prowatke and Klemme, 2006). Apatite-group minerals generally have a $P6_3/m$ hexagonal space group symmetry (Fig. 1.3), deforming to a near-

hexagonal $P2_1/b$ monoclinic structure in the Cl-rich end-member (Mackie *et al.*, 1972). The volatiles OH, F and Cl are held within a central anion channel site (the Z site) running parallel to the crystallographic c -axis (Fig. 1.3; see Chapter 3 for further crystallographic description; Elliott, 1994; Hendricks *et al.*, 1932).

1.2.1. Volatile incorporation

Halogens and OH are essential structural constituents in apatite and are incorporated as part of an exchange equilibrium (Candela, 1986; McCubbin *et al.*, 2015b; Webster and Piccoli, 2015). In stoichiometric crystals, these volatiles total two atoms per unit cell (Hughes *et al.*, 2014; Mackie and Young, 1974). Terrestrial igneous apatites are generally F-rich, with lesser Cl and minor OH, reflecting the relative compatibilities of these different volatiles in apatite (McCubbin *et al.*, 2015a; Piccoli and Candela, 2002). The thermodynamics of apatite-melt volatile exchange (and consequences for interpreting magmatic volatile budgets) are discussed in detail in Chapters 4, 5 and 6 but, importantly, the presence of a structural volatile site in the apatite formula precludes the use of Nernstian partition coefficients for interpreting magma compositions from apatite analyses (e.g. Boyce *et al.*, 2014). It is misleading to interpret changes in any one volatile component without considering changes in the concentration of the other two species, and the apatite-melt volatile relationship is thus better described by exchange coefficients (i.e. the ratio of two partition coefficients; McCubbin *et al.*, 2015a; Piccoli and Candela, 1994). In this thesis, apatite compositions are therefore presented on ‘mole fraction ratio plots’, showing crystal compositions in $X_{\text{Cl}}/X_{\text{OH}}$ versus $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{Cl}}/X_{\text{OH}}$ versus $X_{\text{F}}/X_{\text{Cl}}$ space (where X_{F} , X_{Cl} and X_{OH} are mole fraction F, Cl and OH, respectively). This permits identification of trends in all three exchange reactions that contribute to filling the apatite volatile site.

In addition to halogens and OH, CO_3^{2-} may partition into igneous apatite, typically in concentrations of no more than a few hundred ppm (up to ~1 wt% in rare pegmatitic or carbonatitic environments; Binder and Troll, 1989; Liu and Comodi, 1993). This may be incorporated either through substitution with the Z site anion component (usually accompanied by the formation of a vacancy) or as part of a coupled substitution with the phosphate (PO_4^{3-}) group (Fleet and Liu, 2003; Fleet and Liu, 2005; Fleet *et al.*, 2004; Tacker, 2008). Carbonate substitution in apatite is more prevalent in biominerals than in geological samples (e.g. Barralet *et al.*, 1998; Penel *et al.*, 1998).

Sulphur does not partition into the apatite Z site, instead substituting for PO_4^{3-} as an SO_4^{2-} group (Pan and Fleet, 2002). This occurs either as a coupled substitution with SiO_4^{4-} (Liu and Comodi, 1993; Rouse and Dunn, 1982) or with Na^+ (Chapter 6; Peng *et al.*, 1997). In either case, SO_4^{2-} incorporation is strongly dependent on oxygen fugacity and may also vary slightly in response to changes in pressure and temperature (Parat and Holtz, 2004; Parat and Holtz, 2005; Peng *et al.*, 1997).

1.2.2. Volatile diffusion

Halogens can diffuse rapidly through the apatite anion channel, principally by occupation of interstitial sites in the crystal structure (Jay *et al.*, 2011; Jay *et al.*, 2012). Diffusivities are consequently faster parallel to the crystallographic *c*-axis than *a*-axis, and increase at higher pressures and temperatures (Brenan, 1993). However, to date, diffusion measurements have only been published on natural apatites at 1 atm and 1 GPa (Brenan, 1993; Cherniak, 2010). Preliminary unpublished data suggest that halogen diffusivities under magmatic conditions (i.e. a few hundreds of MPa) may be significantly closer to the existing high pressure (1 GPa) estimates (Brooker R.A., personal communication) but this remains unconstrained. Fast diffusion results in the alteration of apatite volatile

zoning profiles on short timescales (Boyce and Hervig, 2008). Importantly, it also permits apatite microphenocrysts to remain in equilibrium with their host liquids on short timescales (days to a few years) under magmatic conditions (i.e. $>800^{\circ}\text{C}$; Chapter 5; Brenan, 1993). Sulphur and CO_3^{2-} diffusion rates have not yet been determined experimentally in apatite.

1.2.3. Previous applications in igneous systems

Owing to its ability to incorporate all major magmatic volatile species, apatite has recently received increasing attention as a potential magmatic volatile ‘probe’. Primarily, it has been used to investigate magmatic volatile budgets in lunar (Boyce *et al.*, 2014; Boyce *et al.*, 2010; Greenwood *et al.*, 2011; McCubbin *et al.*, 2011; McCubbin *et al.*, 2015b) and other extraterrestrial (Greenwood *et al.*, 2008; McCubbin and Jones, 2015; McCubbin and Nekvasil, 2008; Patiño Douce and Roden, 2006) environments. Terrestrial apatites have primarily been used to assess pre-eruptive magmatic SO_2 concentrations, due to the relative simplicity of crystal-melt partitioning (Dietterich and de Silva, 2010; Parat *et al.*, 2002; Scott *et al.*, 2015; Streck and Dilles, 1998). However, in some cases, apatites have been used to interpret the H_2O or halogen contents of pre-eruptive volcanic or plutonic systems on Earth (Boudreau and McCallum, 1989; Boyce and Hervig, 2008; Boyce and Hervig, 2009; Candela, 1986; Piccoli and Candela, 1994). The work presented in this thesis builds on these studies, developing the analytical techniques and theoretical understanding required to interpret the apatite record of pre-eruptive magmatic processes. Campi Flegrei is used as a case study to explore the application of these techniques.

1.3. The Campi Flegrei volcanic system

The Phlegrean Volcanic District in the Campanian region, central-southern Italy, includes the Campi Flegrei, Ischia and Procida volcanoes, as well as a number of submarine vents

in the Bay of Naples (Orsi *et al.*, 1996). Campi Flegrei is by far the largest volcano in the region, comprising a nested caldera system, with a maximum diameter of ~13 km (Barberi *et al.*, 1991). The main caldera structure is defined by partially-submerged collapse scarps that formed during the Campanian Ignimbrite (CI) and Neapolitan Yellow Tuff (NYT) eruptions (Fig. 1.4; D'Antonio *et al.*, 1999b; Orsi *et al.*, 1996). The caldera encompasses the town of Pozzuoli, and the city of Naples is close to the eastern border (Fig. 1.4). The Bay of Naples is to the South. It is one of the most active volcanoes in Europe, having produced >60 eruptions since the NYT event at 15 kyr (Smith *et al.*, 2011).

1.3.1. Petrogenesis and tectonic setting

The geodetic and geochemical processes of magma generation in the Mediterranean are complex (see Harangi *et al.*, 2006), but petrogenesis at the central Italian volcanoes is attributed to northwest subduction of the Ionian oceanic plate (Faccenna *et al.*, 2007; Mazzeo *et al.*, 2014). In the Phlegrean region, the slab is at about 400-450 km depth (Frepoli *et al.*, 1996; Sartori, 2003), and magma ascent occurs due to regional-scale crustal thinning, caused by the relative motions of the Italian peninsula and the extending Tethyan back arc basin (D'Antonio *et al.*, 2007; Patacca and Scandone, 1989; Tonarini *et al.*, 2004). Consequently, melts have a composition reflecting the mid-ocean ridge basalt (MORB)-like asthenospheric mantle wedge, variably overprinted by a slab-derived fluids (D'Antonio *et al.*, 1999a; D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2011; Tonarini *et al.*, 2004).

Since the Pliocene, the regional tectonic deformation has given rise to two populations of normal faults and fractures in Phlegrean Volcanic District, striking NE-SW and NW-SE (Fig. 1.4; Bartole *et al.*, 1984; Orsi *et al.*, 1999; Orsi *et al.*, 1996).

Extensional deformation along these lineations has formed a disconnected graben structure that transects Campi Flegrei (Orsi *et al.*, 1999). Both the distribution of Campi Flegrei vents and morphologies of the NYT and CI caldera collapse scarps have been significantly influenced by these geomorphological structures (Di Vito *et al.*, 1999; Orsi *et al.*, 1996; Smith *et al.*, 2011). In addition to tectonic deformation, Campi Flegrei is a type-example of bradyseismic, volcano-induced uplift (Chiodini *et al.*, 2003; Di Vito *et al.*, 1999; Lyell, 1837). This has caused significant additional fracturing and the re-activation of regional faults, particularly during recent volcanic resurgence within the NYT caldera (Orsi *et al.*, 1996).

1.3.2. Volcanic history

The time at which volcanism initiated at Campi Flegrei is unknown, as the oldest volcanic products are not exposed at the surface and have not been reached in drill cores (Scandone *et al.*, 1991). However, the earliest dated units formed at >60 kyr (Pappalardo *et al.*, 1999). These pre-CI eruptions occurred over a wide area within the Campanian region (Orsi *et al.*, 1996) and include both lava domes (e.g. Cuma and Punta Marmolita) and explosive tephra deposits (Pappalardo *et al.*, 1999). The CI eruption occurred at ~39 kyr, producing part of the current caldera depression (Fig. 1.4; Fedele *et al.*, 2011). The eruption ejected ~300 km³ of ash and pumice (~125 km³ dense rock equivalent [DRE]), dispersed over a region of ~3.7·10⁶ km² (Costa *et al.*, 2012; Marti *et al.*, 2016). Distal deposits have been identified as far away as southwest Russia (Pyle *et al.*, 2006). It represents the single largest European eruption in the past 200 kyr and has been implicated in triggering a significant volcanic winter and altering the behaviour patterns of Paleolithic humans (Black *et al.*, 2015; Costa *et al.*, 2012; Fedele *et al.*, 2003; Fedele *et al.*, 2008; Lowe *et al.*, 2012; Marti *et al.*, 2016; Sparks, 2005).

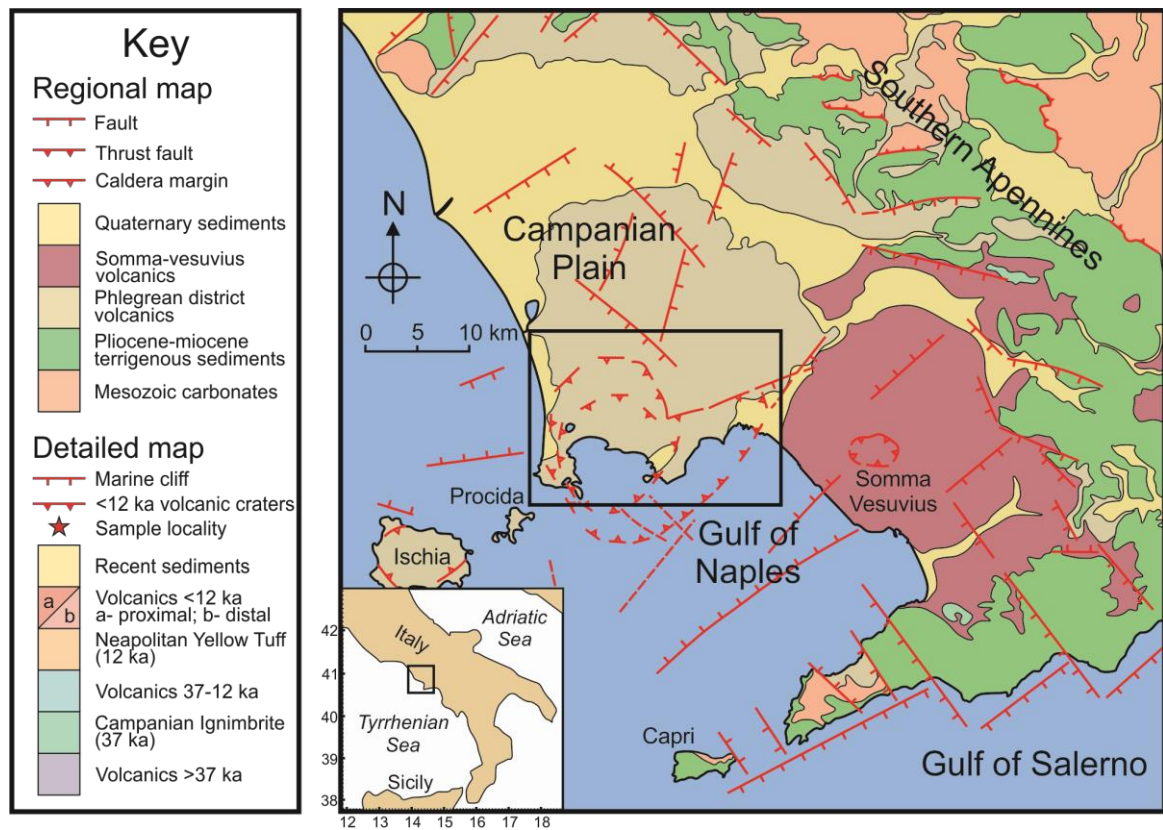


Figure 1.4 | (previous page) Geological maps of the Phlegrean Volcanic District, adapted from Orsi *et al.* (1996). Top: Regional map of the Phlegrean Volcanic District and surrounding area, showing major tectonic structures, regional-scale geology and the position of the CI and NYT calderas. Inset shows the location of the Campanian region within Italy. Bottom: Detailed geological map of the Campi Flegrei caldera area, showing major geological features. Sampling locations refer to eruptions in Chapters 5 and 6, and are as follows: 1.- Fondi di Bala, 2.- Monte Nuovo, 3.- Academia and Mt Olibano, 4.- Astroni 1, 5.- Pisani 1, 6.- Minopoli 1, 7.- Pomici Principali. With the exception of the lava eruptions (Table 6.1), sampling localities are from Smith *et al.* (2011).

Few studies have investigated the period of activity at Campi Flegrei between the CI and NYT eruptions. Multiple (possibly >9) explosive pyroclastic events occurred within the CI caldera in this period, collectively grouped as the ‘Tufi Biancastri’ (Orsi *et al.*, 1996). Some of these have been recognised in distal tephra records (Tomlinson *et al.*, 2012; Wulf *et al.*, 2004), including the widespread Y-3 tephra that is found in the eastern Mediterranean region (Albert *et al.*, 2015). The NYT eruption occurred at ~15 kyr (Deino *et al.*, 2004), forming the second of the two nested calderas that comprise the current Campi Flegrei structure (Fig. 1.4; Orsi *et al.*, 1996). Although significantly smaller than the CI event, the NYT eruption produced >40 km³ DRE of material, covering a region of >1000 km² (Deino *et al.*, 2004).

In the 15 kyr following the NYT event, Campi Flegrei eruptions can be broadly separated into three ‘epochs’, defined by periods of more intense activity, separated by quiescence (Di Vito *et al.*, 1999). Vent locations for these eruptions are within the pre-existing NYT caldera, largely along regional faults or the caldera boundaries (Di Vito *et al.*, 1999; Isaia *et al.*, 2009). Eruptions at these vents produced the cones and craterous morphology that typifies the current Campi Flegrei caldera floor (Orsi *et al.*, 1996). Notable morphological features include the Agnano Plain and Lake Averno craters (Fig. 1.4), which formed following the Agnano-Monte Spina and Averno eruptions, respectively (De Vita *et al.*, 1999; Di Vito *et al.*, 2011).

Epoch 1 occurred between ~ 15 and 10.6 kyr and produced 30-32 explosive eruptions, with a typical periodicity of ~ 70 yr (Di Vito *et al.*, 1999; Smith *et al.*, 2011). The Plinian Pomici Principali eruption was the largest of these, dispersing $\sim 0.85 \text{ km}^3$ DRE of tephra towards the northeast (Lirer *et al.*, 2001; Smith *et al.*, 2011), significantly beyond the Campanian region (Tomlinson *et al.*, 2012). Six low-magnitude explosive eruptions occurred in Epoch 2, between ~ 9.6 and 9.1 kyr, with an average periodicity of ~ 65 yrs (Di Vito *et al.*, 1999; Smith *et al.*, 2011). There was a long period (~ 4 kyr) of quiescence after Epoch 2. 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 $0.02\text{-}0.1 \text{ km}^3$, DRE; Smith *et al.*, 2011). However, uniquely within the past 15 kyr, this epoch also produced 4 effusive lava domes (Di Vito *et al.*, 1999; Melluso *et al.*, 1995). The large, Plinian Agnano-Monte Spina eruption also occurred in the middle of



Figure 1.5 | Contemporary woodcut image of the 1538 AD Monte Nuovo eruption, by Delli Falconi (in 1539 AD). The depiction clearly shows the eruption damaging buildings in nearby settlements (now Pozzuoli and Naples). It was originally published by Toledo (1539). This digitised version is from Morhange *et al.* (2006).

Epoch 3 (sometimes used to define Epoch 3a and 3b subdivisions; Isaia *et al.*, 2009). This eruption occurred in two Plinian phases, producing a similar volume of material to Pomici Principali (i.e. $\sim 0.85 \text{ km}^3$, DRE; Smith *et al.*, 2011; De Vita *et al.*, 1999). The most recent eruption at Campi Flegrei was Monte Nuovo in 1538 AD (Fig. 1.5; Di Vito *et al.*, 1987). This occurred after a >3 kyr dormant period (Piochi *et al.*, 2005), substantially greater than the typical inter-eruption time interval, and is therefore considered post-Epoch 3 (Smith *et al.*, 2011). Before the 1538 AD eruption, there were continual earthquakes, fumarolic emissions and uplift events in the Campi Flegrei area (Piochi *et al.*, 2005). Historic accounts indicate that these intensified within three months of the eruption, and in particular within the final 8-9 days (Guidoboni and Ciuccarelli, 2011).

Smith *et al.* (2011) provide a full stratigraphy of Campi Flegrei eruptions from the past 15 kyr. Tomlinson *et al.* (2012) outline the stratigraphy of the past 60 kyr. Details of temporal variability in the major and trace element and isotopic compositions of Campi Flegrei eruptive products are discussed in Chapter 6 (Section 6.1.1.). Similarly, further information regarding the specific eruptions analysed in this thesis are given in Chapters 5 and 6.

1.3.3. Current unrest and future risk

Campi Flegrei is one of the most hazardous volcanoes on Earth and is currently showing significant signs of unrest. The Neapolitan area experiences persistent earthquake activity, bradyseismicity and fumarolic emissions (Chiodini *et al.*, 2010; Chiodini *et al.*, 2003; De Martino *et al.*, 2014; Di Luccio *et al.*, 2015), with discrete episodes of intense activity ('seismic crises') in 1950-52, 1970-72, 1982-84 and 2012-13 (D'Auria *et al.*, 2015). In 1982, significant uplift and seismicity prompted the evacuation of $\sim 40,000$ people from the town of Pozzuoli (Barberi *et al.*, 1984). Since 2005, Campi Flegrei has been

undergoing continual uplift (Fig. 1.6), accompanied by seismicity, opening of new fumarolic vents (e.g. Pisciarelli; Fig. 1.7) and a change in the composition of surface gas emissions (Chiodini *et al.*, 2015; De Martino *et al.*, 2014). It is therefore imperative to understand pre-eruptive processes and controls on the timing and style of volcanic activity.

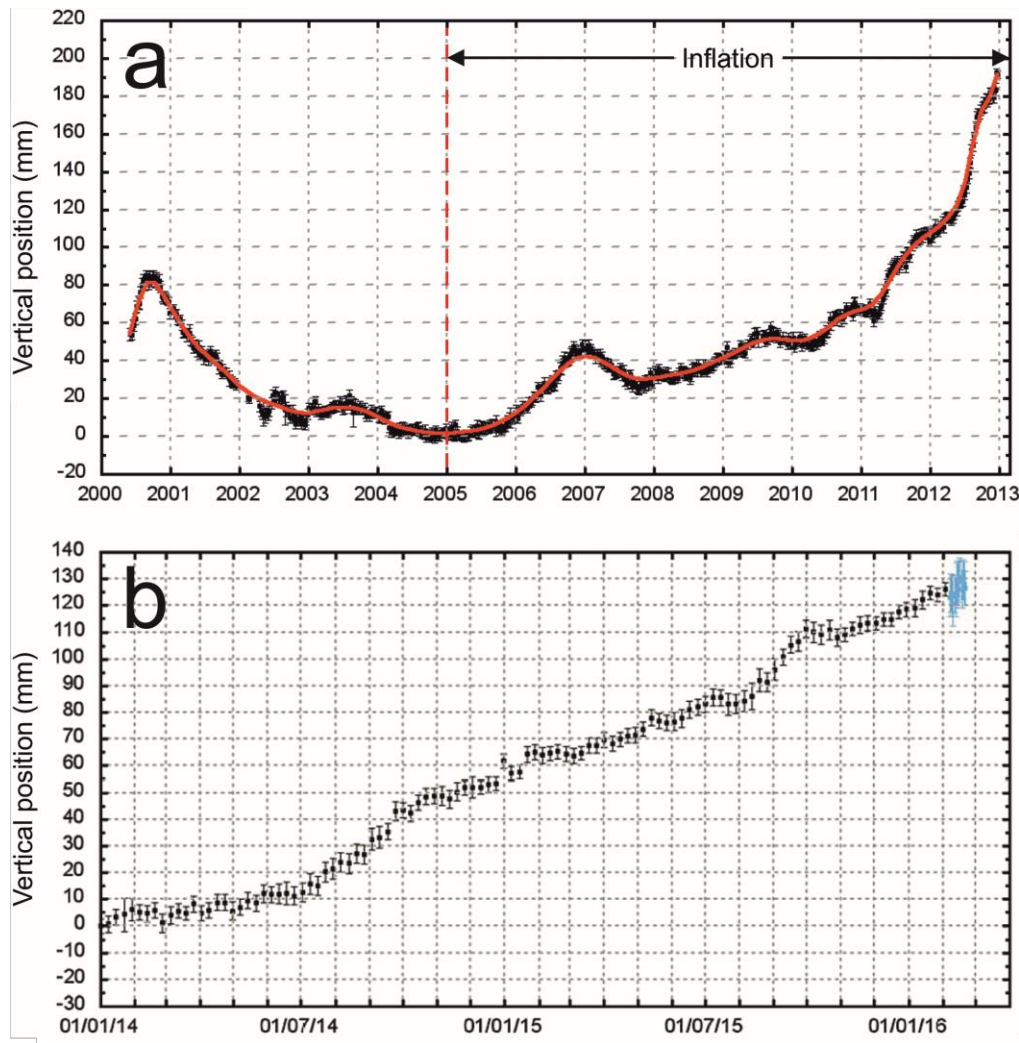


Figure 1.6 | Continuous GPS monitoring data from Campi Flegrei. a, Long-term monitoring data (April 2000 – 30 November 2012), showing the onset of the recent inflation episode (red dashed line), adapted from INGV (2013). **b,** Recent monitoring data (1 January 2014 – 22 February 2016), adapted from INGV (2016). All measurements were made at the RITE GPS Station at Rione Terra, Pozzuoli. Black points show weekly average deformation. Blue points show unprocessed daily measurements. The solid red line shows a rolling average (period unspecified).

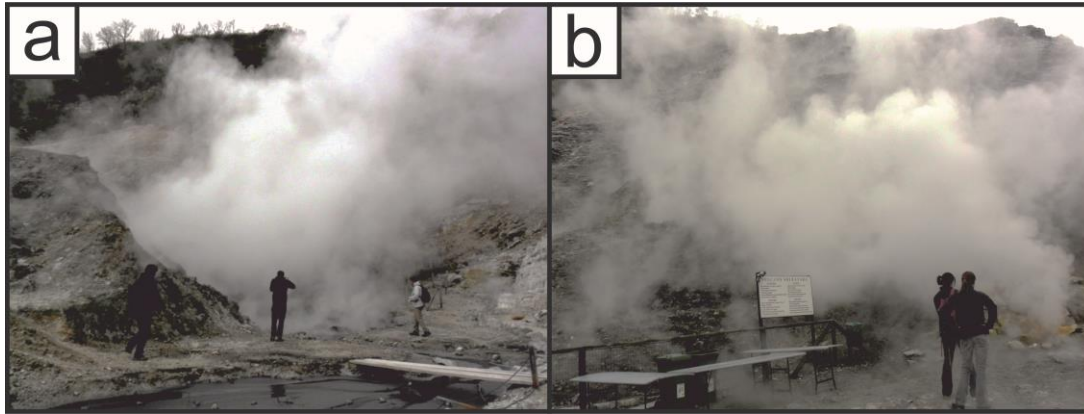


Figure 1.7 | Fumarolic gas emissions at Campi Flegrei. **a**, Geothermal activity at Pisciarelli that began in 2004 and has intensified in recent years (Chiodini *et al.*, 2015). **b**, Long-lived fumarole system at Solfatara. These photos were taken during fieldwork for this thesis in 2013. The scale is given by the people.

The risk posed by the Campi Flegrei system is accessibly encapsulated by its highest ‘devastation potential’ (1000) in the game Volcano Top Trumps. The 1538 AD Monte Nuovo eruption hugely affected the local population: damaging buildings, destroying crops and wildlife, and killing at least 30-32 people (Fig. 1.5; Di Vito *et al.*, 1987; Dvorak and Gasparini, 1991; Guidoboni and Ciuccarelli, 2011). Today, 350,000 people live within the NYT caldera (Orsi *et al.*, 2004; Selva *et al.*, 2012) and, by a recent estimate, 2.5 *million* people in the Neapolitan area would be immediately affected in the event of a medium-magnitude (i.e. deposit cover of 100-500 km²) eruption (Carlino *et al.*, 2015; Orsi *et al.*, 2004). Despite this, a 2013 survey of residents living in the ‘red zone’ found that 76% of people were aware of an active volcano at Campi Flegrei, but fewer than 27% thought that this was their major volcanic risk (compared to 71% for Vesuvius), and only 17% knew of an Emergency Plan (Ricci *et al.*, 2013).

1.3.4. Case study rationale and hypotheses

Campi Flegrei was selected as the case study for this thesis for a number of reasons: firstly, although matrix glass compositions range from basaltic-trachyandesites to phonolites and trachytes (51.7-63.8 wt% SiO₂; e.g. Smith *et al.*, 2011), apatite is present

as an accessory phase in almost every erupted rock type (D'Antonio *et al.*, 1999b). Furthermore, the melts feeding different eruptions are thought to be related primarily through fractional crystallisation of a single shoshonitic parental magma (Civetta *et al.*, 1991; Villemant, 1988; Chapter 6). The apparent null-effect of processes such as crustal assimilation in controlling the liquid line of descent (Civetta *et al.*, 1991; D'Antonio *et al.*, 2007) reduces the number of variables in the interpretation of apatite compositions. Second, Campi Flegrei has produced a range of eruption styles in the past 15 kyr, from large plinian events to effusive lava domes (Di Vito *et al.*, 1999; Smith *et al.*, 2011). The cause of this variability is largely unknown but, through understanding spatiotemporal variability in pre-eruptive volatile compositions, apatite analysis may contribute towards identifying this control. Finally, Campi Flegrei is a highly hazardous system and apatite may provide new insights into pre-eruptive volatile systematics, aiding volcano monitoring and improving civil protection.

1.4. Outline of thesis

The principal aims of this thesis are to develop the use of apatite as a petrologic method for determining magmatic volatile contents, and to use this to gain a better understanding of pre-eruptive processes in the Campi Flegrei system. The apatite record is compared with melt inclusion compositions to explore the different information that can be attained from these magmatic volatile ‘probes’. The thesis is divided into three main themes:

1. **Analysis (Chapters 2 and 3)** - What is the best analytical method for accurate and reproducible light element (i.e. volatile) measurement in apatite?
2. **Interpretation (Chapter 4)** - What controls the volatile compositions of igneous apatites and how might these be disentangled to interpret magmatic processes?
3. **Application (Chapter 5 and 6)** - What information can apatite provide about pre-eruptive processes in the Campi Flegrei system?

Chapter 2 outlines the analytical methodologies used to measure the major, trace and volatile element compositions of natural apatites and glasses presented in Chapters 5 and 6. This chapter includes an outline of the sample preparation methods and details of electron microprobe (EPMA) and SIMS operating conditions. Analytical uncertainties are presented for each of the elements analysed. These methodologies are not relevant to Chapter 3, which has a separate methods section. In Chapter 2, SIMS apatite analyses are calibrated using independently characterised apatite standards. The independent standard compositions were measured by M.C.S. Humphreys.

Chapter 3 is a stand-alone study that explores analytical problems in the measurement of apatite volatile concentrations by EPMA. This is motivated by the observation that halogen X-ray count rates vary through time during apatite electron-beam exposure (Goldoff *et al.*, 2012; Stormer *et al.*, 1993), limiting the accuracy of measurements. Although this effect is widely reported in the literature it remains poorly understood. In this chapter, I identify the causes and mechanisms behind the effect, using a SIMS depth profiling technique, combined with temperature-controlled X-ray diffraction (XRD) experiments and Monte Carlo statistical simulations of electron-matter interactions. The XRD data were collected, processed and described by R.D. Johnson. I integrated the results with the other parts of the study and used them in the discussion. This chapter is published in *American Mineralogist* as Stock *et al.* (2015), doi: 10.2138/am-2015-4949.

Chapter 4 is a theoretical study that develops thermodynamic models to predict the compositional evolution of the apatite volatile component as a function of magmatic fractional crystallisation in the presence of different fluids. This builds on early work by Candela (1986). The chapter includes a detailed description of the model inputs and assumptions. Although the theory is widely applicable in different volcanic systems, the

input values used in this thesis are specifically relevant to Campi Flegrei. The model outputs are ‘families of curves’ that can be compared with natural datasets. In combination with published methods for predicting the compositional evolution of apatite as a function of pressure and temperature (Piccoli and Candela, 1994), these can be used to qualitatively constrain magmatic fluid systematics during apatite crystallisation, or while crystals were in equilibrium with the melt.

The remainder of the thesis is devoted to identifying information that can be attained through the novel use of apatite as a magmatic volatile ‘probe’. The analytical and theoretical advancements from Chapters 3 and 4 are applied to obtain new constraints on pre-eruptive processes at Campi Flegrei. Some of the samples analysed were collected by V.C. Smith and R. Isaia before this project began (see Section 6.2. for details). Chapter 5 uses texturally-constrained apatite and glass analyses, in combination with Rhyolite-MELTS thermodynamic models (Gualda *et al.*, 2012), to develop a novel temporal record of magmatic volatile evolution in the build-up to the Astroni 1 eruption. Results indicate that the magma chamber remained persistently volatile-undersaturated until late in the crystallisation history of the evolving magma. Furthermore, volatile saturation may only occur on very short timescales, on the order of days to a few years before eruption. Late-stage saturation in volatiles likely triggered the Astroni 1 eruption. These findings have significant implications for volcano monitoring, which are outlined at the end of this chapter. A version of this chapter is published in *Nature Geoscience* as Stock *et al.* (2016), doi: 10.1038/ngeo2639.

Chapter 6 compares apatite and glass data from eight different eruptions of Campi Flegrei in the past 15 kyr. In combination with a compilation of literature data, melt inclusion and matrix glass compositions are used to investigate the liquid line of descent of Campi Flegrei melts. Variability in apatite microphenocryst volatile compositions is

interpreted to construct a three-stage model of magmatic fluid evolution on short pre-eruptive timescales. This record is compared with melt inclusions, showing that the glass compositions are altered at shallow crustal levels on ascent. Finally, systematic compositional variability in apatite microphenocrysts is used to investigate potential long-term changes in the pre-eruptive volatile contents of Campi Flegrei melts and to explore the link between magmatic volatile concentrations and the style of volcanic activity in the system. Data suggest that the volatile concentrations of the primitive melts feeding the Campi Flegrei system changed through time, correlating with isotopic variability in the different epochs of activity. Variability in pre-eruptive volatile contents may contribute towards understanding the diversity of eruptive styles at Campi Flegrei, with explosive mafic eruptions fed by volatile-rich magmas and lava dome-forming melts containing low pre-eruptive H₂O concentrations. A version of this chapter is in preparation for submission to the *Journal of Petrology*.

Chapter 2

Analytical methods

Much of the material in this chapter is presented as supplementary methods in:

Stock M.J., Humphreys M.C.S., Smith V.C., Isaia R., and Pyle D.M., 2016.

Late-stage volatile saturation as a potential trigger for explosive volcanic eruptions.

Nature Geoscience, 9, 249-254, doi: 10.1038/ngeo2639.*

This chapter provides details of the sample preparation techniques and analytical methods used for measurement of mineral and glass compositions in Chapters 5 and 6. Chapter 3 has an independent, stand-alone methods section.

2.1. Sample preparation

Samples from all of the studied volcanoclastic deposits (i.e. explosive eruptions) and the Accademia lava dome (see Table 6.1) were crushed, homogenised and wet sieved to remove the fine (<44 µm) component. They were then dried in an oven (~40 °C) before mineral separation. Clinopyroxene and biotite phenocrysts were hand-picked from the 250-500 µm size fraction. Apatite microphenocrysts were separated from the 44-250 µm

*Secondary ion mass spectrometer apatite analyses in this chapter are calibrated using independently characterised apatite F, Cl and H₂O standards. The independent standard compositions were measured by M.C.S. Humphreys for a separate study (unpublished).

size fraction using heavy liquid and magnetic separation techniques in the Faculty of Earth and Life Sciences, VU University, Amsterdam and the Department of Earth Sciences, University of Oxford, respectively. Diluted, density-controlled diiodomethane was used to remove material $<3 \text{ g cm}^{-3}$ and $>3.3 \text{ g cm}^{-3}$. The remaining sample was passed through a Franz magnetic separator to remove any residual magnetic material. This method produced an almost pure apatite separate. Crystals and matrix glass ash grains were mounted in epoxy resin, with clinopyroxenes mostly on the (010) and biotites mostly on the (100) crystal faces, before being ground and polished for analysis.

Lava dome samples (Accademia and Mt Olibano; Table 6.1) were cut to remove weathered outer layers before being mounted and prepared as polished thin sections (30 μm thickness).

2.2. Sample mapping

All samples were carbon coated to a thickness of $\sim 30 \text{ nm}$ and mapped, using an FEI Quanta 650 FEG scanning electron microscope (SEM), with a 20 kV, $\sim 6\text{--}7 \text{ nA}$ beam in the Department of Earth Sciences, University of Oxford. Backscattered electron (BSE) maps were created for sample navigation. These were also used for identification and examination of apatite and melt inclusions within phenocryst phases. Only apatite inclusions away from cracks and fully enclosed by their host phenocryst were analysed, to ensure that they were trapped during phenocryst growth and were unable to subsequently re-equilibrate with the melt/fluids. Furthermore, as far as possible, apatite crystals were selected for compositional analysis where the *a*- or *b*-axis was in the plane of the mount, in order to reduce the potential for diffusional modification during analysis (Goldoff *et al.*, 2012; Stormer *et al.*, 1993; Chapter 3). Melt inclusions were rejected if they showed evidence of post-entrapment crystallisation or if they were touching cracks in their host

phenocryst, which may have provided pathways for volatile leakage (although the absence of cracks cannot be verified in the third dimension). Ash grains were screened to identify microlite-free regions for compositional analysis.

Energy-dispersive spectrometry (EDS) phosphorus maps (x215 magnification, 14% image overlap, 2048 pixel wide resolution, 5 μ s pixel dwell time, 8 iterations) were created for thin section samples. These were overlain on the BSE images, thus permitting easy identification of apatite microphenocrysts in the microcrystalline (trachytic texture) groundmass of lava dome samples.

2.3. Electron microprobe analysis

Prior to electron microprobe analysis (EPMA), samples were briefly re-ground and polished to remove any potential compositional alteration induced by electron-beam exposure during SEM mapping (Goldoff *et al.*, 2012; Stormer *et al.*, 1993; Chapter 3). Major and trace element (including halogen) compositions of minerals (apatites and biotites) and glasses were analysed using a JEOL 8600 wavelength-dispersive electron microprobe (EPMA) at the Research Laboratory for Archaeology and the History of Art (RLAHA), University of Oxford. The instrument was calibrated with appropriate mineral and oxide standards for each set of beam conditions. Samples were carbon coated (~30 nm thickness) simultaneously with secondary standards, in order to avoid variability in light element X-ray attenuation. In total, over 300 glass analyses and 1,200 apatite analyses were acquired on samples from eight different eruptions (Table 6.1). For each element analysed, the background was determined by counting for half of the on-peak count time on either side of the peak.

Apatite: Apatite analyses were collected at 15 kV, using a low beam current (10 nA), defocussed spot (5 μ m diameter) and the lowest possible halogen count times, with

halogens always analysed first. This routine limits the potential for time-dependent variability in halogen X-ray counts during analysis (Goldoff *et al.*, 2012; Stormer *et al.*, 1993; Chapter 3), while maintaining sufficient count rates to achieve reasonable precision for low-concentration elements (i.e. Cl). Elements analysed (and corresponding on-peak count times in parentheses) include: F (60 s), SiO₂ (60 s), Na₂O (60s), Al₂O₃ (30 s), P₂O₅ (20 s), Cl (120 s), CaO (20 s), and SO₂ (120 s). All sulphur was measured as SO₂ after comparison of the peak position in natural samples with the peak positions in anhydrite (CaSO₄) and galena (PbS) standards.

Glass: For glass analysis, care was taken to minimise the risk of Na and Si migration during electron-beam exposure (Humphreys *et al.*, 2006), again by using a low voltage (15 kV), low beam current (6 nA) and defocussed spot (10 µm diameter) for major element analysis. Elements analysed using these operating conditions (and corresponding on-peak count times in parentheses) include: SiO₂ (30 s), Al₂O₃ (30 s), Na₂O (12 s), MgO (30 s), P₂O₅ (60 s), CaO (30 s), K₂O (30 s), TiO₂ (30 s), Cl (50 s), MnO (40 s), and FeO (30 s). All Fe was measured as FeO (i.e. FeOt).

The 6 nA glass analytical routine (above) generates sufficient count rates for measurement of most elements, while minimising the potential for electron-beam induced sample damage (Humphreys *et al.*, 2006). However, SO₂ and P₂O₅ are in low abundance in Campi Flegrei glasses (typically <0.2 wt%) and higher beam currents are required to increase count rates (reducing detection limits and analytical uncertainties) for reliable analysis of these elements. A sub-set of glasses were therefore examined for these low concentration elements in a second, separate analysis, using a 30 nA, 15 kV electron-beam with a defocussed spot (10 µm diameter). Measurements were made as close to the original analysis position as possible. Elements analysed (and corresponding on-peak count times in parentheses) include: F (90 s), P₂O₅ (90 s), Cl (90 s), and SO₂ (90 s). An

average matrix glass or melt inclusion major element composition from each eruption was used in the matrix correction routine for these analyses (varying the input major element composition between the most mafic and most evolved composition from each eruption did not change the results outside of uncertainty). Fluorine is below EPMA detection limits even at high beam currents and secondary ion mass spectrometry (SIMS) was used to measure this element. There is good agreement between Cl concentrations in 6 nA and 30 nA analyses. In general, there is less scatter in the 6 nA dataset (presumably because of reduced electron-beam induced volatile migration; Humphreys et al., 2006) and this is therefore used for most Cl glass analyses in this thesis. However, the higher beam current (30 nA) analyses are used where Cl is present only in low concentrations (typically <0.6 wt%), in melt inclusions from more mafic eruptions (Pomici Principali, Pisani 1, Minopoli 1; Chapter 6).

Biotite: Biotite analyses were collected at 15 kV, 15 nA and using a defocussed spot (5 μm diameter). Elements analysed (and corresponding on-peak count times in parentheses) include: F (60 s), Na_2O (20 s), SiO_2 (20 s), Al_2O_3 (20 s), MgO (20 s), Cl (50 s), K_2O (20 s), CaO (20 s), TiO_2 (20 s), FeO (20 s), and MnO (20 s).

Totals in glass analyses were typically in the range 95 to 99% and are not normalised in this thesis, unless otherwise stated. A few analyses had lower totals (~90% minimum) but were not excluded unless they also showed anomalous major element compositions, suggesting accidental analysis of crystals (e.g. melt inclusion host phenocrysts or microlites). Apatite totals were 96 to 102%, with totals >100% likely reflecting electron-beam induced halogen migration in near end-member fluorapatite (Chapter 3). Biotite totals were >94%. Again, mineral data were excluded where they showed evidence of accidental analysis of other phases (e.g. host crystals). Typical 1σ precision is 9% for MgO and 7% for Cl relative in glass analyses, based on counting

statistics. For other elements, uncertainties are generally <5-10% (higher for low concentration elements; Table 2.1). In mineral analyses, typical 1σ precision is <10% relative for most elements (Table 2.1). The reproducibility of secondary standards is excellent (Table 2.2).

EPMA counting statistic uncertainties						
	Glass		Apatite		Biotite	
	Absolute (wt%)	Relative (%)	Absolute (wt%)	Relative (%)	Absolute (wt%)	Relative (%)
SiO ₂	0.42	1	0.05	7	0.27	1
Na ₂ O	0.26	7	bdl	bdl	0.05	13
MgO	0.06	9	-	-	0.17	1
Al ₂ O ₃	0.23	1	bdl	bdl	0.16	1
P ₂ O ₅	0.02 ^a	21 ^a	0.45	1	-	-
SO ₂	0.02 ^{a,b}	25 ^{a,b}	0.03	9	-	-
K ₂ O	0.20	2	-	-	0.15	2
CaO	0.12	4	0.50	1	bdl	bdl
TiO ₂	0.08	16	-	-	0.12	3
MnO	0.09	69	-	-	bdl	bdl
FeOt	0.25	7	-	-	0.35	3
F	0.05 ^c	37 ^c	0.13 ^c	5 ^c	0.08	7
Cl	0.06	7	0.03 ^c	3 ^c	0.02	14

Table 2.1 | Representative EPMA precision estimates, based on counting statistics. All precision estimates are one standard deviation (1σ) and are shown both as absolute and relative concentrations. Where no precision is given, elements were not analysed in this study. bdl = consistently below detection limit. MnO is typically below detection limit in glasses but a precision is given as it is presented in Figures 6.5 and 6.6 for comparison with literature data.

^a Refers to data collected using 30 nA EPMA glass operating conditions. All other glass data were collected at 6 nA.

^b Excludes matrix glasses, where SO₂ concentrations are typically below detection limit.

^c SIMS data are primarily used for these elements in this thesis.

EPMA secondary standard reproducibility						
	StHs6/80-G		ATHO-G		GOR132-G	
	wt%	1 σ	wt%	1 σ	wt%	1 σ
SiO ₂	63.30	0.48	75.20	0.59	45.56	0.28
Na ₂ O	4.58	0.09	4.17	0.12	0.83	0.06
MgO	1.93	0.06	0.10	0.02	22.05	0.19
Al ₂ O ₃	17.66	0.22	12.22	0.19	10.99	0.15
P ₂ O ₅	0.14	0.04	-	-	-	-
K ₂ O	1.31	0.04	2.73	0.07	0.03	0.01
CaO	5.24	0.09	1.69	0.05	8.38	0.08
TiO ₂	0.71	0.04	0.25	0.03	0.30	0.02
MnO	0.07	0.03	0.10	0.04	0.16	0.04
FeOt	4.45	0.10	3.27	0.12	10.29	0.2
Cl	-	-	0.04	0.01	-	-
Total	99.38		99.76		98.59	
n		15		15		15

Table 2.2 | Compositions of secondary standards (MPI-DING reference glasses) used in EPMA. Independent characterisation of these standards can be found in Jochum *et al.* (2006). Absolute precision estimates are given as one standard deviation of multiple analyses (1 σ). n= number of repeat analyses, measured over multiple EPMA sessions during data collection for Chapters 5 and 6.

2.4. Ion microprobe analysis

Samples were briefly ground and re-polished prior to ion microprobe (SIMS) analysis, in order to remove any surficial halogen modification induced by EPMA (Chapter 3). They were then gold coated to a thickness of ~30 nm.

All apatite and glass samples were analysed for H₂O, F, Cl and trace elements using a Cameca ims-4f ion microprobe at the Edinburgh Ion Micro-Probe Facility (EIMF), University of Edinburgh. A sub-set of glasses from Astroni 1 were additionally analysed for CO₂. Peak positions were verified before each analysis and a combination of

static magnet and (B1) electromagnetic fields was applied to compensate for any misalignment between H and other, heavier elements. A liquid nitrogen cold trap was applied to the sample chamber to improve the vacuum and reduce backgrounds for volatile elements, and blocks were allowed to outgas for >10 hours prior to analysis. Mass 0.7 was analysed to monitor the electron multiplier background count rate (<0.01 cps). All analyses were collected using a $^{16}\text{O}^-$ primary ion beam with a ~15 keV net impact energy (10.7 keV primary and 4.5 keV secondary). Apatite data were mostly collected using a 5 nA beam current, giving a surface spot diameter of ~15-20 μm but for smaller apatite inclusions the beam current was reduced to 2.5 nA, giving a surface spot of ~10-15 μm . Secondary ions were analysed with a 25 μm image field. Samples were pre-sputtered for ≥ 3 min before analysis to remove any surface contamination and for magnet calibration. During this period, the beam was rastered over a 15 μm^2 area for larger apatite analyses and a 10 μm^2 area for small apatite inclusions. Glass volatile data were collected in two separate analyses of the same spot. H_2O , F and other trace elements were collected in the first analysis, using a 4 nA beam current with a 25 μm image field. A field aperture was applied, limiting the imaged area to the central 8-10 μm , to eliminate contamination from the crater edges, and to reduce backgrounds. These analyses were pre-sputtered for ≥ 3 min over a 10 μm^2 area. In a sub-set of Astroni 1 apatites, CO_2 was measured in a second analysis, using a 4 nA beam current and 60 μm image field. A field aperture was applied, reducing the imaged area to the central 20 μm . CO_2 analyses were pre-sputtered for ≥ 2 min over a 15 μm^2 area within the hole produced by the earlier H_2O analysis. Exactly the same procedure was used for standards and unknowns. A 75 eV energy offset (40 eV window) was used for apatite and glass H_2O analyses, with a 50 eV offset (40 eV window) for glass CO_2 analyses.

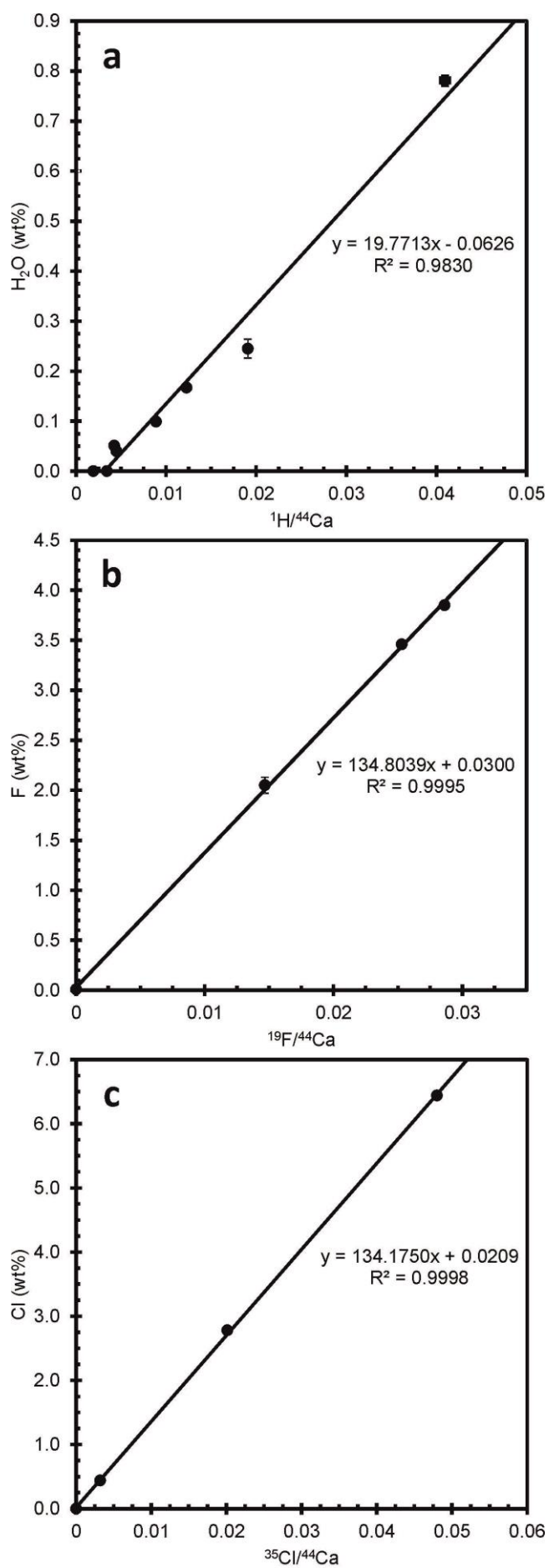


Figure 2.1 | (previous page) Calibration data for apatite SIMS analyses. Points show representative daily standard analyses for calibration of apatite (a) H₂O, (b) F and (c) Cl. Lines show linear regressions through each data set, with corresponding R² values. Standards are independently calibrated natural and synthetic apatites, with synthetic apatite compositions from Schettler *et al.* (2011). Where shown, error bars represent are 1 σ precision; otherwise uncertainties are less than the size of the data points. Average absolute deviations are 0.00015, 0.00013 and 0.00020 for ¹H/⁴⁴Ca, ¹⁹F/⁴⁴Ca and ³⁵Cl/⁴⁴Ca, respectively.

The following ions were measured for 10 cycles in apatite analyses: ¹H, ¹²C, ²⁵Mg/2, ¹⁶O, ¹⁹F, ²³Na, ²⁶Mg, ³⁰Si, ³¹P, ³⁵Cl, ³⁷Cl, ³⁹K, ⁴⁴Ca. Counts were normalised to ⁴⁴Ca and averaged over the first 5 cycles for halogens and the final 5 cycles for ¹H. These were converted to concentrations using a calibration curve populated by independently characterised apatite standards (Fig. 2.1). Calibration curves were created at the start of each day or whenever beam conditions were altered. Background volatile concentrations were determined by analysis of anhydrous, low-Cl and low-F synthetic apatites.

The following ions were measured for 8-10 cycles in the first glass analyses: ¹H, ⁷Li, ¹¹B, ¹²C, ²⁵Mg²⁺, ¹⁶O, ¹⁹F, ²⁶Mg, ³⁰Si, ³¹P, ³⁵Cl, ³⁷Cl, ³⁹K, ⁴²Ca, ⁴⁴Ca, ⁴⁵Sc, ⁴⁷Ti. Counts were normalised to ³⁰Si and averaged over the first 5 cycles for ¹⁹F and the final 5-7 cycles for ¹H, with the same number of cycles run in standards and unknowns. ¹H was converted to H₂O concentrations using calibration curves derived from a series of characterised rhyolitic glasses (Fig. 2.2), which were created at the start of each day. Background H₂O concentrations were monitored through the analysis of clinopyroxene host crystals. The ¹H ion yield correlates positively with the SiO₂ content of silicate glasses, hence a working curve of ¹H/³⁰Si yields H₂O concentration for glasses with variable SiO₂ contents, with no requirement for further correction (Blundy and Cashman, 2005). Fluorine and other trace elements were calibrated against NIST SRM610 glass, with ⁴⁴Ca as the internal standard for all analyses, based on EPMA of the same spot.

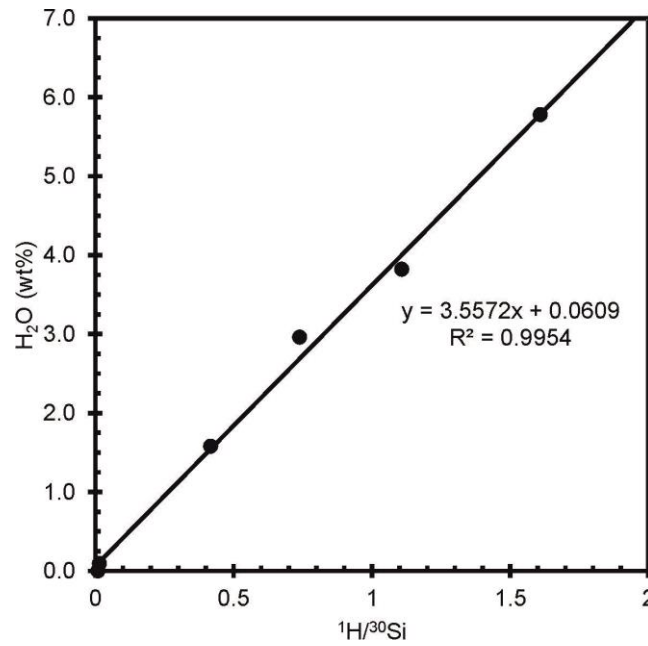


Figure 2.2 | Calibration data for SIMS analysis of H_2O in hydrous glasses. Points show a representative daily analysis of independently calibrated natural and synthetic rhyolite standards, for calibration of H_2O in melt inclusions and matrix glasses. An average linear regression through the data set is shown, with corresponding R^2 value. Fully propagated 1σ precision is less than the size of the data points. The average absolute $^1\text{H}/^{30}\text{Si}$ deviation is 0.0042.

$^{24}\text{Mg}^{2+}$, $^{12}\text{C}^+$, $^{40}\text{Ca}^{2+}$ and ^{30}Si were measured for 15 cycles in the second Astroni 1 glass analyses. Counts were normalised to ^{30}Si over the final 8 cycles and ^{12}C was converted to CO_2 , using a calibration curve defined prior to analysis, populated by characterised basaltic glasses with similar CO_2 contents to the unknowns (Fig. 2.3). Backgrounds were monitored on clinopyroxene host crystal within the same block. As the ^{12}C ion yield varies as a function of glass SiO_2 content a correction is applied to account for the difference between the known SiO_2 content of the standards and that of the unknowns, measured by EPMA.

In apatite analyses, typical relative precision is 12% for H_2O , 5% for F and 2% for Cl, based on a 90% confidence interval on the regression of calibration standards. These uncertainties have been fully propagated in calculating $X_{\text{Halogen}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios. In

glass analyses, precision is 6% and 9% relative for H₂O and CO₂ respectively, based on statistical assessment of the calibration regression, with a 90% confidence interval, and 3% relative for F, based on counting statistics.

For major, trace and halogen elements, there is good relative agreement between SIMS and EPMA analyses of the same apatite grains, melt inclusions or matrix glasses (Appendix Figs A4.1, A5.1). This provides validation for the methods outlined here and demonstrates that any electron-beam induced damage to the apatite crystal structure was eradicated on re-grinding.

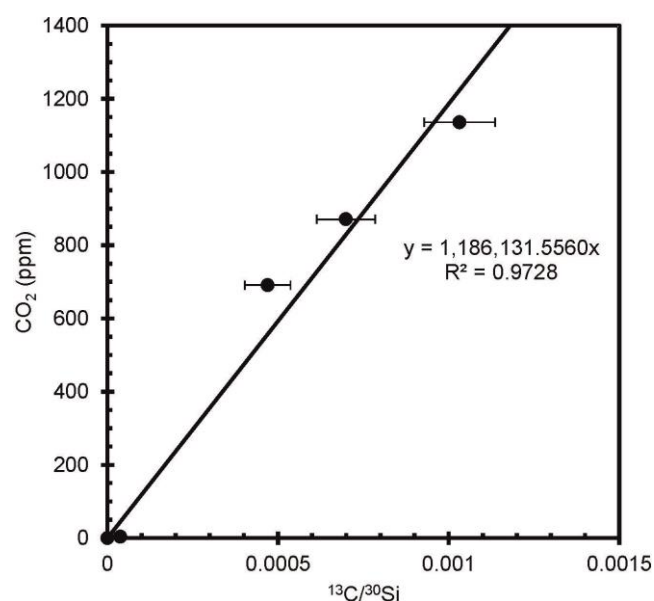


Figure 2.3 | Calibration data for SIMS analysis of CO₂ in hydrous glasses. Points show analyses of independently calibrated natural basaltic standards, for calibration of CO₂ in melt inclusions. Standards were background-corrected prior to calibration and subsequent SiO₂ correction. A zero-intercept linear regression is shown, with corresponding R² value. Allowing a non-zero intercept does not significantly change the calibration slope. Error bars are 1 σ precision; otherwise uncertainty is less than the size of the data points. The average absolute $^{13}\text{C}/^{30}\text{Si}$ deviation is 0.00044.

Chapter 3

New constraints on electron-beam induced halogen migration in apatite

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New constraints on electron-beam induced halogen migration in apatite.

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Fluorine and Cl X-ray count rates are known to vary significantly during electron probe microanalysis (EPMA) of apatite. Since the rate, timing and magnitude of this variation are a function of apatite orientation and composition, as well as EPMA operating conditions, this represents a significant problem for volatile element analysis in apatite. Although the effect is thought to be an intrinsic crystallographic response to electron-beam exposure, the mechanisms and causes of the count rate variability remain unclear. I tackle this by examining directly the effects of electron-beam exposure on apatite, by performing secondary ion mass spectrometry (SIMS)

*The XRD data presented in this chapter were collected, processed and described by R.D. Johnson. I integrated the results with other parts of this study and used them in the discussion.

depth profiles of points previously subject to electron-beam irradiation. During irradiation of fluorapatite, oriented with the *c*-axis parallel to the electron-beam, halogens become progressively concentrated at the sample surface, even under a relatively low power (15 nA, 10-15 kV) beam. This surface enrichment corresponds to an observed increase in EPMA *FKα* X-ray count rates. After prolonged irradiation, the surface region starts to lose halogens and becomes progressively depleted, corresponding with a drop in EPMA count rates. Under normal EPMA operating conditions there is no halogen redistribution in fluorapatite oriented with the *c*-axis perpendicular to the electron-beam, or in chlorapatite. I infer that anionic enrichment results from the migration of halogens away from a centre of charge build-up caused by the implantation of electrons from the EPMA beam, assisted by the thermal gradient induced by electron-matter interactions. The process of surface enrichment is best explained by halogen migration through interstitial crystallographic sites in the *c*-axis channel. This suggests that once the thermal and electric fields are removed, halogens may relax back to their original positions on very long timescales or with sample heating.

3.1. Introduction

Apatite group minerals are important in a diverse range of research areas. They represent the most common naturally occurring phosphate minerals on Earth and are present as accessory phases in most igneous rocks, as well as in sedimentary, metamorphic and ore-forming systems (e.g. Belousova *et al.*, 2002; Piccoli and Candela, 2002; Shemesh, 1990; Spear and Pyle, 2002). Apatites are integral to many biologic hard tissues, comprising the inorganic component of bones and teeth (Wopenka and Pasteris, 2005; Young and Brown, 1982). They represent a potentially stable host for the disposal of nuclear waste (Dacheux *et al.*, 2004) and the incorporation of U and Th also permits the use of apatite in

radiometric (Zeitler *et al.*, 1987) and fission track dating (Gleadow *et al.*, 2002). This variety of applications is largely facilitated by an extraordinarily high degree of flexibility in the apatite crystal lattice, which permits the incorporation of numerous trace components (Pan and Fleet, 2002).

The general formula of igneous apatite is $\text{Ca}_5(\text{PO}_4)_3\text{Z}$, where Z is F^- (fluorapatite), Cl^- (chlorapatite) or OH^- (hydroxylapatite; Elliott, 1994). Coupled substitutions also allow incorporation of CO_3^{2-} and S^{6+} in trace amounts (Pan and Fleet, 2002); thus apatite can incorporate each of the major volatile species present in magmatic systems (i.e. H_2O , CO_2 , SO_2 , F and Cl). Through the application of appropriate partition or exchange coefficients (e.g. Boyce *et al.*, 2010; Mathez and Webster, 2005; Peng *et al.*, 1997; Webster *et al.*, 2009b) and with an adequate understanding of volatile diffusion rates (Brenan, 1993), measurements of apatite composition can be used to assess pre-eruptive magmatic volatile contents. Thus, petrologic studies are increasingly using variations in apatite composition to interpret magmatic, degassing and ore-forming processes in terrestrial (e.g., Boyce and Hervig, 2008; Boyce and Hervig, 2009; Dietterich and de Silva, 2010) and extraterrestrial (e.g., Boyce *et al.*, 2014; Boyce *et al.*, 2010; Patiño Douce and Roden, 2006) environments.

Electron probe microanalysis (EPMA) represents the cheapest, easiest and most commonly accessible technique for apatite chemical analysis, allowing direct measurement of F, Cl and S concentrations and crude calculation of water concentrations ‘by difference’, assuming stoichiometry (Pyle *et al.*, 2002). Furthermore, the EPMA technique has a high spatial resolution, permitting quantitative analysis on micrometre length-scales. This is critical in the analysis of natural apatites, which commonly occur as 100-300 μm acicular grains, and in the analysis of individual zones within larger apatite crystals. However, many EPMA-derived apatite F concentrations reported in the literature

exceed 3.75 wt% (the stoichiometric limit for pure fluorapatite), attesting to significant uncertainties in the technique (Pyle *et al.*, 2002 and references therein). Apatite EPMA is subject to significant anisotropic, time-dependent variation in $FK\alpha$ and $ClK\alpha$ X-ray count rates during prolonged electron-beam exposure (Stormer *et al.*, 1993), and this largely accounts for erroneous halogen concentration measurements (Pyle *et al.*, 2002). Similar temporal variability in X-ray count rates is observed during EPMA of natural glasses (Humphreys *et al.*, 2006; Lineweaver, 1963) and feldspars (Autefage and Couderc, 1980), where alkali element X-ray counts drop exponentially during electron-beam exposure. However, in apatite, halogen X-ray count rates rise rapidly on initial beam exposure before more slowly decreasing below initial values (Stormer *et al.*, 1993).

Several studies have investigated the time-dependent variation in apatite halogen X-ray counts, with the aim of optimising the reliability of apatite volatile analysis by EPMA (Goldoff *et al.*, 2012; Henderson, 2011; Stormer *et al.*, 1993). The effect is most pronounced when the incident electron-beam is oriented parallel to the crystallographic c -axis and is minimised when the beam is parallel to the a - or b -axis (Stormer and Pierson, 1993). In addition to this crystallographic control, count rate variability is also dependent upon the apatite composition. The magnitude of the increase in $FK\alpha$ counts is lower in Cl-rich varieties than in end-member fluorapatite, but does not change systematically with increasing Cl content in intermediate compositions (Goldoff *et al.*, 2012). Conversely, the increase in $ClK\alpha$ count rates is more pronounced in more Cl-rich apatites (Goldoff *et al.*, 2012). Electron-beam conditions also significantly affect halogen count rate variability. Varying the electron-beam accelerating voltage has little effect on the magnitude or rate of the initial increase in $FK\alpha$ counts, but it appears to control the rate at which counts subsequently decrease (Stormer *et al.*, 1993) and the absolute number of halogen X-rays produced per unit time, for a fixed current (Goldoff *et al.*, 2012). Irradiation with larger

electron-beam diameters reduces the rate of change in halogen X-ray count rates through irradiation (Stormer *et al.*, 1993) and the initial increase in X-ray counts is faster under higher beam currents (Goldoff *et al.*, 2012). Henderson (2011) reports that the variability in halogen X-ray count rates can be reduced by rastering the electron-beam or cryogenically cooling the sample during irradiation. One important observation is that re-analysis of the same point on an apatite crystal after a 16 hour pause in irradiation showed no recovery in X-ray counts, suggesting that the effect induced by the electron-beam is stable over long time periods at ambient temperature (Stormer *et al.*, 1993).

Most of the previous studies focused on optimisation of the apatite EPMA procedure, rather than on constraining the physical processes responsible for the time-dependent variation in halogen X-ray count rates. Migration is thought to occur through a vacancy-mediated mechanism, in response to the generation of an electric field within the sample, induced by electron implantation from the EPMA beam (Stormer *et al.*, 1993). In this model, during the initial increase in X-ray count rates F is thought to rise through the sample and react with the surface, where $FK\alpha$ X-rays experience less matrix attenuation. The subsequent drop in count rates is suggested to result from the absorption of a critical energy, breaking the bonds holding F on the sample surface and causing F ions to volatilise into the vacuum (Stormer *et al.*, 1993). Contamination and degradation of the carbon coat (Buse and Kearns, 2014) on the apatite surface may also significantly contribute to the decrease in halogen X-ray counts (Stormer *et al.*, 1993). However, these hypotheses have never been tested directly.

In this study, I used secondary ion mass spectrometry (SIMS) to depth-profile regions of apatite crystals that had previously been subjected to electron-beam irradiation for different amounts of time. The novelty of this approach is that it allows us to observe directly any halogen redistribution caused by electron-beam irradiation under different

conditions. The main aim of this investigation is to quantify any temporal variability in the location and degree of halogen redistribution within irradiated samples to constrain the processes responsible for the observed time-dependent variability in halogen X-ray count rates during EPMA, and hence test the mechanisms proposed by Stormer *et al.* (1993). This investigation follows a similar approach to that of Humphreys *et al.* (2006), in which SIMS depth profiling was successfully applied to determine alkali migration mechanisms in natural glasses.

Apatite sample materials		
wt%	Durango fluorapatite ^a	Bamle chlorapatite ^b
P ₂ O ₅	40.78	41.23
CaO	54.02	52.73
SiO ₂	0.34	0.05
Na ₂ O	0.23	0.40
FeO _t	0.05	0.08
MnO	0.01	0.01
SrO	0.07	0.06
SO ₃	0.37	
F	3.53	0.08
Cl	0.41	6.37
Total	98.24 ^c	99.54 ^c
$X^{\text{Ap}}_{\text{Fluorapatite}}^{\text{d}}$	0.93	0.02
$X^{\text{Ap}}_{\text{Chlorapatite}}^{\text{d}}$	0.06	0.94
$X^{\text{Ap}}_{\text{Hydroxylapatite}}^{\text{d}}$	0.01	0.04

Table 3.1 | Published major and trace element compositions of the Durango (fluorapatite) and Bamle (chlorapatite) standards used in the EPMA experiments.

Note: The calculated mole fractions of fluorapatite, chlorapatite, and hydroxylapatite are also given.

^a Data from Young *et al.* (1969).

^b Data from Carlson *et al.* (1999), monoclinic chlorapatite.

^c Total adjusted for F and Cl in place of O.

^d Mole fraction of F, Cl and OH in crystal.

3.2. Experimental methods

3.2.1. Apatite sample materials

Experiments in this study were conducted using large single crystals of near-end-member fluorapatite and chlorapatite. The fluorapatite end-member was from Cerro de Mercado, Durango, Mexico (referred to as Durango), with the chlorapatite from Ødegården Quarry, Bamble, Norway (referred to as Bamble). Table 3.1 gives the compositions of the apatite standards used. Although not perfectly homogeneous, Durango apatite is routinely used as a standard reference material (e.g., Boyce and Hervig, 2009) and Bamble apatite has been proposed as a potential standard in microanalytical studies of apatite halogen concentrations (Marks *et al.*, 2012). Crystallographic orientation was carefully controlled, and checked through the measurement of apparent cleavage angles on the polished surface, and observation of crystal form.

3.2.2. Electron microprobe irradiation

Apatite samples were mounted in a single epoxy resin block and exposed to an electron-beam using a JEOL 8600 4-spectrometer electron microprobe, controlled by SAMx software, in the Research Laboratory for Archaeology and the History of Art, University of Oxford. To test the effect of varying apatite composition and crystal orientation both fluorapatite and chlorapatite were irradiated, with the fluorapatite oriented both *c*-axis parallel and perpendicular to the incident electron-beam. Prior to irradiation the resin block was polished and carbon coated to a standard thickness of 15 nm, monitored on a polished brass bar. Some thin polishing scratches were preserved in order to re-locate irradiated points accurately. The positions of irradiated points were documented using a reflected light microscope attached to the EPMA instrument. Apatite crystals were not

Electron-beam operating conditions				
Operating condition	'Goldoff' ^a	'Low power'	'Routine'	'Extreme'
Accelerating voltage (kV)	10	10	15	20
Probe current (nA)	4	15	15	30
Beam diameter (μm)	10	5	5	Focussed

Table 3.2 | Summary of the electron-beam operating conditions used in this study.

^a The recommended conditions of Goldoff *et al.* (2012), given for comparison.

imaged using SEM, in order to avoid any premature electron-beam exposure. Electron-beam conditions and irradiation times were varied systematically between experiments, generally within a realistic range for quantitative analysis. Accelerating voltages were varied from 10 to 20 kV, with beam currents ranging between 10 and 30 nA. The beam diameter was 5 μm except where a focused electron-beam was used to provide intense electron bombardment (Table 3.2). Beam exposure times were varied from 10 s to 555 s, with most irradiations conducted for <360 s, as for typical analyses. Irradiation times were monitored using an external timer and a Faraday cage was manually inserted at the end of each irradiation to prevent prolonged electron-beam exposure during data processing. For each irradiation, time scans of raw X-ray counts ($FK\alpha$, $ClK\alpha$, $CaK\alpha$ and $PK\alpha$) were collected simultaneously on the four spectrometers to observe the time-dependent count rate variability under different operating conditions.

3.2.3. Secondary ion mass spectrometry depth profiling

Following electron-beam exposure, irradiated areas were analysed by SIMS, with a time gap of 32-39 days between EPMA irradiation and SIMS analysis. The carbon coat was first removed by briefly wiping the sample with methanol. This technique was used, rather than re-polishing, to avoid removal of material from the crystal surfaces. The samples were then sputter-coated with Au for 200 s, resulting in a coat thickness of ~30

nm. The SIMS beam was manually lined up with each EPMA spot for each of the experiments by comparison with reflected light images, and using an inclined reflected light microscope attached to the SIMS instrument. In most cases there was no visible mark left from the EPMA irradiation, so scratches left on the sample surface during polishing were used to guide identification of the position of irradiated areas. The ion-beam was used to sputter continuously down through the irradiated areas to create depth profiles showing the distribution of elements in damaged areas, as well as adjacent, non-irradiated parts of the crystal. These non-irradiated profiles were run for the same number of cycles as irradiated profiles and provide baseline values for each sample. Baseline profiles were also run at the start and end of each day and when moving between crystals, to check for instrument drift.

All SIMS analyses were conducted using the CAMECA ims-4f ion microprobe, controlled by Charles Evans and Associates PXT interface and software, at the Ion Microprobe Facility, University of Edinburgh. A 0.2 nA O^- primary ion-beam was used, with a net impact energy of 15 kV, yielding a beam diameter of 10-15 μm . The ion-beam was not rastered on the sample surface and no field aperture was applied. Secondary ions were extracted at +4.5 keV energy, with no energy offset and a ± 40 eV energy window. Mass 4.5 was analysed to monitor the electron multiplier background count rate. $^1H^+$, $^{12}C^+$, $^{16}O^+$, $(^{16}O^1H)^+$, $^{19}F^+$, $^{23}Na^+$, $^{31}P^+$, $^{37}Cl^+$ and $^{42}Ca^+$ were collected in each cycle for 5, 6, 3, 6, 6, 5, 1, 6 and 2 s, respectively. The number of cycles was kept constant at 70, corresponding to a counting time of ~ 1 hour, because trial baseline profiles with greater cycle numbers showed large inconsistencies in baseline counts at >70 -75 cycles, likely related to edge effects or fractionation of secondary ions escaping from deep pits.

The SIMS instrument was calibrated for the analyte secondary ions prior to each depth profile, on non-irradiated areas close to the actual analysis position. To avoid

removal of potentially important surface layers, the depth profiles were acquired with no pre-sputter period; the first result in each depth profile is therefore affected by sputtering through the Au coat, seen as anomalously low concentrations of elements such as P in both baseline and irradiated depth profiles. The first cycle was therefore removed from the depth profiles and is not considered in further discussion. After one cycle the baseline profiles have approximately constant P and are therefore considered free of Au coat contamination.

All SIMS data are presented as counts per second (CPS) for each isotope, normalised to Ca. This approach removes artefacts in the depth profiles related to fluctuations in the primary ion-beam. The CPS/Ca for each point in the irradiated depth profile was then normalised to the baseline CPS/Ca value at the same point (cycle number), permitting easy identification of differences between irradiated and non-irradiated depth profiles. Baseline profiles were all highly reproducible. This approach removes any charging, edge or matrix effects that may occur during depth profiling and cancels out any artefacts imposed by possible minor inhomogeneity in the starting materials.

3.2.4. Sputter rate calibration

SIMS sputtering rates are related to the primary ion-beam conditions, physical properties of sample media, and any existing topography on the sample surface. It must therefore be determined under conditions individual to each study. To do this, a series of calibration SIMS pits was created on non-irradiated areas of the fluorapatite standard, in both orientations, as well as the chlorapatite standard. Calibration pits were created by running for 10, 20, 30, 50, and 70 cycles.

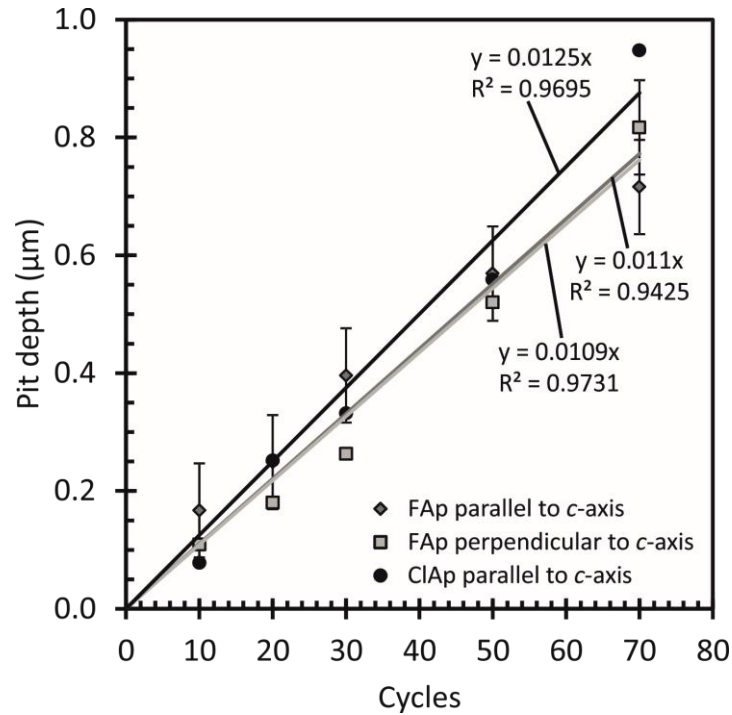


Figure 3.1 | SIMS sputtering rate calibration. Measured depths of calibration SIMS pits in fluorapatite parallel to the *c*-axis, in fluorapatite perpendicular to the *c*-axis, and in chlorapatite parallel to the *c*-axis sputtered for different numbers of cycles. Best-fit lines are used to calibrate sputter rate in irradiated and baseline depth profiles, allowing conversion of cycle number to depth. Vertical bars show the error imposed by the z-axis step distance. Otherwise this is smaller than the size of the marker. FAp = Durango; ClAp = Bamble.

The depths of the calibration pits were measured using a 3D scanning NanoFocus μ Surf white light confocal optical profiler in the Department of Materials, University of Oxford. The system was operated using a 50x objective lens, with a vertical-axis step of 0.01-0.08 μm , depending on the absolute scan range in the z-direction. The profiler was calibrated on a pitted glass reference standard. The certified precision, estimated from multiple calibration measurements, was $\pm 0.01\%$. The maximum widths of the SIMS pits at the surface are approximately 10-15 μm and thus significantly exceed the nominal diameter of the electron probe spot. This is necessary to sample the whole EPMA

interaction volume with the SIMS beam but may slightly dampen the observed electron-beam induced compositional variations. There is a good linear correlation between the number of cycles and the maximum depth of the SIMS pits (Fig. 3.1). Fluorapatite and chlorapatite show a difference in sputtering rate, but sputter rates were almost identical for fluorapatite parallel and perpendicular to the *c*-axis (Fig. 3.1). In each case, a zero-intercept linear regression through the calibration points was used to quantify the sputter rate. This approach gives maximum depths of 0.88, 0.77 and 0.76 μm in 70-cycle SIMS depth profiles measured in chlorapatite parallel to the *c*-axis, fluorapatite parallel to the *c*-axis, and fluorapatite perpendicular to the *c*-axis, respectively (Fig. 3.1).

3.2.5. X-ray diffraction experiments

The published crystal structure of fluorapatite (Elliott, 1994), and associated anisotropic atomic displacement parameters, were refined against single crystal X-ray diffraction (XRD) data, measured on a sample of Durango apatite with approximate dimensions 50 x 50 x 100 μm , using an Oxford Diffraction, Super Nova instrument in the Department of Physics, University of Oxford. An Oxford Cryosystems Cryostream 700 Plus was used to provide *in situ* sample temperatures from 100-500 K. Full spheres of diffraction data were measured at each temperature (100, 200, 300, 350, 400, 450, and 500 K). Data collection and reduction was performed using the Agilent CrysAlis PRO software package, giving integrated intensities of approximately 530 inequivalent reflections at each temperature. The structural refinement was then run against the reduced data sets using FULLPROF (Rodríguez-Carvajal, 1993). Excellent reliability factors of $R_F^2 < 4\%$ were achieved in all refinements.

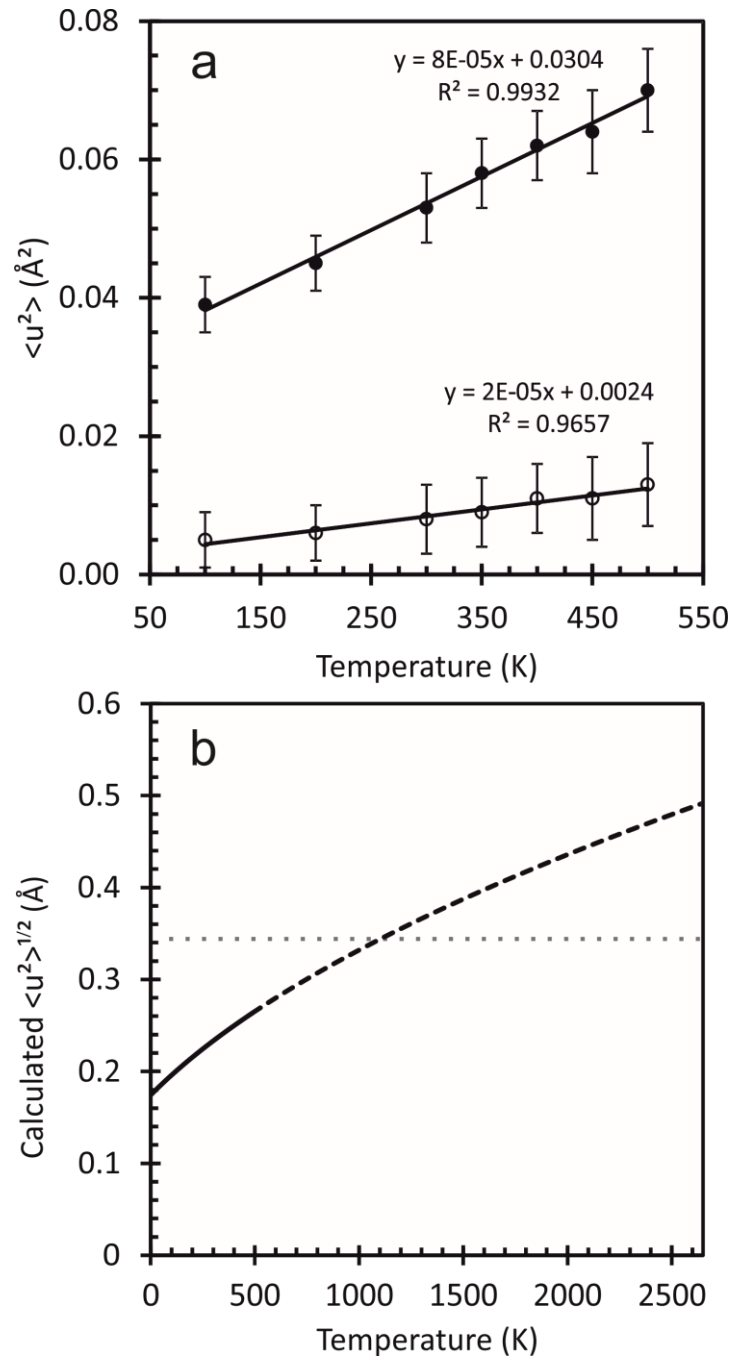


Figure 3.2 | Fluorine atomic displacement parameters in fluorapatite. **a**, Measured instantaneous atomic displacement for F in fluorapatite parallel (filled circles) and perpendicular (open circles) to the *c*-axis at varying temperatures measured by XRD. Error bars show the analytical uncertainty. **b**, Square root of the measured F instantaneous atomic displacement in fluorapatite (solid line), extrapolated to higher temperatures (dashed line). The horizontal dotted line shows 20% of half the interatomic distance.

3.3. Results

3.3.1. X-ray diffraction data

At room temperature, 99% of all measured reflections for the Durango fluorapatite sample were indexed with the lattice parameters $a = b = 9.3955(1) \text{ \AA}$, $c = 6.8801(1) \text{ \AA}$, $\alpha=90^\circ$, $\beta=90^\circ$, and $\gamma=120^\circ$, consistent with those published by (Elliott, 1994). (A CIF file is on deposit at: ammin.geoscienceworld.org, deposit item: AM-15-107.) The diffraction intensities were in agreement with the reflection conditions and Laue class of space group $P6_3/m$, giving $R_{\text{int}} = 4.78\%$. This space group symmetry was consistent across all data sets. The structural model, based upon published atomic fractional coordinates, was refined to high accuracy and with good reliability factors ($R_F^2 = 3.95\%$, $wR_F^2 = 7.25\%$, $R_F = 2.47\%$). The apatite crystal structure has 10 calcium ions in the unit cell. Six of these (Ca2 sites) are located on mirror planes at $z=1/4$ and $z=3/4$ (Wyckoff position 6h), equivalent by the 6_3 symmetry operation, and forming two calcium plaquettes with a trigonal planar geometry. In fluorapatite, F anions are also located on the mirror planes in the centre of the plaquettes, hence surrounded by (and bonded to) three nearest neighbour Ca cations. In contrast, Cl in chlorapatite is located between the mirror planes with six nearest neighbour Ca cations. Thus, in apatite, Z-site species occupy a channel-like structure of Ca ions that extends along the crystallographic c -axis (Elliott, 1994). Fluorine thermal ellipsoids, defined with a 90% probability, have an elongate, cigar shape, with the major axis extending along the c -axis channel.

Within the temperature range 100-500 K, F is the only atom in this sample that shows a significant anisotropic change in the shape of the thermal ellipsoids. In order to quantify temperature-dependent changes in the delocalisation of F ions, I calculate the anisotropic atomic displacement parameters ($\langle u^2 \rangle$) of F atoms at different temperatures

(Fig. 3.2a). Parallel to the c -axis, $\langle u^2 \rangle$ increases linearly with temperature, demonstrating a convergence of the F thermal ellipsoids and a probabilistic reduction in the distance between F atoms. However, even at 500 K, 90% thermal ellipsoids do not meet and F remains ordered within the crystal lattice. Perpendicular to the c -axis F $\langle u^2 \rangle$ is isotropic and does not vary outside of uncertainty within the measured temperature range. The $\langle u^2 \rangle^{1/2}$ value, calculated from the XRD results, gives the root-mean-square value of the atomic displacement at the temperatures analysed in these experiments (Fig. 3.2). This can be linearly extrapolated to higher temperatures. The results show that at >1100 K the atomic displacement of F in the c -axis direction exceeds 20% of half the interatomic distance (where the interatomic spacing is half of the c -axis lattice parameter; Fig. 3.2b). Above this temperature, the Lindemann criterion states that F will become delocalised within the c -axis channel (Chakravarty *et al.*, 2007).

3.3.2. Electron microprobe time scans

X-ray count rates were collected every 1.4-1.7 s under electron-beam conditions typical of normal analysis, as well as under more severe electron-beam conditions with a high energy density, which would be expected to induce high count rate variability. The electron-beam conditions used in experiments in this study are summarised in Table 3.2. The ‘routine’ beam conditions are slightly adapted from the recommended operating procedure of Goldoff *et al.* (2012) (Table 3.2), using 15 nA instead of 4 nA to achieve adequate precision for minor elements (Fe, Mn, Mg, S) and for F and Cl concentrations in natural near-end-member chlorapatite and fluorapatite, respectively. Reducing the spot size from 10 μm to 5 μm gives greater flexibility in the size of natural grains to be analysed, and had little impact on the amount of halogen count rate variability. Goldoff *et al.* (2012) recommend analysis using a 10 kV accelerating voltage, but acknowledge that

15 kV is required for quantification of heavy elements (e.g. Fe). I therefore tested both of these conditions ('low power' and 'routine' conditions, respectively) in fluorapatite oriented with the *c*-axis parallel to the electron-beam.

My X-ray count rate time scans broadly agree with the results of previous studies (Goldoff *et al.*, 2012; Stormer *et al.*, 1993). There was no change in PK α and CaK α count rates within any of the time scans collected under 'routine' or 'low power' conditions

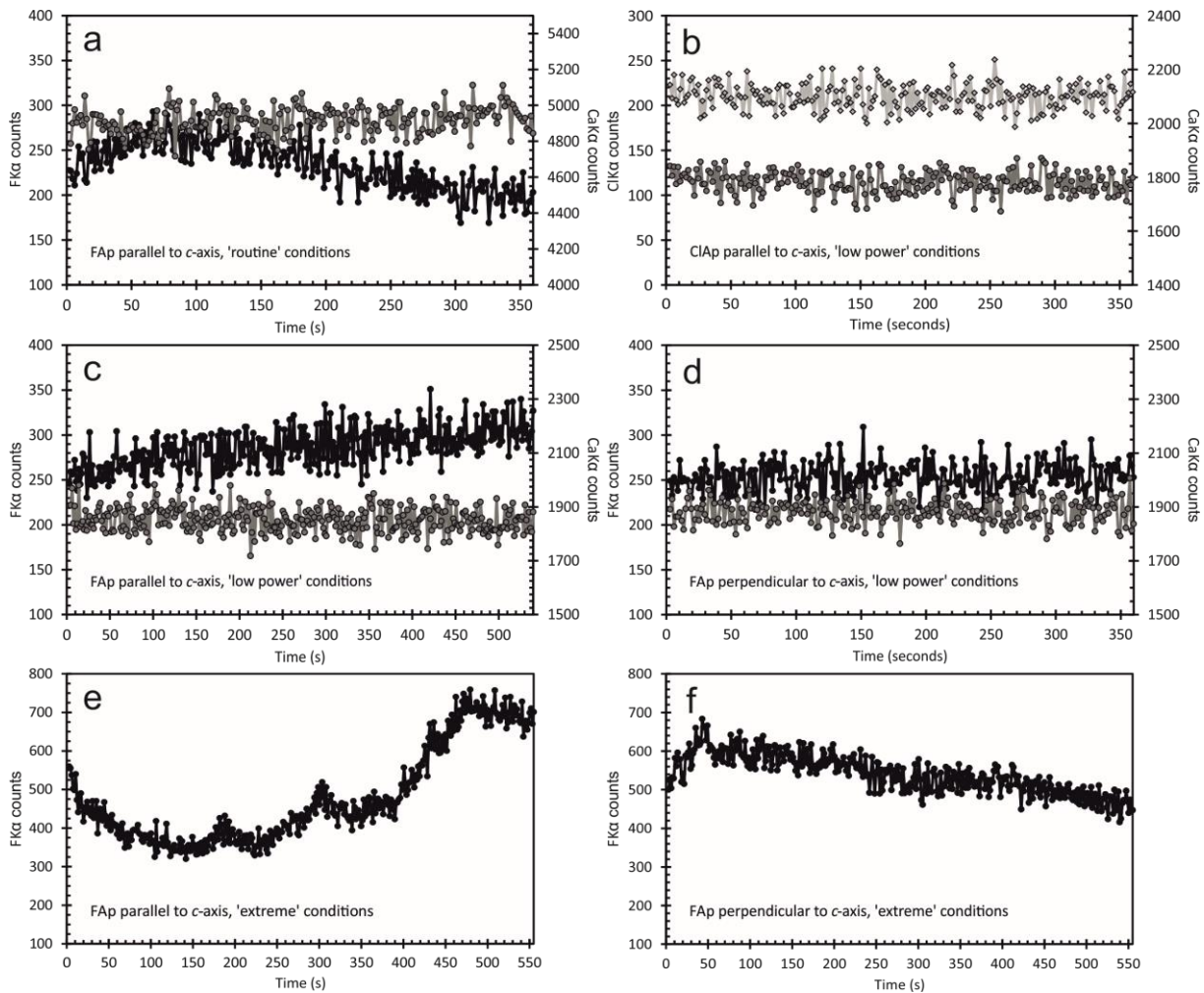


Figure 3.3 | Electron microprobe time scans. Time scans show the change in F (black circles), Cl (light grey diamonds), and Ca (medium grey circles) K α count rates through protracted electron-beam irradiation. Panels **a**, **c** and **e** show count rate variability in fluorapatite parallel to the *c*-axis under 'routine', 'low power' and 'extreme' electron-beam operating conditions, respectively. Perpendicular to the *c*-axis, fluorapatite shows constant count rates under 'low power' conditions (**d**) but variable X-ray count rates under 'extreme' conditions (**f**). Chlorapatite parallel to the *c*-axis shows constant X-ray count rates under 'low power' conditions (**b**).

(Fig. 3.3). In fluorapatite, analysed parallel to c -axis under ‘routine’ conditions, the $FK\alpha$ count rates rise rapidly on initial electron-beam exposure (Fig. 3.3a). They reach a maximum, after the first 80 s of analysis, at which time $FK\alpha$ X-ray counts are ~30% higher than initial values. The peak in intensity is followed by a drop in count rates down below the initial values over the following 280 s of electron-beam exposure. As previously reported (Stormer *et al.*, 1993), changing the electron-beam accelerating voltage from 15 to 10 kV extends the period over which $FK\alpha$ X-ray counts increase. In fluorapatite, analysed under ‘low power’ conditions, $FK\alpha$ increased continually over 540 s of analysis, with X-ray counts ~30% higher than initial values at the end of the irradiation (Fig. 3.3c). Although $FK\alpha$ did not start to decrease within this time scan, the experiments of Stormer *et al.* (1993) suggest that this would happen with continued irradiation. Under both ‘routine’ and ‘low power’ electron-beam conditions $ClK\alpha$ count rates are below the detection limit in fluorapatite.

Under ‘low power’ analytical conditions $FK\alpha$ counts in fluorapatite oriented with the c -axis perpendicular to the incident electron-beam are comparable to starting values in time scans for crystals oriented with their c -axis parallel to the beam, but count rates do not change during the experiment (Fig. 3.3d).

The chlorapatite time scans were measured only under ‘low power’ operating conditions, where the crystal was oriented with the c -axis parallel to the incident electron-beam (Fig. 3.3b). Under these conditions there was no change in the $ClK\alpha$ X-ray count rates over 360 s of analysis. Count rates remained approximately constant, close to initial values. This is in contrast to the data presented by Goldoff *et al.* (2012), in which Cl-rich apatites show a drop in $ClK\alpha$ X-ray counts with time using a 10 kV beam. Under these beam conditions $FK\alpha$ was below the detection limit in chlorapatite.

Under ‘extreme’ electron-beam conditions, time scans show a different trend for $FK\alpha$ in fluorapatite (Fig. 3.3e,f). Fluorapatite, oriented with the c -axis parallel to the electron-beam, shows an anomalously high initial value followed by a decrease of 40-50% in $FK\alpha$ over the first 140 s of electron-beam exposure. After reaching a minimum, counts sharply increase again, exceeding initial values and showing erratic fluctuations for the remainder of the experiment (Fig. 3.3e). Fluorapatite analysed with the electron-beam oriented perpendicular to c -axis shows an increase in $FK\alpha$ counts of 25% over the first 50 s of electron-beam exposure (Fig. 3.3f). After this, count rates decrease gradually, below initial values, for the remainder of the 555 s irradiation.

3.3.3. Baseline SIMS depth profiles for fluorapatite and chlorapatite

Figure 3.4 shows baseline profiles for fluorapatite and chlorapatite in different orientations. In these non-irradiated profiles the concentrations of most elements are constant with depth, showing homogeneity in the apatite composition within the sampled region. The only baseline profile that shows significant variability is F/Ca in chlorapatite. This has an elevated F/Ca ratio at the surface, which declines exponentially with depth. This is reproducible and this trend is therefore cancelled out in the baseline-normalised profiles. Chlorapatite from the Bamble deposit suffered late-stage metasomatic albitisation that caused patchy, pseudomorphic replacement of chlorapatite with more F-rich apatite, focused along crystal fractures (Engvik *et al.*, 2009; Marks *et al.*, 2012). When the chlorapatite sample was prepared for mounting it probably broke along pre-existing fractures. Thus, baseline depth profiles likely demonstrate the effects of metasomatism close to a fracture surface.

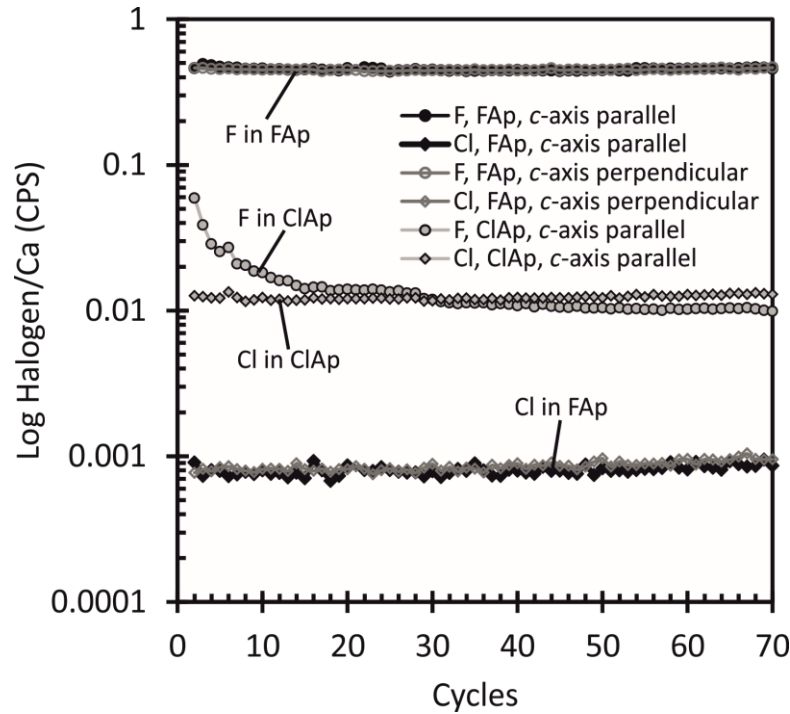


Figure 3.4 | Baseline SIMS depth profiles. Concentration profiles, measured by SIMS, in fluorapatite parallel to the *c*-axis (black), fluorapatite perpendicular to the *c*-axis (medium grey), and chlorapatite parallel to the *c*-axis (light grey), where the apatite crystals have not previously been subject to electron-beam irradiation, showing F (circles) and Cl (diamonds). These analyses represent the fluorapatite and chlorapatite baseline profiles, against which irradiated depth profiles are normalised. Data are normalised to Ca (counts per second, i.e. CPS), in order to cancel any fluctuations in the primary ion-beam or artefacts related to changes in pit shape with depth.

3.3.4. Fluorapatite SIMS depth profiles parallel to *c*-axis

3.3.4.1. 'Low power' EPMA conditions; 10 kV, 15 nA, 5 μ m beam

For all irradiation times these depth profiles show a significant enrichment in halogen/Ca ratios at the surface, which decays exponentially with depth, back down to baseline values (Fig. 3.5a,b). (Baseline-normalised SIMS depth profile results are provided in Appendix 1.) Maximum surface F/Ca enrichment increases approximately linearly with exposure time during the analysis, reaching 2.7 times baseline levels after 540 s of irradiation. The F/Ca ratios return to baseline values at depths of $\sim 0.1 \mu$ m in profiles irradiated for 10-120

s and at 0.2 μm in the profile irradiated for 540 s (Fig. 3.5a). Trends in Cl/Ca ratios under these conditions are difficult to interpret due to background noise. A maximum surface enrichment of 3.7 times baseline Cl/Ca is observed after 540 s of irradiation (Fig. 3.5b). All other profiles show no surficial Cl/Ca enrichment above baseline values.

3.3.4.2. 'Routine' EPMA conditions; 15 kV, 15 nA, 5 μm beam

Using 'routine' EPMA operating conditions, irradiated depth profiles show a similar trend of surface halogen/Ca enrichment to that of the 'low power' experiments (Fig. 3.5c,d). The degree of surface F/Ca enrichment increases with electron-beam exposure time, reaching 3.2 times baseline levels after 120 s, but declines to 1.6 times baseline levels after 360 s. The F/Ca ratios return to baseline values at 0.1 μm in profiles irradiated for 30-360 s and 0.2 μm in profiles irradiated for 10-20 s. The Cl/Ca ratios at the surface of the fluorapatite sample are noisy but appear to increase to a maximum 2.3 times baseline levels after 60 s of irradiation, then decline to 1.5 times baseline levels after 360 s (Fig. 3.5d). The return to baseline values is achieved within ~ 0.1 -0.2 μm of the sample surface in all depth profiles.

3.3.5. Effect of crystal orientation

In contrast to depth profiles of fluorapatite irradiated parallel to *c*-axis, there is no significant compositional variability in profiles of irradiated fluorapatite oriented with the beam perpendicular to the *c*-axis (Fig. 3.6a,b). Under 'low power' analytical conditions there is no enrichment in F/Ca above baseline values in any of the irradiated depth profiles. The Cl/Ca ratio shows a small surficial inflection outside of uncertainty in the profile irradiated for 10 s but is constant, at baseline levels, in all other profiles.

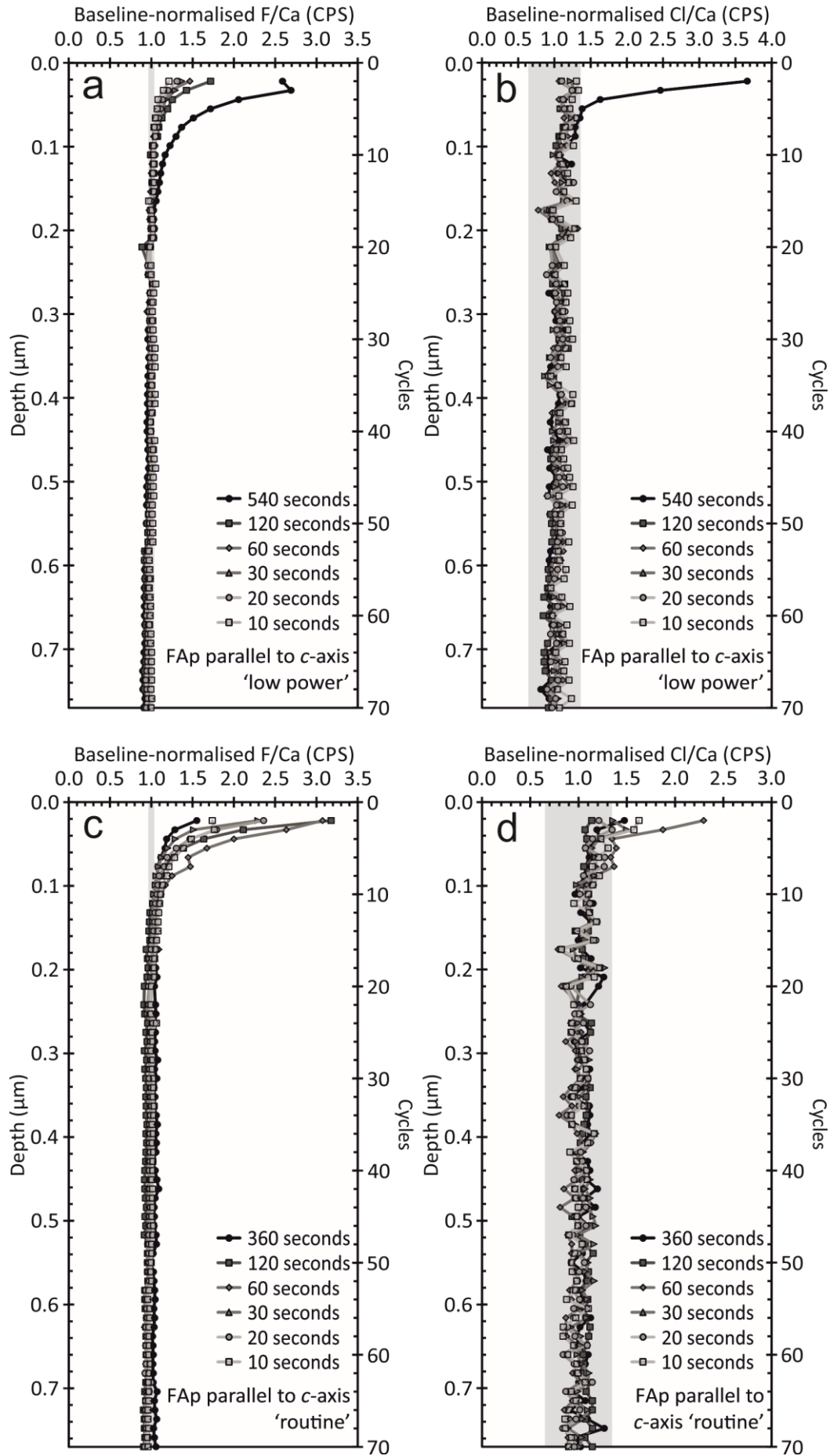


Figure 3.5 | (previous page) Fluorapatite SIMS depth profiles irradiated parallel to *c*-axis. Secondary ion mass spectrometry data showing chemical depth profiles for (a) F and (b) Cl in fluorapatite parallel to the *c*-axis, irradiated under ‘low power’ electron-beam conditions. Panels (c) and (d) show SIMS depth profiles for F and Cl, respectively, in fluorapatite parallel to the *c*-axis, irradiated under ‘routine’ electron-beam conditions. Symbols denote the different lengths of time that profiles were exposed to an electron-beam (see legend for details). All plots are presented as baseline-normalised halogen/Ca (counts per second, i.e. CPS), to remove any artefacts imposed by the primary ion-beam, pit geometry, or sample inhomogeneity. Baseline values are those shown in Figure 3.4. Fully propagated, two standard deviation counting uncertainties are presented as grey bars along the line baseline-normalised halogen/Ca ratio = 1.0.

3.3.6. Effect of crystal composition

In the chlorapatite crystal, irradiated under ‘low power’ electron probe operating conditions, there is no significant compositional variability with depth in the sample (Fig. 3.6c,d). Minor depletion, slightly outside of uncertainty, is seen $<0.080\ \mu\text{m}$ below the surface in the F/Ca ratio of some irradiated depth profiles (Fig. 3.6c). However, this is not seen in all depth profiles and may therefore reflect a subtle compositional difference in the Bamble sample between the positions of the irradiated and baseline profiles, such that the depletion is an artefact imposed during baseline normalisation, rather than an effect of electron-beam irradiation. Furthermore, although F/Ca is constant at depth within chlorapatite samples, the absolute ratio varies between 0.8 and 1.1, slightly outside of uncertainty. This variability also likely reflects slight lateral inhomogeneity in the sample. The Cl/Ca ratio stays approximately equal to baseline values, even after 360 s of electron-beam irradiation (Fig. 3.6d).

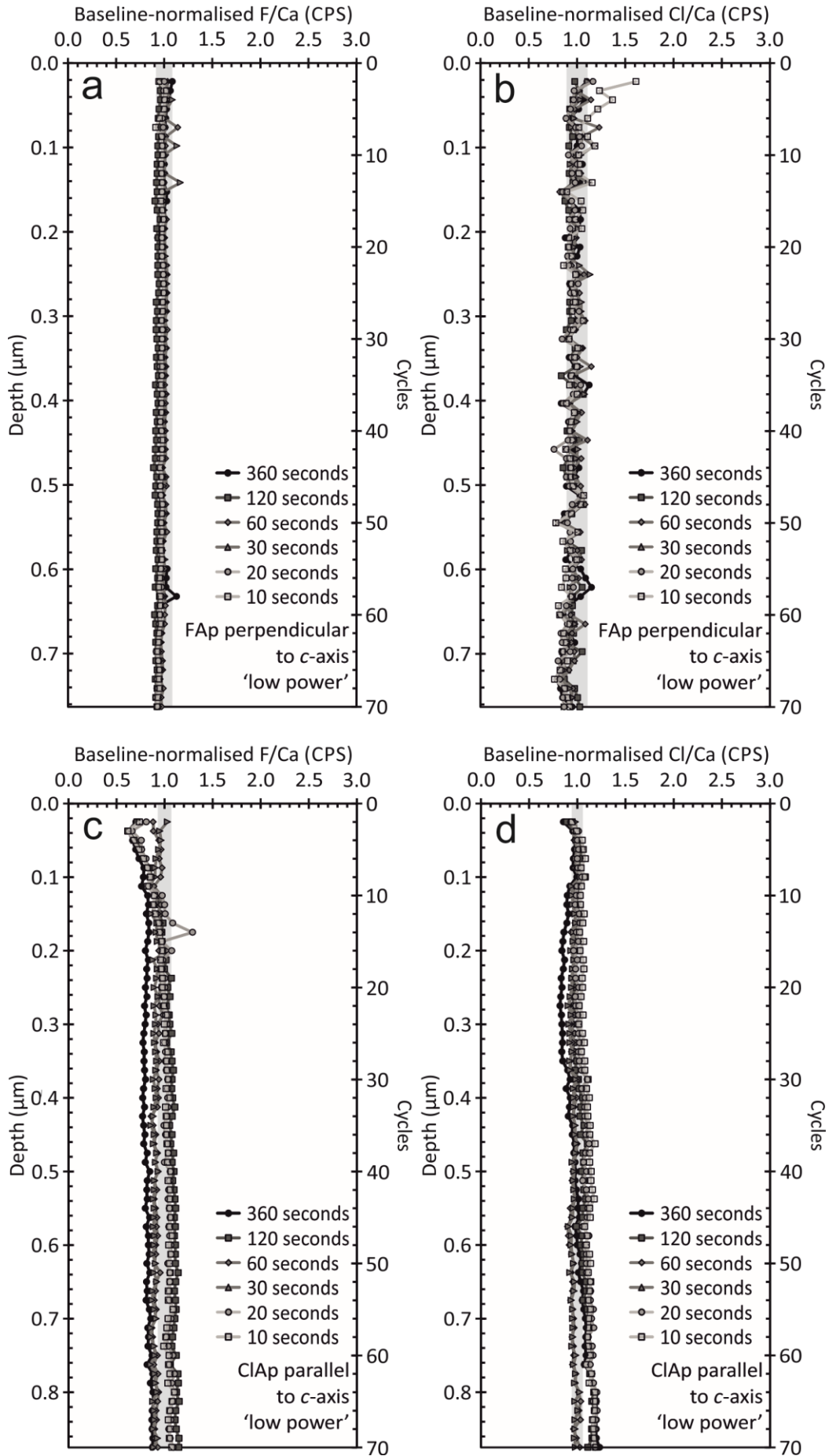


Figure 3.6 | (previous page) SIMS depth profiles of chlorapatite irradiated parallel to *c*-axis and fluorapatite irradiated perpendicular to *c*-axis. Secondary ion mass spectrometry data showing chemical depth profiles for (a) F and (b) Cl in fluorapatite perpendicular to the *c*-axis, irradiated under 'low power' electron-beam conditions. Panels (c) and (d) show SIMS depth profiles for F and Cl, respectively, in chlorapatite parallel to the *c*-axis, irradiated under 'low power' electron-beam conditions. Symbols denote the different lengths of time that profiles were exposed to an electron-beam (see legend for details). Data are presented as in Figure 3.5. Fully propagated two standard deviation counting uncertainties are presented as grey bars along the line baseline-normalised halogen/Ca ratio = 1.0.

3.4. Discussion

The difference between irradiated and non-irradiated SIMS profiles demonstrates that changes in the surface concentration of halogens must be a result of electron-beam exposure. Furthermore, the degree of F/Ca enrichment seen at the surface of irradiated fluorapatite, oriented with the *c*-axis parallel to the electron-beam, correlates very well with the increase in $FK\alpha$ X-ray count rates (Fig. 3.7). Minor discrepancies are interpreted as resulting from slight misalignment of SIMS and EPMA points. If the SIMS depth profile does not fully sample the region affected by electron-beam irradiation this effectively 'dilutes' the signal and apparently reduces the effects of EPMA irradiation in the SIMS profiles. The data confirm that the variation in X-ray count rate during EPMA is related to migration of halogens in the vicinity of the sample surface. My data also show surface enrichment in Cl after prolonged beam exposure parallel to *c*-axis (Fig. 3.5), which indicates that this is a generic mechanism of halogen migration within the apatite channel and is not restricted to F. The degree of surficial Cl enrichment does not appear to vary systematically with F enrichment, within the limitations of my dataset, though I would anticipate that this might be evident if greater precision were possible.

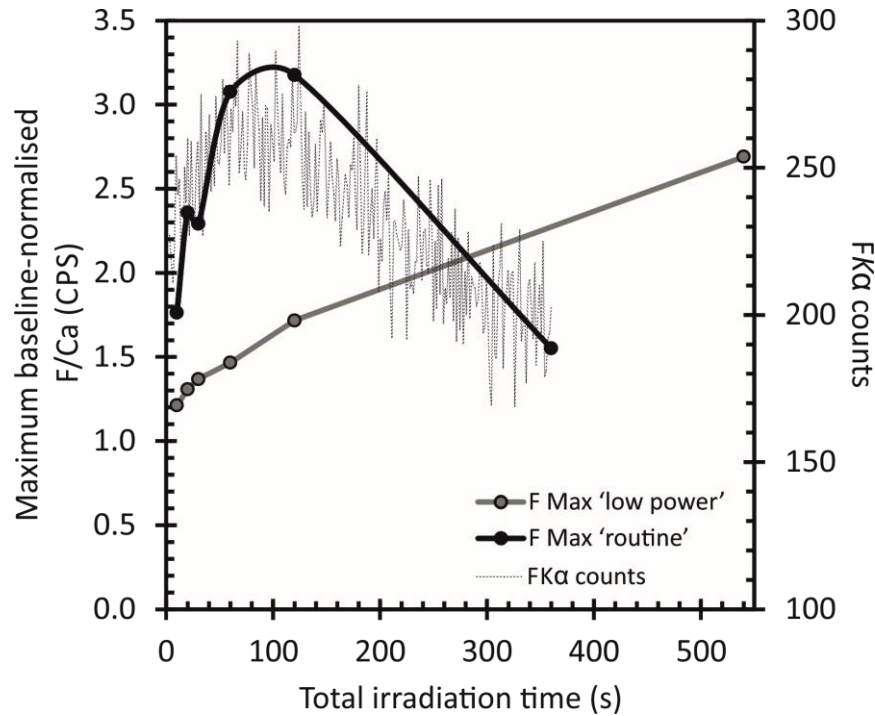


Figure 3.7 | Comparison of surface F enrichment measured by SIMS and FKα counts measured by EPMA. Scatter graph showing the maximum surface F/Ca ratio (F max) in SIMS depth profiles of fluorapatite, oriented with the *c*-axis parallel to the electron-beam, irradiated under 'routine' (black circles) and 'low power' (grey circles) electron-beam conditions. Data are presented as in Figure 3.5. Fully propagated two standard deviation counting uncertainties are less than the size of the marker. The FKα EPMA time scan for fluorapatite irradiated under 'routine' conditions parallel to the *c*-axis is shown for comparison (thin, dashed black line).

The main physical effects of electron-beam exposure are sample heating and the generation of an electric field within the sample. In a thermally and electrically insulating medium, such as apatite, the thermal and electrical fields operate over approximately the size of the interaction volume region. It therefore seems likely that any excess halogens identified close to the sample surface in irradiated profiles are sourced from this region. In the following section, I consider the effects of sample heating and electric fields induced by electron-beam exposure under 'low power', 'routine' and 'extreme' electron-beam conditions. I then use this information to interpret the mechanisms responsible for the variability in halogen X-ray count rates observed during EPMA.

3.4.1. Physical effects of the electron-beam

3.4.1.1. *Electron implantation*

The CASINO programme (Hovington *et al.*, 1997) uses Monte Carlo statistical simulations to compute probabilistic electron trajectories within a sample medium, giving information on the maximum depth of electron penetration and the region of highest charge density (i.e. the region of maximum electron deposition). The results of simulations run for pure fluorapatite and chlorapatite using the ‘low power’ and ‘routine’ electron-beam conditions are summarised in Figure 3.8 and Table 3.3. This model demonstrates that, for a given electron-beam current and spot size, the maximum depth of electron penetration, and the centre of the electron interaction volume, increase with increasing accelerating voltage and are similar in both fluorapatite and chlorapatite, as predicted by Kanaya and Okayama (1972). Furthermore, at a constant accelerating voltage, the strength of the electric field will increase at higher beam currents, as increasing numbers of negatively charged electrons are deposited within the interaction volume. Because the strength of an electric field decreases radially with increasing distance, the electric field at the sample surface will be weaker at higher accelerating voltages.

3.4.1.2. *Halogen X-ray generation*

During EPMA, a proportion of the X-rays generated as a result of interactions between the incident electrons and the sample medium is attenuated by the sample matrix. This is related to the material density and the wavelength of the X-rays (Reed, 2005). In general, X-rays generated at greater depths are more likely to be attenuated. CASINO simulations (Hovington *et al.*, 1997) demonstrate that for pure fluorapatite all $FK\alpha$ X-rays generated

at depths >0.87 , >1.59 and >1.94 μm are attenuated for the 10, 15 and 20 kV electron-beams, respectively. The intensity of the emitted X-rays is at a maximum close to the sample surface and decreases exponentially with depth (Fig. 3.8). $\text{ClK}\alpha$ X-rays have a higher energy than $\text{FK}\alpha$ X-rays and so the degree of attenuation is much lower for a given composition and set of beam conditions. In apatite, under a 10 kV electron-beam, 90% of the emitted $\text{ClK}\alpha$ X-rays are derived from the top 0.46 μm of the sample (cf. 0.37 μm for

Electron-matter interaction models					
Simulation conditions	Maximum electron penetration depth (μm) ^a	Depth of maximum electron density (μm) ^a	ΔT_{VC} (K) ^b	ΔT_{R} (K) ^c	Maximum depth of F enriched region (μm)
Fluorapatite 'low power'	0.9	0.5	7.2	10.8	0.21
Chlorapatite 'low power'	0.9	0.5	-	-	-
Fluorapatite 'routine'	1.9	0.8	10.8	16.2	0.19
Fluorapatite 'extreme'	3.1	1.5	28.7	43.3	-

Table 3.3 | Summary of model outputs, showing the simulated electron penetration and average heating under different electron-beam operating conditions. The maximum depth of F enrichment in fluorapatite parallel to the *c*-axis is shown for comparison. Fluorapatite density = $3.10 \text{ g}\cdot\text{cm}^{-3}$, Chlorapatite density = $3.17 \text{ g}\cdot\text{cm}^{-3}$. Thermal conductivity for fluorapatite = $0.0133 \text{ W}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$ (Shan *et al.*, 2013). Focused electron-beam diameter = 0.2 μm .

^a Modelled for pure fluorapatite or chlorapatite using the CASINO simulation (Hovington *et al.*, 1997).

^b Estimate of electron-beam induced heating averaged over the entire interaction volume from Vassamillet and Caldwell (1969).

^c Estimate of electron-beam induced heating averaged over the entire interaction volume estimate from Reed (2005).

FK α at 10 kV) and all ClK α X-rays generated at depths $>0.93\text{ }\mu\text{m}$ are attenuated. In other words, FK α X-ray counts reflect variability in the concentration of F very close to the sample surface, above the depth of maximum charge density, while ClK α counts reflect a bulk average of the Cl concentrations extending deeper into the sample and within the electron interaction volume.

3.4.1.3. Electron-beam induced heating

Inelastic collisions during electron-sample interactions convert a significant portion of the electron-beam energy into heat within the sample, through excitation of lattice oscillations (Nouiri *et al.*, 2006). The amount of heat generated within the interaction volume increases with higher beam power (current $\cdot$ accelerating voltage), and with decreasing spot size and thermal conductivity. Empirical expressions derived by Vassamillet and Caldwell (1969) and Reed (2005) both give a ΔT of a few degrees, averaged over the interaction volume, for the electron-beam conditions used in the EPMA irradiations, assuming an apatite thermal conductivity of $0.0133\text{ W}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$ (Table 3.3; Shan *et al.*, 2013). However, because the number of electron-matter interactions decreases outwards from the centre of the interaction volume, neither model adequately addresses the spatial variability of the beam-induced thermal field. Monte Carlo simulations of electron trajectories in GaAs, taking into account this spatial variability in the electron density, demonstrate an exponential decrease in ΔT with depth through the interaction volume, with the steepness of the thermal gradient dictated by the accelerating voltage (Nouiri *et al.*, 2006). Shan *et al.* (2013) further show that the degree of surface heating increases with prolonged electron-beam exposure, due to more electron-matter interactions. These models demonstrate the principle that electron-beam exposure may induce a steep thermal gradient within the interaction volume (Fig. 3.8). After 384 s of

irradiation, under a 16.5 kV, 1 nA electron-beam, apatite crystals may experience a temperature rise of ~ 30 K close to the sample surface, which decays to <5 K within the top ~ 0.3 μm (Shan *et al.*, 2013). However, Nouiri *et al.* (2006) demonstrate that small changes in the primary beam current can greatly increase the degree of surface heating, particularly at lower accelerating voltages. I therefore consider it feasible that the crystals in this study may experience a temperature rise of >200 K close to the sample surface.

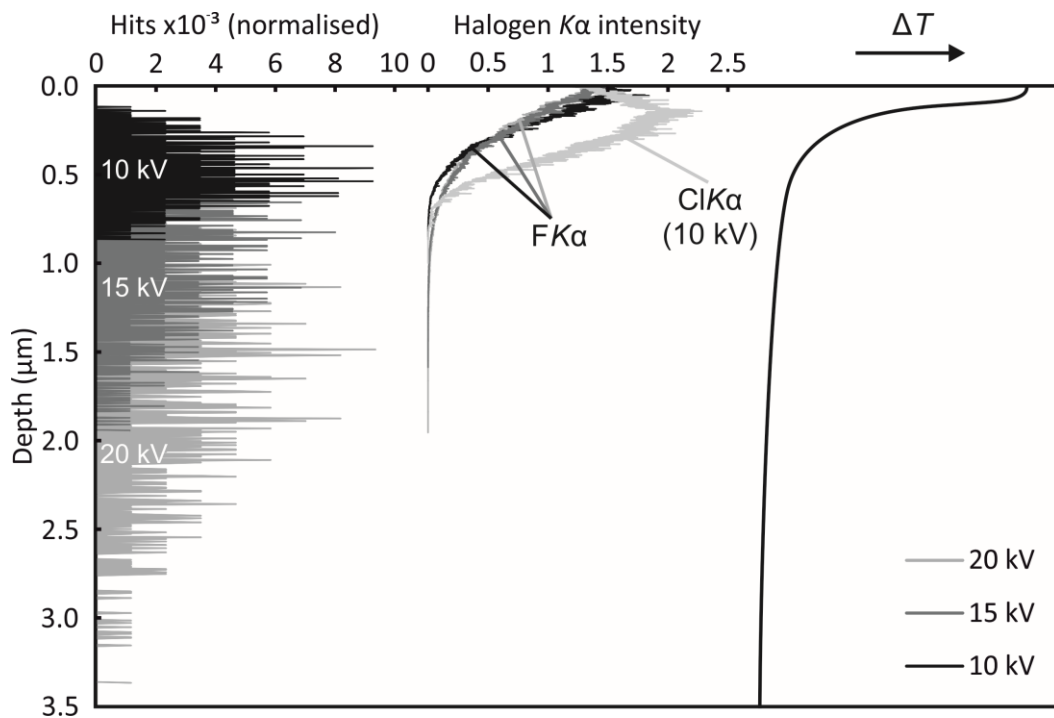


Figure 3.8 | Summary diagram showing the combined effects of electron-beam exposure under different electron-beam operating conditions. Left: Histogram showing the implantation depths of electrons in apatite, modelled using the CASINO Monte Carlo simulation (Hovington *et al.*, 1997). Light grey = ‘extreme’ conditions (20 kV), medium grey = ‘routine’ conditions (15 kV), and black = ‘low power’ conditions (10 kV). **Center:** intensity of halogen X-rays, generated within the sample that are emitted at the surface (i.e. unattenuated), calculated using CASINO (Hovington *et al.*, 1997). Greyscale as above. The labelled light grey line shows Cl X-ray attenuation in chlorapatite under ‘low power’ conditions. **Right:** schematic thermal gradient within fluorapatite during electron-beam irradiation at 16.5 kV, adapted from Shan *et al.* (2013).

3.4.2. New constraints on the halogen migration mechanism in fluorapatite

Fluorine remains localised in all of my XRD results, demonstrating that thermally-induced diffusion alone cannot occur at the temperatures experienced during electron-beam irradiation. Therefore, surface halogen enrichment must be related to the combined influence of the thermal and electric fields imposed by the beam. This is consistent with the greater electrical conductivity of apatite at higher temperatures, explained by charge transfer through anionic migration (Laghzizil *et al.*, 2001). The observed mobility of halogen anions is likely facilitated by their local crystallographic environment.

During electron-beam exposure a number of physical mechanisms may be responsible for the transportation of halogen ions along the *c*-axis channel:

(1) Vacancy-mediated migration (Tse *et al.*, 1973; Welch and Royce, 1973). This mechanism requires the presence of intrinsic vacancies within the apatite crystal structure, which either exist as a result of Frenkel defects (Jay *et al.*, 2012), or Schottky defects, in which two F⁻ vacancies are charge-balanced by a Ca²⁺ vacancy (Den Hartog *et al.*, 1972). In this mechanism, vacancies would move towards the centre of the interaction volume to charge-balance implanted electrons from the EPMA beam, and interchange of vacancies with Z-site anions would result in the migration of halogens away from the charge centre (Tse *et al.*, 1973).

(2) The halogen anions may be repelled away from the centre of charge build-up, as a result of the electric field generated by electron implantation, in a process similar to alkali migration in glass (Humphreys *et al.*, 2006). This is somewhat similar to mechanism (1) but does not require pre-existing vacancies to facilitate migration. Recent molecular dynamics simulations demonstrate the potential for *c*-axis halogen migration in apatite via

interstitial sites (Jay *et al.*, 2012). This mechanism results in the formation of a Frenkel defect in the original halogen position, and would require ‘storage’ of excess F in metastable interstitial sites.

(3) Halogen migration could be driven by an electric potential induced through an independent change in the crystal structure, resulting in loss of negative charge. If, for example, electron-beam induced heating were to cause dissociation and loss of oxygen anions from the apatite surface, as is observed during the irradiation of volcanic glasses (Lineweaver, 1963), then halogens within the *c*-axis channel might migrate towards the surface in order to compensate the loss of charge.

The SIMS depth profiles permit some interpretation of the physical mechanisms responsible for halogen migration during electron-beam irradiation of apatites. In the experiments that show the highest degree of surface enrichment there is up to three times more F than in baseline profiles. Given that the Durango apatite is known to be close to end-member stoichiometric fluorapatite (Young *et al.*, 1969), it is unlikely that the surface layer would contain sufficient vacancies to accommodate the additional F introduced into this region through mechanism (1). Furthermore, the SIMS data appear to negate the possibility that halogen diffusion is induced by the surficial loss of other anionic species through mechanism (3). The only other major anionic component within the apatite crystal structure is O^{2-} and baseline-normalised O/Ca are constant (within error) in irradiated depth profiles. I therefore suggest that EPMA-induced halogen migration is most likely to occur through an interstitial mechanism (2), facilitated by the availability of metastable interstitial sites located within the column anion channel and close to the average halogen crystallographic position.

The molecular dynamics simulations of Jay *et al.* (2012) suggest that F diffusivity through the interstitial mechanism is log linear with $1/T$ for $1100 < T < 1500$ K. This is

substantially in excess of the maximum anticipated temperature of electron-beam induced heating under the beam conditions used in this study. However, the simulations were only run for 20 ps. Assuming that this relationship remains true at lower temperatures, F diffusion through an interstitial mechanism could occur at the temperatures of EPMA-induced heating, albeit on longer times scales than were accessed by Jay *et al.* (2012). Furthermore, their simulations only consider thermally assisted migration and do not account for the effect imposed by the electric field generated during EPMA.

Fluorapatite is weakly conductive in an electric field and conductivity has been shown to increase with temperature (Laghzizil *et al.*, 2001). The electrical properties of apatite are anisotropic, suggesting that the crystallographic response to an external electric field is associated with Z-site ion migration, parallel to the *c*-axis (Royce, 1974; Welch and Royce, 1973). These electrical properties have been interpreted as both migration through a vacancy-mediated mechanism (Royce, 1974) and through the occupation of interstitial sites (Laghzizil *et al.*, 2001).

Molecular dynamics simulations have not been performed to investigate Cl⁻ or OH⁻ migration in apatite. These anions are larger than F⁻ and do not fit in the same position within the *c*-axis channel (Hughes and Rakovan, 2002). The SIMS depth profiles demonstrate the potential for surficial Cl⁻ enrichment during electron-beam exposure, indicating the possibility for *c*-axis Cl migration in agreement with Brennan (1993). As with F, the degree of Cl enrichment at the sample surface precludes diffusion through a vacancy-mediated mechanism and may be facilitated by the occupation of interstitial sites. However, in the ‘low power’ irradiated depth profiles, Cl enrichment outside of analytical uncertainty is only detected after very long beam exposure times, which may reflect a higher activation energy for Cl migration. Hydroxide concentrations do not show significant surface enrichment in any irradiated depth profiles parallel to the *c*-axis. This

largely reflects the high analytical uncertainties, although I cannot exclude that a high activation energy is also required for migration of large OH molecules, as suggested by Tse *et al.* (1973), and/or that OH migration requires a different mechanism than halogen migration (Laghzizil *et al.*, 2001).

Stormer *et al.* (1993) demonstrate that there is no relaxation in EPMA count rates after a 16 hour break in electron-beam irradiation. In this study, surficial halogen enrichment is preserved for up to 39 days between EPMA irradiation and SIMS analysis. Previous studies on apatites and silicates with the apatite structure have detected excess anionic species in interstitial sites within the *c*-axis channel by nuclear magnetic resonance (Sansom *et al.*, 2006) or by XRD (Hughes *et al.*, 2014; Mackie and Young, 1974). This suggests that longer-term occupation of these interstitial sites is possible. However, after removal of the thermal and electric fields halogen anions occupying interstitial sites in the enriched region of irradiated apatites are likely highly unstable or metastable. Diffusion rates will be very slow at room temperature, but I suggest that heating of irradiated crystals should cause relaxation of the surface enrichment profiles.

3.4.2.1. Mass-balance considerations and asymmetry in halogen migration

Unfortunately, due to limitations in the SIMS technique, it was not possible to depth-profile right through the interaction volume in any of the irradiated points. If migration were in response only to an electric field (i.e. in the absence of any directional thermal field), I would expect an equal enrichment in halogen concentrations above and below the interaction volume. However, there is little evidence of depletion within the interaction volume region, beneath the maximum depth of surface enrichment. Assuming mass-balance, the depletion is insufficient to supply the required amount of F for equal accumulation below the interaction volume, suggesting that more F has migrated up than down. I would predict that the rapid decrease in the thermal effect with increasing depth

prevents effective migration below the interaction volume. Instead, the steep thermal gradient would enable halogens to migrate upwards more easily and hence become more enriched at the surface than below the interaction volume. This thermal control may be one explanation for why cooling samples during analysis can improve the accuracy of EPMA results (Henderson, 2011).

3.4.2.2. Decreasing halogen enrichment at long irradiation times

After prolonged electron-beam exposure the amount of F in the enriched surface region decreases. This cannot be related to the electric field as this stabilises rapidly within the sample (Cazaux, 1986). Apatite crystals were carbon coated and grounded during electron-beam irradiation, so I can exclude sample charging effects, which would progressively decrease the depth of maximum electron deposition by reducing the effective accelerating voltage (Reed, 2005). I also reject suggestions that the decrease in X-ray counts, observed in EPMA time scans, may result from external factors such as beam contamination or destruction of the carbon coat (Stormer *et al.*, 1993). Beam contamination would result in deposition of graphite on the sample surface, increasing light element X-ray attenuation (Buse and Kearns, 2014). However, there is very good agreement between the decrease in X-ray counts and the reduction in halogen concentrations in the enriched layer (Fig. 3.7), indicating that the decrease in halogen X-ray counts is an intrinsic crystallographic response to electron-beam exposure. After prolonged irradiation under ‘extreme’ electron-beam conditions, I see a general increase and irregular fluctuations in F X-ray counts (Fig. 3.3e), accompanied by observable damage to the sample surface and formation of a shallow pit. I attribute this to instabilities in the absorbed beam current, related to degradation of the carbon coat and sample breakdown. These effects are not seen for the ‘low power’ or ‘routine’ conditions.

Instead, I suggest that breakdown of the apatite structure, by non-stoichiometric loss of CaZ_2 ($Z = \text{F}, \text{Cl}, \text{OH}$; Den Hartog *et al.*, 1972 and references therein) as a result of progressive sample heating, is responsible for the eventual decrease in X-ray count rates and decreasing surface halogen/Ca. Under my ‘extreme’ conditions, craters were eventually observed to form at the sample surface during irradiation. I interpret this as the result of thermally-driven breakdown of the crystal structure. An increase in the accelerating voltage of the incident electron-beam reduces the initial temperature rise at the sample surface (Nouiri *et al.*, 2006). Thus, higher accelerating voltages increase the time taken for the sample surface to reach the temperature above which halogen loss from the surface exceeds the rate of enrichment.

3.4.3. Anisotropy of migration

Under ‘low power’ and ‘routine’ EPMA operating conditions I only detected halogen migration when the crystals were oriented *c*-axis parallel to the incident electron-beam. Despite the three dimensional nature of the electric field, halogens do not appear to migrate (either laterally along the *c*-axis or parallel to the *a*-axis) when the crystal is oriented with its *c*-axis perpendicular to the beam. If halogens were moving laterally along the *c*-axis (i.e. normal to the electron-beam), this would be seen as a decrease in EPMA X-ray counts and potentially a measurable, near-surface depletion in SIMS depth profiles. If halogens were moving parallel to the *a*-axis (and thus parallel to the beam) this would cause a surficial enrichment and increase in EPMA X-ray counts. I interpret this as further evidence of the necessity for combined thermal and electric fields in order to facilitate migration. Only under ‘extreme’ electron bombardment is a variation in X-ray count rates induced in samples oriented with the beam perpendicular to the *c*-axis (Fig.

3.3f). I interpret this as migration in the a -axis direction, induced by the ‘extreme’ electron-beam conditions.

3.4.4. The role of apatite composition

In chlorapatite, oriented with the c -axis parallel to the electron-beam, $\text{ClK}\alpha$ does not show any systematic count rate variability in EPMA time scans and there is no evidence of surface F or Cl enrichment in the SIMS depth profiles, even after prolonged electron-beam exposure. In contrast, Goldoff *et al.* (2012) report variation in halogen X-ray counts in some Cl-rich apatites, but the relationship between the degree of halogen count rate variability and the Cl content of the crystal is non-linear. It has been reported that stoichiometric end-member chlorapatite has a monoclinic structure, with a $P2_1/b$ space group (Elliott, 1994). However, for non-stoichiometric chlorapatite, containing vacancies or other substituents, such as the natural samples in this study, the crystal retains a hexagonal $P6_3/m$ symmetry overall (Hughes *et al.*, 2014). In either case, the c -axis column remains effectively unaltered, with the loss of symmetry related to the ordering of halogen displacements along $[0,0,1]$ relative to the mirror planes (Hughes *et al.*, 2014). In hexagonal fluorapatite, F ions sit directly on the mirror planes, permitting migration through the occupation of interstitial lattice sites, between the two Ca triangles, at low activation energies (Jay *et al.*, 2012). Larger Cl ions are accommodated above or below the mirror planes and in binary F-Cl apatites the incorporation of Cl can act to push F off of the mirror plane to maintain sufficient distance between anions (Hughes *et al.*, 2014). The presence of anionic species in the space between the two mirror planes along the anion column alters the geometry of interstitial sites along the column. It is this incorporation of halogens at positions off the mirror plane, combined with the larger radius of Cl^- relative to F^- , that I believe inhibits c -axis migration in chlorapatite. In binary

and Cl-rich apatites, the ease with which interstitial sites are occupied will be dependent on small changes in composition and the presence of vacancies. This may explain the non-linearity between apatite Cl content and halogen migration observed by Goldoff *et al.* (2012).

3.5. Implications

I have demonstrated that halogen migration can occur in apatite in response to sample heating and the application of an electric field, particularly where these effects occur together. This is important for our understanding of the materials properties of apatite group minerals and elucidates the migration mechanisms for volatile species.

This study reinforces the conclusions from previous work, and highlights the necessity for careful analysis of apatite volatile contents by EPMA. The choice of electron-beam conditions must be governed by the required precision for all elements, but take into account that it is combined sample heating and the electric field, induced by electron-beam irradiation, that cause halogen migration. Alone, neither of these effects appears capable of inducing migration under normal EPMA operating conditions. This explains why sample cooling, using a cryogenic or Peltier cooling stage, represents a promising method by which the quality of apatite halogen measurements may be improved (Henderson, 2011). If this is not viable, analyses should be performed with the electron-beam oriented perpendicular to the *c*-axis, using beam conditions that minimise the deposited energy density. Furthermore, electron-beam induced migration of halogens is highly dependent on the apatite composition. Thus, any correction for halogen migration (e.g. through linear projection to the time-zero intercept), must be done for appropriate crystal compositions, and under identical electron-beam conditions used for analysis. Importantly, the common approach of calculating apatite OH contents ‘by

difference', assuming that the Z-site is fully occupied by F, Cl and OH (Pyle *et al.*, 2002), will be severely compromised by electron-beam damage. My data show that the error will be non-linear with irradiation time, and compounded by uncertainties in F and Cl contents, depending on the apatite composition and orientation, the EPMA counting time, and electron-beam conditions. I therefore strongly recommend that OH should be analysed directly, either by SIMS or by Fourier transform infrared spectroscopy wherever possible.

The results of this study suggest that electron-beam induced halogen redistribution will relax, given sufficient time or with sample heating, but this is likely to require very long timescales at ambient conditions. Therefore, any electron-beam-based sample mapping (e.g. backscatter electron imaging, cathodoluminescence and/or EPMA element mapping) that is undertaken *prior* to EPMA analysis is likely to cause lasting damage to the crystal. Although no evidence is seen for irradiation-induced OH migration in my results, OH-bearing-apatites are likely to be affected by similar issues. The effect of electron-beam irradiation on apatite carbon contents is also unconstrained. Therefore, SIMS analyses, when performed, should be completed before electron-beam exposure.

The results of this study imply that halogen migration occurs through the occupation of interstitial crystal sites. Molecular dynamic simulations have been run for F migration in pure fluorapatite, but my work highlights a need to extend this to other species (e.g. Cl and OH) in fluorapatite, as well as in binary (F, Cl) and Cl-rich apatites, where my data suggest an impediment to migration.

Finally, this work also has implications for apatite fission track studies where the annealing rate is known to be dependent on the crystal halogen content (Carlson *et al.*, 1999). Migration mechanisms, similar to those described here, could be invoked to explain the temporal and temperature dependent variability of annealing between

fluorapatite and chlorapatite. The similarity of the migration mechanisms invoked for EPMA-induced migration and those responsible for fission track annealing is consistent with the anisotropy of the annealing rate, whereby diffusion is believed to occur more rapidly parallel to the *c*-axis (Green and Durrani, 1977). Zeitler *et al.* (1987) identified a time-dependent decrease in the ^4He content of apatite with low-temperature heating in a vacuum. In principle, helium loss from the sample surface could occur through a similar mechanism to that described here for halogen-group elements.

Chapter 4

Modelling the volatile evolution of magmas and corresponding apatite

4.1. Introduction

Interpreting pre-eruptive magma fluid systematics from apatite volatile analyses is not straightforward. Previous studies have attempted to apply Nernst-type partition coefficients in an attempt to relate magma and apatite volatile concentrations (e.g. Boyce *et al.*, 2010). However, experimental partition coefficients often fail to reproduce dissolved magmatic volatile abundances from apatite analyses in natural systems (Boyce *et al.*, 2014; Doherty *et al.*, 2014; Webster *et al.*, 2009b). This is not surprising, as F, Cl and OH are integral constituents in the apatite crystal structure, and stoichiometric crystals must be filled by a combination of these anion components (Hughes and Rakovan, 2002; Pan and Fleet, 2002). Volatile concentrations in apatite are therefore not independent of one another (Candela, 1986) and, although crystal compositions do vary as a function of changes in the melt composition, the apatite-melt volatile relationship is non-Nernstian (Boyce *et al.*, 2014; McCubbin *et al.*, 2015a; Webster and Piccoli, 2015); an increase in the apatite OH component may, for example, either reflect an increase in magmatic H₂O concentration, or a decrease in the abundance of halogens.

Instead of Nernst-type partitioning, the apatite-melt volatile relationship is more accurately described as an exchange equilibrium between F, Cl and OH, analogous to olivine-melt Fe and Mg partitioning (Roeder and Emslie, 1970; Toplis, 2005). This can be written in the general form:



where Y and Z represent two different end-member apatite components and superscripts Ap and m denote the apatite and melt phases, respectively (McCubbin *et al.*, 2015a). At equilibrium, the ratio of the activities of two volatile components (Cl-F, OH-F, or OH-Cl) in the melt is proportional to the activities of those volatile components in the apatite phase, multiplied by an exchange coefficient (K):

$$K_{Z-Y(P,T)} = \frac{a_Y^m}{a_Z^m} \cdot \frac{a_Z^{Ap}}{a_Y^{Ap}} \quad (\text{eq. 4.2})$$

where a is activity, P is pressure, and T is temperature (McCubbin *et al.*, 2015b). In combination, equations of this form can describe the crystal-melt volatile relationship, accounting for the interdependence of apatite volatile components.

In the melt phase, F, Cl and H₂O concentrations evolve differently during fractional crystallisation in the presence (or absence) of magmatic fluids, and apatite compositions in equilibrium with the melt should therefore evolve distinctly, depending on the nature of the fluid-melt volatile exchange. If the crystal-melt exchange coefficients are known, apatite analyses may be a useful tool for assessing pre-eruptive magmatic fluid systematics. In this chapter, I develop a two-step semi-quantitative approach to determining the theoretical compositional evolution of apatite during crystallisation in the presence of magmatic fluids. In the first step, I model variations in the F, Cl and H₂O concentrations of silicate melts as a function of the extent of crystallisation. Fractional

crystallisation models are created to describe variations in the partitioning of these volatile components in the presence of different fluid phases. In the second step, I calculate the volatile composition of apatite in equilibrium with the melt at each stage of the crystallisation models using the isobaric, isothermal, quasichemical formulation of the crystal-melt relationship described by Candela (1986). The same approach is used to calculate the compositional evolution of apatite during volatile-undersaturated crystallisation and the effect of late-stage fluorite saturation on evolving apatite compositions.

The modelling approach outlined in this chapter can be compared directly with empirical data to determine the thermodynamic properties of mineral-melt volatile exchange, and hence the nature of the magmatic fluid phase at the time of apatite crystallisation or crystal-melt re-equilibration. Although the approach could be applied widely to assess fluid systematics in different volcanic environments, the models presented here focus on evolved phonolitic systems, similar to Campi Flegrei. I use these models to interpret empirical apatite analyses from Campi Flegrei in Chapters 5 and 6.

4.2. Fluid phase terminology and processes

Before modelling the compositional evolution of magmatic volatiles, it is necessary to define terminology describing magmatic fluid systematics, and the fluid phases that may coexist with silicate melts in sub-volcanic systems. In the magmatic, hydrothermal and fluid inclusion literature, fluid phases can be described ambiguously and the same terminology is often applied to describe compositionally variable liquids. Here, I categorise fluid phases based on the thermodynamics of their volatile exchange with a coexisting silicate melt. My classification is similar to that of Heinrich (2005), in which fluid phases are defined on the basis of their relative physical properties (i.e. density).

However, it does not require prior quantitative knowledge of phase compositions or stability, thus providing a more useful basis for modelling the evolution of volatile species during magmatic fractionation.

As a first-order subdivision, magmatic systems may either be volatile-undersaturated or saturated in one or more fluid phase. ‘Fluid’ is a generic term that broadly refers to any liquid or vapour that coexists with a silicate melt. In natural magmatic systems, fluids are generally composed of H₂O and chloride salts (Heinrich, 2005), as well as CO₂ and sulphur species. In Campi Flegrei, melt inclusion analyses consistently demonstrate that the system contains very low CO₂ concentrations (Arienzo *et al.*, 2010; Marianelli *et al.*, 2006; Chapter 5). For this reason, and due to its

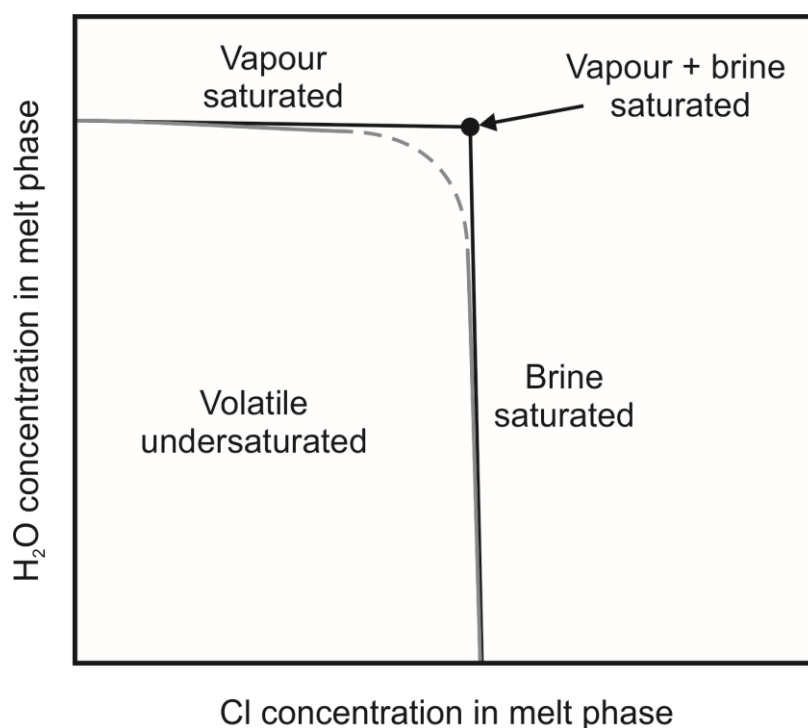


Figure 4.1 | Schematic diagram showing H₂O and Cl concentrations in a silicate melt, adapted from Webster (2004). Lines show the solubilities of H₂O and Cl under subcritical (black line) or supercritical (grey line) conditions. At these lines, the melt will be saturated in a single fluid phase. The solid lines show regions of Henrian vapour-melt Cl partitioning or brine-melt H₂O partitioning. The dashed line shows the region of non-Henrian supercritical hydrosaline fluid-melt partitioning (see discussion in text). At the black point, both a vapour and brine may co-exist with the silicate melt.

considerably greater influence on apatite compositions, I focus on modelling the (Na,K)Cl-H₂O binary electrolyte system, with only passing reference to the effect of CO₂. ‘Volatile saturation’ refers to the point at which the concentration of a dissolved magmatic volatile species is at its solubility limit. An increase in the volatile content of the system will cause exsolution of one or two fluid phases, which will coexist with the silicate melt. Further volatile enrichment will increase the volume of the fluid phase but the volatile content of the silicate melt will remain constant (i.e. ‘buffered’) at fixed pressure and temperature (Fig. 4.1).

Although chloride and chlorine saturation strictly refer to the solubility of Cl⁻ and pure Cl₂ respectively, it is the convention in the magmatic literature is to use these terms interchangeably (Lowenstern, 2000). I use ‘Cl saturation’ herein specifically to refer to

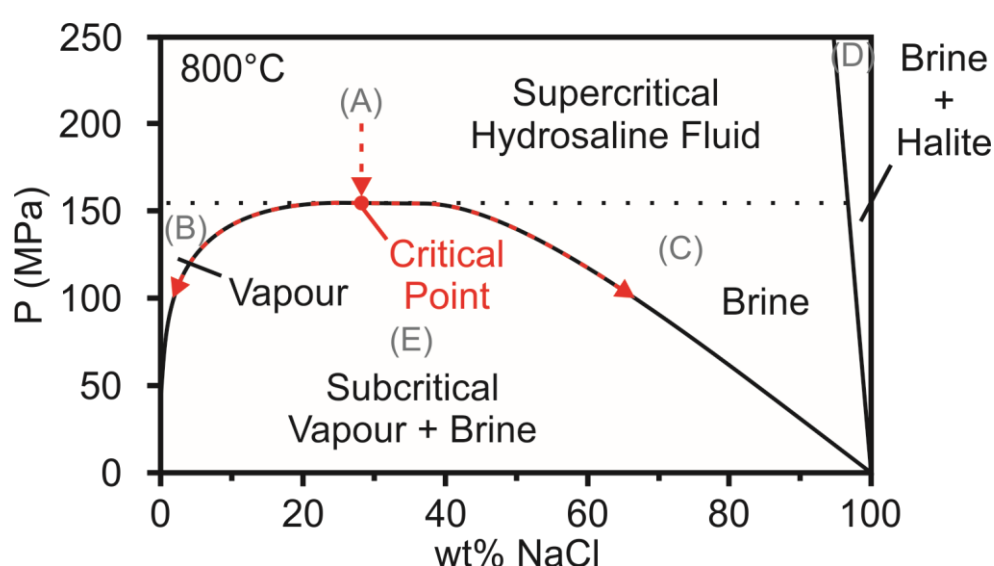


Figure 4.2 | Experimentally derived NaCl-H₂O binary phase diagram at 800 °C, adapted from Driesner and Heinrich (2007). Solid black lines show phase boundaries, dotted black line shows the division between supercritical hydrosaline fluids, dense brines and low-density vapours. Letters in parenthesis show different liquid compositions: (A) is a supercritical hydrosaline fluid, (B) is a vapour, (C) is a brine, (D) is a molten salt melt, and at (E) both a brine and immiscible vapour phase will co-exist. The red dashed line shows the evolution of liquid (A) during depressurisation from 200 MPa to 100 MPa- at the critical point the fluid will un-mix forming a dense brine and low-density vapour. At 100 MPa these contain 67 wt% and 2 wt% NaCl, respectively.

the solubility of the Cl^- ion, rather than Cl_2 gas. Chlorine saturation in an anhydrous melt will cause exsolution of molten salt, composed predominantly of Na^+ , K^+ and Cl^- (Aiuppa *et al.*, 2009a; Lowenstern, 2000). At low magmatic H_2O concentrations, H_2O will partition into this Cl-rich fluid, forming a hypersaline ‘brine’ (Fig. 4.2; Webster and De Vivo, 2002). Water saturation is characterised by the exsolution of a magmatic aqueous phase (Larsen and Gardner, 2004; Schmidt and Behrens, 2008; Webster *et al.*, 1999). At low Cl concentrations, Cl partitioning into the aqueous phase is, or can be approximated as, Henrian (Fig. 4.3; Signorelli and Carroll, 2000) and under these conditions I refer to the low density, low salinity fluid as a magmatic ‘vapour’ (Figs 4.1, 4.2).

Numerous studies have demonstrated that the (Na,K)Cl- H_2O system is characterised by a miscibility gap under typical sub-volcanic pressures and temperatures (i.e. $\sim 850^\circ\text{C}$, $\sim 200\text{ MPa}$; Driesner and Heinrich, 2007; Heinrich *et al.*, 2004; Shinohara, 1994; Signorelli and Carroll, 2000; Webster, 1997a). Under subcritical conditions, the silicate melt can coexist with two fluid phases (Signorelli and Carroll, 2000): a brine and immiscible vapour phase (Fig. 4.2). Under these conditions of ‘two-fluid stability’, the Cl and H_2O content of the vapour and brine are fixed at a given pressure and temperature and, according to the Gibbs’ phase rule, the composition of the coexisting silicate melt must also be invariant, causing non-Henrian fluid-melt volatile partitioning (Fig. 4.3; Signorelli and Carroll, 2002). Under supercritical conditions, the silicate melt can only coexist with a single fluid phase. Although low-Cl fluid-melt partitioning is approximately Henrian, at moderate-to-high Cl concentrations this assumption becomes increasingly invalid, as there is a greater increase in the Cl content of the fluid phase than the melt as Cl becomes concentrated in the system (Fig. 4.3; Lowenstern, 2000; Signorelli and Carroll, 2000). I define ‘supercritical hydrosaline fluids’ as those where fluid-melt Cl partitioning is non-Henrian, to distinguish them from vapours, in which the Cl content of

the fluid is low and can be adequately described by a true Nernstian partition coefficient. Note: this definition follows the convention in the magmatic literature to categorise ‘supercritical’ fluids as those where there is no distinction between vapour and brine phases. This is distinct from the more common use of the term ‘supercritical’ in the chemical literature to define a fluid that displays both liquid- and gas-like physical properties (Heinrich, 2005).

Phase stability relations in the system (Na,K)Cl-H₂O are a complex function of pressure, temperature and salinity (Driesner and Heinrich, 2007; Heinrich, 2005;

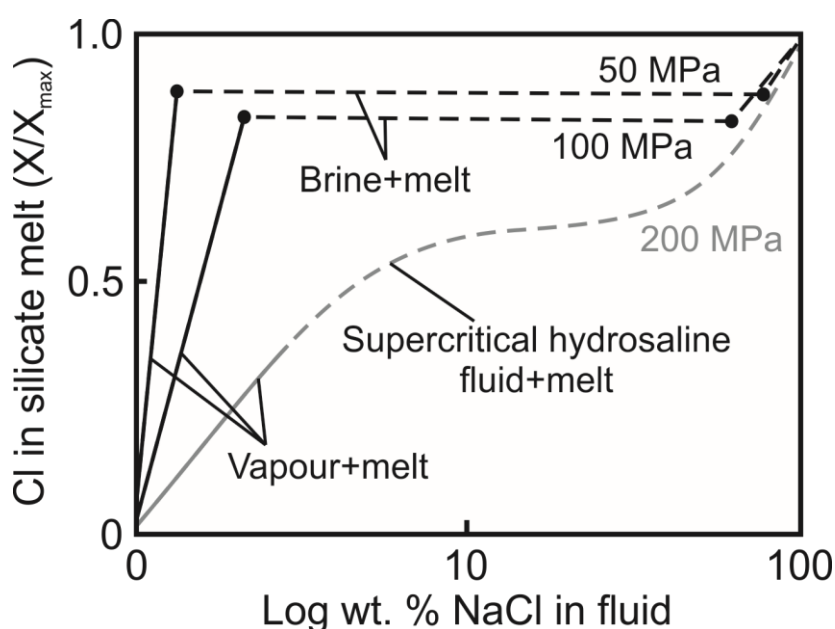


Figure 4.3 | Schematic diagram showing relative concentrations of Cl in exsolved magmatic fluid phase(s) versus the silicate melt, adapted from Lowenstern (2000). Chlorine in the melt is shown relative to the maximum concentration at saturation (X/X_{max}). Solid lines show the region where fluid-melt Cl partitioning can be approximated as Henrian (see Signorelli and Carroll 2000). Dashed lines show where fluid-melt Cl partitioning is non-Henrian and cannot be described using a Nernstian partition coefficient (see discussion in text). Under subcritical conditions (black lines), both a brine and vapour coexist with the silicate melt after Cl saturation, buffering Cl in the melt. Black points show the end-member fluid compositions. Under supercritical conditions (grey line) only a single fluid phase coexists with the silicate melt and fluid-melt Cl partitioning is non-linear at moderate and high Cl concentrations. Based on data from Metrich and Rutherford (1992), Lowenstern (1994), Shinohara (1994) and Webster (1997a), with fluid compositions from Sourirajan and Kennedy (1962).

Signorelli and Carroll, 2000; Signorelli and Carroll, 2002). The transition between subcritical and supercritical conditions occurs at the ‘critical point’, below which two fluid phases can coexist. Experimental data show that at magmatic temperatures (i.e. 860-880 °C), the critical point for NaCl-H₂O liquids occurs between 150 and 200 MPa (Lowenstern, 2000; Signorelli and Carroll, 2000) and increases with temperature (Anderko and Pitzer, 1993; Signorelli and Carroll, 2000). This is supported by thermodynamic modelling, which predicts the critical point to occur at a maximum pressure of 158 MPa at 800 °C and 218 MPa at 1000 °C in the range 0-100% NaCl fluid (Driesner and Heinrich, 2007). The effect of KCl on the fluid phase stability has not been investigated under magmatic conditions, but low-temperature studies suggest that higher KCl may slightly increase the critical pressure (Anderko and Pitzer, 1993; Carroll, 2005).

4.3. Model parameters

In this chapter, variations in apatite volatile compositions are modelled as the result of changing F, Cl and H₂O concentrations in the silicate melt, under isobaric and isothermal conditions. In addition to the effects of changing magmatic volatile content, changes in apatite composition during crystallisation are induced by variations in pressure and temperature. The effects of these parameters on apatite compositions are calculated in Chapter 5 (Section 5.4.3.; Fig. 5.2). Further uncertainty is caused by the assumption of ideality in apatite solid solution. The validity and implications of this assumption are discussed in Section 4.6. Important parameters in these models include: the mineral-melt partition coefficients; the solubility of halogens and H₂O in the silicate melt; and fluid-melt volatile partition coefficients. The values of these parameters, relevant to the Campi Flegrei system, are discussed below. The symbols used in this modelling are summarised in Table 4.1.

List of symbols	
C	Concentration*
a	Activity
Φ	Pertaining to a mineral phase
φ	Fraction of melt remaining
D	Nernst partition coefficient
$\bar{D}$	Bulk Nernst partition coefficient
$\hat{D}$	“Apparent” partition coefficient
K	Equilibrium constant
X	Mole fraction
W	Mass fraction
P	Pressure
T	Temperature
N	Moles O from H ₂ O plus moles of O from anhydrous melt component per kg of melt
m (superscript)	Melt phase
Ap (superscript)	Apatite phase
0 (superscript)	Initial value in the melt phase at the onset of crystallisation
s (superscript)	Value of at saturation
c/m (superscript)	Partitioning between all crystal phases and the melt phase
Φ /m (superscript)	Partitioning between an individual mineral phase and the melt phase
v/m (superscript)	Partitioning between the vapour and melt phases
b/m (superscript)	Partitioning between the brine and melt phases
f/m (superscript)	Partitioning between the fluid(s) and melt phases
i (subscript)	Generic term denoting a component (i.e. F, Cl or OH)

Table 4.1 | Definition of symbols used in fractional crystallisation models.

* In all equations C is in units of weight fraction.

4.3.1. Mineral-melt partition coefficients

Volatile elements are incorporated into the crystal structure of hydrous minerals. However, these minerals are typically only minor constituents in magmatic phase assemblages and when this is true, F, Cl and H₂O are concentrated in the melt during fractional crystallisation. The partitioning of halogens and OH between minerals and the melt is described by their bulk partition coefficients, defined as:

$$\bar{D}_i^{c/m} = \sum_{\Phi} W^{\Phi} D_i^{\Phi} \quad (\text{eq. 4.3})$$

where $\bar{D}_i^{c/m}$ is the bulk partition coefficient of component i (i.e. F, Cl or OH) between all crystal phases (i.e. the bulk crystal phase) and the melt phase, Φ pertains to an individual mineral phase and W is mass fraction. The volatile partition coefficients for each crystal phase are calculated from:

$$D_i^{\Phi/m} = \frac{C_i^{\Phi}}{C_i^m} \quad (\text{eq. 4.4})$$

where $D_i^{\Phi/m}$ is the partition coefficient of component i between mineral phase Φ and the melt, and C is concentration in weight fraction. If no hydrous or halogen-bearing minerals are on the liquidus, $\bar{D}_F^{c/m} \approx \bar{D}_{Cl}^{c/m} \approx \bar{D}_{H_2O}^{c/m} \approx 0$. However, during hydrous mineral precipitation both W^{Φ} and D_i^{Φ} have a positive value and thus $\bar{D}_F^{c/m} \neq \bar{D}_{Cl}^{c/m} \neq \bar{D}_{H_2O}^{c/m} \neq 0$. This was not considered in the apatite compositional modelling of Candela (1986), in which halogens were treated as perfectly incompatible during volatile-undersaturated crystallisation, as fluid-melt volatile partitioning has a much greater effect on apatite compositional evolution than mineral-melt partitioning.

Both apatite and biotite crystallise at Campi Flegrei and can account for up to ~10% and ~16% of the modal crystallising assemblage respectively, according to thermodynamic modelling (Bohrson *et al.*, 2006; Cannatelli, 2012; Fowler *et al.*, 2007; Chapter 5). Halogens and H₂O are therefore not perfectly incompatible and bulk partition coefficients should be used. Melt inclusion studies have shown that halogens become concentrated in the melt during magmatic differentiation in Campi Flegrei (e.g. Arienzo *et al.*, 2010; Fourmentraux *et al.*, 2012; Chapters 5 and 6). Melt inclusions cannot easily be used to determine the behaviour of H₂O, due to the potential for post-entrapment compositional modification (Chapter 5). However, Campi Flegrei apatites are generally OH-poor (Chapter 6) and biotites have low H₂O contents relative to the melt at *biotite-in* (Section 5.4.3.; Appendix 2), so crystallisation would remove only small amounts of H₂O from the melt and H₂O should behave incompatibly during volatile-undersaturated crystallisation. Thus, for H₂O and halogens $0 < \bar{D}_i^{c/m} < 1$. Experimental data consistently show that F partitions more strongly into apatite than Cl does, and Cl is concentrated in the crystal phase relative to OH (i.e. $K_{D\text{ Cl-F}}^{c/m} > K_{D\text{ OH-Cl}}^{c/m} > K_{D\text{ OH-F}}^{c/m}$, where K_D is the ratio of apatite-melt Nernstian partition coefficients for two volatile components) for a wide range of melt compositions (Boyce *et al.*, 2014; McCubbin and Jones, 2015; McCubbin *et al.*, 2015a; Webster and Piccoli, 2015). This is supported by analyses of Campi Flegrei apatites, which always contain F > Cl > OH (Chapter 6). Biotite-melt volatile partitioning has a complex dependence on the crystal composition (Icenhower and London, 1997; Zhu and Sverjensky, 1992) but Campi Flegrei biotites are always comparatively OH-rich and halogen depleted (Fabbrizio *et al.*, 2009; Appendix 2). Although Nernstian partition coefficients describe hydrous mineral volatile partitioning poorly (as described in the introduction to this chapter), these observations provide relative constraints on mineral-melt volatile partition coefficients for fractional

crystallisation models; the $\bar{D}_i^{c/m}$ range used to model apatite compositional evolution in this chapter is fictitious, replicating the magmatic compositional evolution as determined from melt inclusions and MELTS models, and is not quantified from observed modal abundances.

4.3.2. Water solubility in alkali melts

The solubility of H₂O in magmatic systems is a complex function of pressure, melt composition and, to a lesser extent, temperature (Holloway and Blank, 1994). In general, H₂O solubility correlates positively with magmatic SiO₂ concentrations (Botcharnikov *et al.*, 2005; Brooker *et al.*, 2001; King and Holloway, 2002; Shishkina *et al.*, 2014) and total alkali (Na + K) content (Carroll and Blank, 1997; Shishkina *et al.*, 2014). However, the alkali effect is more prominent in intermediate and evolved alkalic melts than in mafic alkali systems (Vetere *et al.*, 2014). Slight differences in the solubility relations between different phonolites result from variations in trace element concentrations (Schmidt and Behrens, 2008). Volatile solubilities are interdependent, with H₂O solubility decreasing with increasing magmatic CO₂ (Holloway and Blank, 1994). However, given the low magmatic CO₂ concentrations recorded in melt inclusions (Arienzo *et al.*, 2010; Marianelli *et al.*, 2006; Appendix 3), I assume that the effect of CO₂ on H₂O solubility in Campi Flegrei is minor, and I therefore exclusively use low-CO₂ (≤ 0.01 wt%) or CO₂-free H₂O solubility data. Recent experiments have shown that magmatic Cl and S may also have a minor effect on phonolite H₂O solubility (Webster *et al.*, 2014) but this is poorly constrained and cannot be quantified precisely for a given melt composition.

Magmatic H₂O solubility shows a negative temperature dependence over a wide range of melt compositions from haplobasalts to rhyolites at pressures <500 MPa (Benne and Behrens, 2003; Holtz *et al.*, 1995; Yamashita, 1999). Although this has not been

studied systematically for mafic alkali melts, temperature has only a minor effect on phonolite and trachyte H₂O solubility, varying by 0.1-0.2 wt% per 100 °C within the range 50-200 MPa and 850-1200 °C (Di Matteo *et al.*, 2004; Fanara *et al.*, 2015; Schmidt and Behrens, 2008). Pressure exerts by far the greatest control on magmatic H₂O solubility. For all silicate melt compositions, H₂O solubility increases strongly over the typical pressure range of crustal magma storage (Botcharnikov *et al.*, 2005; Holloway and Blank, 1994; Larsen and Gardner, 2004; Vetere *et al.*, 2011). However, the exact nature of the H₂O solubility law is strongly dependent on melt composition (Holloway and Blank, 1994; Iacono-Marziano *et al.*, 2012).

Experimentally-derived H₂O solubilities for alkali melts are shown over a realistic range of crustal magma storage pressures in Figure 4.4. Trachytes and phonolites, which represent the most evolved melts in the Campi Flegrei system, have similar H₂O solubilities within the pressure range 50-300 MPa at 825-927 °C (Fig. 4.4a). The most primitive shoshonitic melts in the Campi Flegrei system (Vetere *et al.*, 2011) have lower H₂O solubilities than phonolites under equivalent pressure and temperature conditions, with the difference increasing with pressure (up to ~1.5 wt% at 300 MPa; Fig. 4.4b). Although the regression line through all of the available experimental data in Figure 4.4a provides a first-order estimate of phonolite H₂O solubility, there is significant scatter between melts at equivalent pressures and temperatures (up to ~1 wt%), attributed to trace element variability (Schmidt and Behrens, 2008). As no experimental data exist explicitly for Campi Flegrei phonolites (the most common glass composition measured in Chapter 6), I use a H₂O solubility of 7.52 wt% in apatite crystallisation models, which was obtained for a natural, compositionally similar, CO₂-free Vesuvian phonolite, at 200 MPa (similar to the current magma storage pressure at Campi Flegrei, see discussion in Section 5.2.3.) and 927 °C (Webster *et al.*, 2014). This agrees well with H₂O solubility in Campi

Flegrei trachytes under similar conditions (Di Matteo *et al.*, 2004). At the same pressure, Campi Flegrei shoshonites would have a H₂O solubility of ~5 wt% (Fig. 4.4b), based on a regression through the data of Vetere *et al.* (2011).

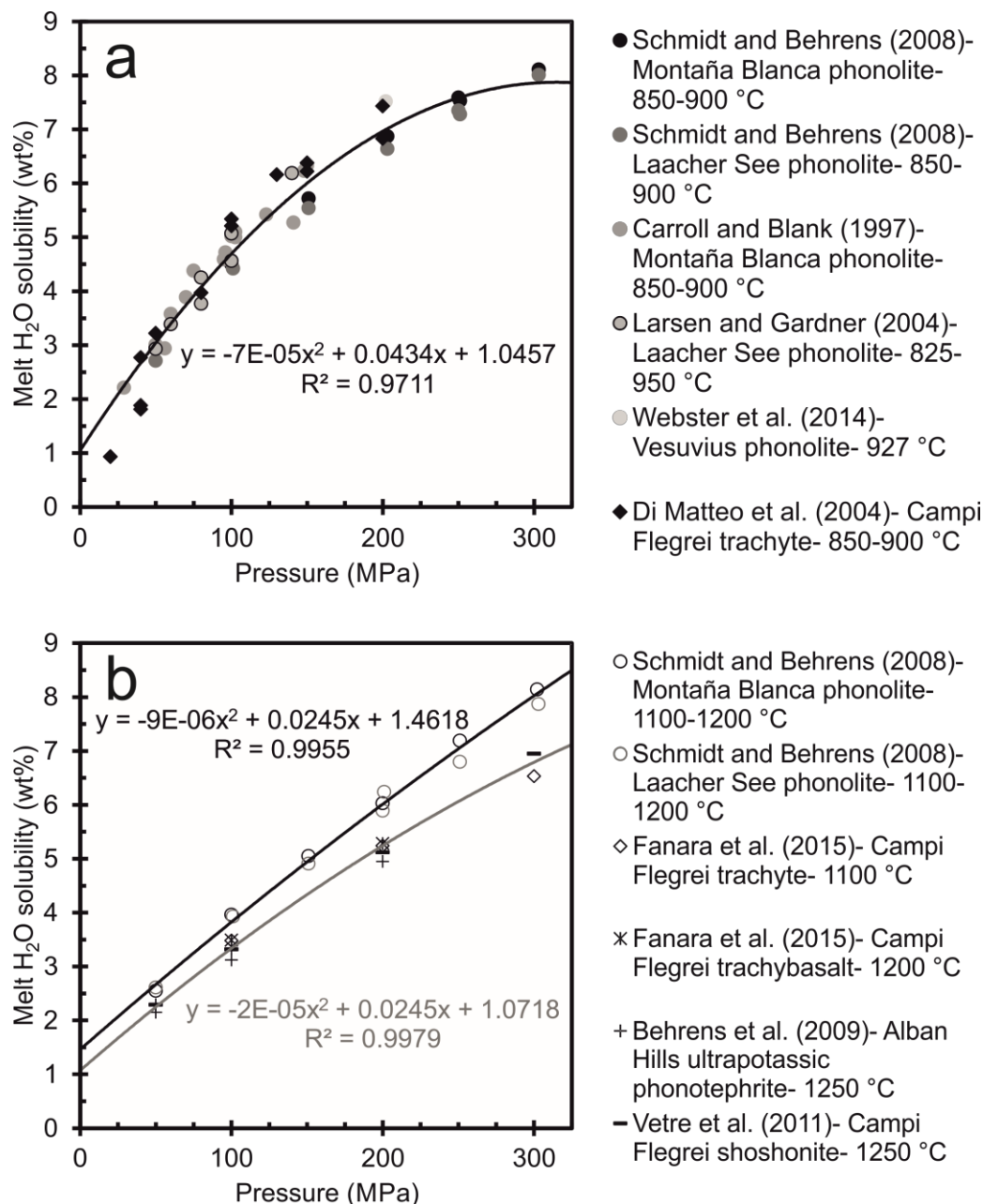


Figure 4.4 | Compilation of experimental H₂O solubility data in low CO₂ or CO₂-free alkali melts at 0 to 300 MPa. a, Phonolite and trachyte H₂O solubilities at low temperature (825-927 °C). **b,** Phonolite, trachyte, phono-tephrite, shoshonite and trachybasalt H₂O solubilities at high temperature (1100-1250 °C). Lines show polynomial regressions through phonolitic (black lines) and shoshonitic experimental data sets (grey line), with associated equations and R² values. Data are distinguished on the basis of melt composition (see legend). Data sources are in the legend.

4.3.3. Halogen solubilities in silicate melt

Magmatic Cl solubility is strongly composition dependent but is generally lower in SiO₂-poor systems (Carroll, 2005; Metrich and Rutherford, 1992; Webster *et al.*, 1999; Webster *et al.*, 2009a). In H₂O-undersaturated melts, Cl solubility correlates positively with increasing CaO, MgO, FeO and Al₂O₃ in the melt, and therefore decreases during magmatic fractionation (Webster *et al.*, 2006; Webster and De Vivo, 2002). Increasing F and decreasing H₂O in the melt also increase Cl solubility, but exert only a minor influence over a large range of volatile concentrations (Webster, 1997a; Webster, 1997b). Applying the 200 MPa Cl solubility model of Webster and De Vivo (2002) to the matrix glass compositions measured in Chapter 6 indicates that Campi Flegrei melts reach Cl saturation at 0.8-1.3 wt%, decreasing from the least evolved to the most evolved samples. These are first-order estimates, as the H₂O concentration of Campi Flegrei melts may be significantly higher than those used in the model calibration (Fig. 6.7). Nevertheless, this demonstrates the potential for very high Cl concentrations in Campi Flegrei magmas, in agreement with Vesuvian phonolite experiments (Webster and De Vivo, 2002). Temperature has no effect on H₂O-undersaturated magmatic Cl solubility within the range 850-1075 °C (Webster, 1997b; Webster and De Vivo, 2002). In H₂O-poor melts, chlorine solubility shows a slight positive correlation with pressure, but the effect is minor in the range 0-200 MPa (<0.1 wt% in haplogranitic melts; Webster, 1997a; Webster, 1997b; Webster and De Vivo, 2002).

In H₂O-saturated melts, Cl solubility similarly varies as a function of melt composition, but is significantly lower than in H₂O-undersaturated systems (Carroll, 2005; Signorelli and Carroll, 2000; Signorelli and Carroll, 2002). As well as decreasing with increasing SiO₂, Cl solubility varies as a function of Na₂O+K₂O/Al₂O₃ and is considerably higher in H₂O-saturated phonolites than in H₂O-saturated rhyolites (Metrich

and Rutherford, 1992; Signorelli and Carroll, 2000). Trachytic Cl solubilities appear unaffected by variability in alkali/alumina ratio (Signorelli and Carroll, 2002) but this may be due to the unconstrained influence of MgO, FeO and CaO concentrations (Carroll, 2005). The effect of temperature on Cl solubility in H₂O-saturated melts has not been investigated in detail, but appears not to be significant for phonolitic or trachytic melts in the range 860-930 °C (Signorelli and Carroll, 2002). The effect of varying pressure is ~30 times more significant in H₂O-saturated melts than in H₂O-undersaturated systems (Webster, 1997a). In H₂O-saturated phonolites and trachytes, Cl solubility decreases from 0.75-0.85 wt% at 50 MPa to ~0.3-0.4 wt% at 200 MPa (Signorelli and Carroll, 2000; Signorelli and Carroll, 2002).

Fluorine solubility is defined here as the concentration of fluorine at fluorite (F⁻) saturation (rather than F₂ gas, as with Cl). Fluorine solubility in silicate melts has not been extensively investigated (Aiuppa et al., 2009a), as the only reported magmatic F⁻ liquids are in upper-mantle xenoliths (Klemme, 2004) or rare granitic systems (Veksler, 2004). However, fluorite crystallisation may buffer the magmatic F concentrations, depending on the melt composition (Dolejš and Baker, 2004). This is important in Campi Flegrei, where primary fluorite has been identified in lava domes (Melluso *et al.*, 2012) and explosive deposits (Chapters 5 and 6). Fluorite stability is a function of $\mu(\text{CaO})$ and $\mu(\text{F}_2\text{O}_{-1})$ in the melt (where μ is chemical potential) and varies systematically with magmatic (Na+K)/Al and (Ca+Na+K)/Al ratios (Dolejš and Baker, 2004; Dolejš and Baker, 2006; Scaillet and Macdonald, 2004). In Ca-rich systems, fluorite saturation occurs early during crystallisation, buffering F at low F concentrations. In low-Ca systems, *fluorite-in* only occurs late-stage, after significant crystallisation and F enrichment in the melt (Dolejš and Baker, 2006). As Campi Flegrei matrix glasses typically contain ~0.2 wt% F (Chapter 6) and the magmas contain fluorite microphenocrysts, I use this as an approximation of F

solubility, in order to assess the effect of F buffering by fluorite in apatite crystallisation models. The F contents of Campi Flegrei melts are consistent with concentrations in other fluorite-saturated magmas (Scaillet and Macdonald, 2004).

4.3.4. Fluid-melt volatile partitioning

Vapour-melt Cl partition coefficients ($D_{\text{Cl}}^{\text{v/m}}$) in phonolitic melts are similar to those in rhyolitic systems and show little variation between peraluminous and peralkaline compositions or with varying trace element concentrations (Signorelli and Carroll, 2000). At low Cl concentrations, phonolite $D_{\text{Cl}}^{\text{v/m}}$ values show a strong positive correlation with pressure, increasing from 0.8 at 50 MPa to 25 at 250 MPa (Signorelli and Carroll, 2000). At higher Cl concentrations, either a brine exsolves under subcritical conditions of two-fluid stability, or fluid-melt partitioning becomes increasingly non-Henrian in the presence of a supercritical hydrosaline fluid. Under these conditions, traditional Nernstian partition coefficients do not adequately describe fluid-melt Cl exchange (Lowenstern, 2000) and the Cl exchange can instead be represented by an ‘apparent’ partition coefficient ($\hat{D}_{\text{Cl}}^{\text{f/m}}$), which is not constant and increases as a function of the total Cl concentration of the system (Signorelli and Carroll, 2000). This either represents total fluid (i.e. vapour + brine)-melt partitioning under subcritical conditions or supercritical hydrosaline fluid-melt partitioning. In either case, given that the non-linearity of fluid-melt exchange is characterised by a more rapid increase in the Cl content of the fluid phase(s) relative to the melt (Carroll and Webster, 1994; Lowenstern, 2000), $\hat{D}_{\text{Cl}}^{\text{f/m}}$ must always be greater than $D_{\text{Cl}}^{\text{v/m}}$ under equivalent pressure and temperature conditions. For H₂O-saturated phonolitic systems, Signorelli and Carroll (2000) report $\hat{D}_{\text{Cl}}^{\text{f/m}}$ values in the

range 13-17 at 50 MPa (subcritical conditions) and 56-140 at 250 MPa (supercritical conditions).

Vapour-melt F partition coefficients ($D_F^{v/m}$) are poorly constrained due to experimental and analytical difficulties (Aiuppa *et al.*, 2009a; Baker and Alletti, 2012) but in general, F is retained in the silicate liquid (Carroll and Webster, 1994; Dingwell and Scarfe, 1983; Webster *et al.*, 2014; Webster, 1990; Webster and Holloway, 1990). Experimental data suggest that $D_F^{v/m}$ may have some compositional dependence, increasing with magmatic Na+K/Al but this is not well established (Carroll and Webster, 1994). $D_F^{v/m}$ is unaffected by pressure in rhyolitic systems (Webster, 1990) but may have a slight temperature dependence (Borodulin *et al.*, 2009; Chevychelov *et al.*, 2005). For some melt compositions, $D_F^{v/m}$ shows non-Henrian behaviour, increasing with total F in the system. However, this is only observed at very high melt F concentrations (>4 wt%; Webster, 1990; Webster and Holloway, 1990), far exceeding those measured in Campi Flegrei glasses (Figs 6.7, 6.8), and has not been recognised in alkali systems (e.g. Webster *et al.*, 2014). Some experiments have identified $D_F^{v/m} > 1$ under magmatic conditions (Alletti, 2008; Chevychelov *et al.*, 2008a), including in Vesuvian phonolites (Chevychelov *et al.*, 2008b). However, these often report experimental difficulties or poor reproducibility (Baker and Alletti, 2012) and are inconsistent with more recent H₂O-saturated experiments on Vesuvian phonolites and trachytes, which show that F is strongly retained within the silicate melt (i.e. $D_F^{v/m} < 1$; Webster *et al.*, 2014). Borodulin *et al.* (2009) conducted a systematic study of evolved alkali melts at 650-1200 °C and 100 MPa, and found $D_F^{v/m}$ consistently between 0.1 and 0.7. Their data have no clear compositional trend, but values at the upper end of this range were obtained in more alkali-rich melts and I use $D_F^{v/m} = 0.7$ for apatite compositional modelling in Campi

Flegrei. Limited experimental data suggest that fluid-melt F partitioning ($D_F^{f/m}$) is independent of fluid Cl concentration (Webster, 1990; Webster and Holloway, 1990). This is confirmed by analysis of natural systems, in which F partitioning into strongly Cl-enriched fluids is negligible (Aiuppa et al., 2009a). I therefore assume that $D_F^{v/m} = D_F^{b/m}$ in Campi Flegrei (where $D_F^{b/m}$ is the brine-melt F partition coefficient).

The partitioning of H₂O into Cl-enriched liquids, in H₂O-undersaturated melts is unknown. Experimental studies show that magmatic H₂O concentrations increase after brine exsolution and that this continues until vapour exsolution (under subcritical conditions) or until formation of a supercritical hydrosaline fluid, as with Cl in H₂O-saturated melts (e.g. Webster, 1997a; Webster, 2004). Under subcritical conditions of ‘two-fluid stability’, hydrothermal brines can contain a wide range of H₂O concentrations (16-73.6 wt% at 700°C; Heinrich *et al.*, 1999; Sourirajan and Kennedy, 1962), suggesting $D_{H_2O}^{b/m} > 0$. In supercritical systems, the apparent fluid-melt H₂O partition coefficient $\hat{D}_{H_2O}^{f/m}$ is presumably greater than $D_{H_2O}^{b/m}$ under equivalent pressure and temperature conditions, as is the case for Cl. However, as $D_{H_2O}^{b/m}$ has never been measured directly, I model a range of values to identify the possible variability in apatite compositional evolution in low-H₂O, Cl-saturated systems.

4.4. Modelling the volatile evolution of the melt

Because apatite is the first hydrous mineral phase to precipitate from Campi Flegrei magmas, I take this as the starting point (i.e. $\phi = 1$, where ϕ is the fraction of melt remaining) for isobaric fractional crystallisation models. Before *apatite-in*, I assume that $\bar{D}_F^{c/m} = \bar{D}_{Cl}^{c/m} = \bar{D}_{H_2O}^{c/m} = 0$. In most models, initial F and Cl concentrations in the melt are set at ~0.4 wt%, based on the most mafic clinopyroxene-hosted melt inclusions measured

in Chapter 6. Due to the potential for melt inclusion re-homogenisation, the initial melt H₂O concentration is estimated from Rhyolite-MELTS models as ~2.5-4.3 wt% at *apatite-in*, depending on the liquidus H₂O concentration (Chapter 5; Fig. 5.4). Model outputs showing the evolution of magmatic H₂O, Cl and F concentrations in the presence of different fluids are presented in Figure 4.5.

During volatile-undersaturated crystallisation, changes in the concentration of all volatile components in the melt can be modelled using the Rayleigh equation:

$$\frac{C_i^m}{C_i^0} = \phi \bar{D}_i^{c/m-1} \quad (\text{eq. 4.5})$$

where superscript 0 denotes the initial concentration of a component in the melt phase. Phase equilibrium experiments on magmas from Campi Flegrei demonstrate that apatite is the only hydrous mineral on the liquidus over a significant crystallisation interval (Bohrson *et al.*, 2006; Cannatelli, 2012; Fowler *et al.*, 2007; Fig. 5.4). Before eruption, biotite starts to co-precipitate with apatite (Bohrson *et al.*, 2006; Cannatelli, 2012; Fowler *et al.*, 2007; Fig. 5.4). When the hydrous mineral phase assemblage changes there is a small change in volatile $\bar{D}_i^{c/m}$ values (there is no change in melt inclusion halogen versus MgO evolution outside of uncertainty at *biotite-in*; Chapter 5; Fig. 5.3), causing only a minor deviation in the liquid lines of descent (Fig. 4.5b; Candela, 1986; Webster *et al.*, 1999). In the absence of a fluid phase, the modelled concentrations of F, Cl and H₂O increase exponentially in the melt phase as crystallisation progresses (Figs 4.5a,b). This results in volatile concentrations far exceeding realistic phonolite solubility estimates at low melt fractions. However, in natural systems under upper crustal conditions, this progressive concentration of volatiles will always be arrested by volatile saturation or eruption.

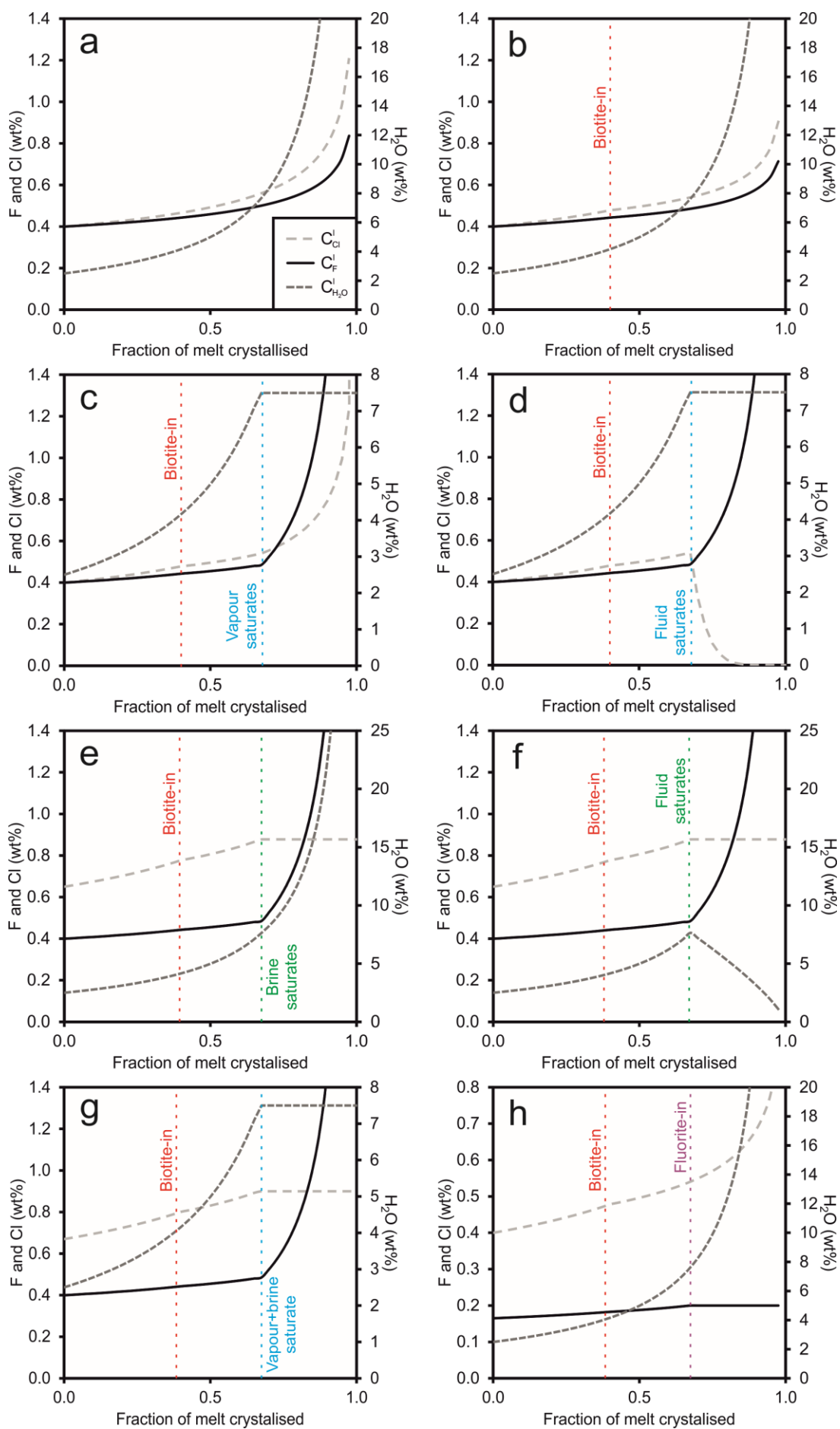


Figure 4.5 | (previous page) Modelled volatile evolution of the silicate melt. Models show the evolution of F (black solid line), Cl (light grey long dash line) and H₂O (dark grey short dash line) in the melt during fractional crystallisation. Unless otherwise stated: $C_{\text{Cl}}^0 = 0.4$ wt%, $C_{\text{F}}^0 = 0.4$ wt%, and $C_{\text{H}_2\text{O}}^0 = 2.5$ wt%; during apatite-only crystallisation $\bar{D}_{\text{Cl}}^{c/m} = 0.65$, $\bar{D}_{\text{F}}^{c/m} = 0.8$ and $\bar{D}_{\text{H}_2\text{O}}^{c/m} = 0.001$; after *biotite-in* $\bar{D}_{\text{Cl}}^{c/m} = 0.8$, $\bar{D}_{\text{F}}^{c/m} = 0.85$ and $\bar{D}_{\text{H}_2\text{O}}^{c/m} = 0.01$; $C_{\text{H}_2\text{O}}^s = 7.5$ wt%; and $D_{\text{F}}^{v/m} = D_{\text{F}}^{f/m} = D_{\text{F}}^{b/m} = 0.7$. The effect of varying these parameters is discussed in the text. In all panels except **a**, *biotite-in* occurs after 40% volatile-undersaturated crystallisation. **a**, Volatile-undersaturated apatite-only crystallisation ($\bar{D}_{\text{Cl}}^{c/m} = 0.75$). **b**, Volatile-undersaturated apatite-only crystallisation, with *biotite-in* after 40% crystallisation. **c**, Volatile-undersaturated crystallisation with vapour saturation after 70% crystallisation ($D_{\text{Cl}}^{v/m} = 9$). **d**, Volatile-undersaturated crystallisation with H₂O-saturated supercritical hydrosaline fluid saturation after 70% crystallisation ($D_{\text{Cl}}^{f/m} = 97$). **e**, Volatile-undersaturated crystallisation with brine saturation after 70% crystallisation ($C_{\text{Cl}}^0 = 0.65$ wt%, $D_{\text{H}_2\text{O}}^{b/m} = 10$, $C_{\text{Cl}}^s = 0.88$ wt%). **f**, Volatile-undersaturated crystallisation with Cl-saturated supercritical hydrosaline fluid saturation after 70% crystallisation ($C_{\text{Cl}}^0 = 0.65$ wt%, $D_{\text{H}_2\text{O}}^{f/m} = 200$, $C_{\text{Cl}}^s = 0.88$ wt%). **g**, Volatile-undersaturated crystallisation with subcritical ‘two phase fluid’ (i.e. vapour + brine) saturation after 70% crystallisation ($C_{\text{Cl}}^0 = 0.67$ wt%, $C_{\text{Cl}}^s = 0.9$ wt%). **h**, Volatile-undersaturated crystallisation with fluorite saturation after 70% crystallisation ($C_{\text{F}}^0 = 0.165$ wt%, $C_{\text{F}}^s = 0.2$ wt%). All models continue to 97.5% crystallisation. Vertical dashed lines show the melt fraction at which mineral phases or different types of fluid saturate.

After vapour saturation in Cl-poor melts, changes in melt volatile compositions are calculated using the approach of Candela (1986). Under these conditions, F and Cl concentrations in the melt are given by:

$$C_i^m = C_i^0 \cdot \varphi^{[(D_i^{v/m} \cdot C_{\text{H}_2\text{O}}^s) - 1]} \quad (\text{eq. 4.6})$$

where $C_{\text{H}_2\text{O}}^s$ is the concentration of H₂O at saturation and halogens are extracted into successive aliquots of the vapour phase as crystallisation progresses. The concentration of H₂O in the melt is buffered in the presence of a vapour and is described by:

$$C_i^m = C_i^s \quad (\text{eq. 4.7})$$

where C_i^s is the concentration of component i in the melt at saturation. Thus, with continued isobaric crystallisation the concentration of H_2O in the melt remains constant at its solubility limit (Fig. 4.5c). As $D_F^{v/m} \ll C_{\text{H}_2\text{O}}^s$ (where C is in units of weight fraction) under magmatic conditions, F is concentrated in the melt phase following vapour saturation. $D_{\text{Cl}}^{v/m}$ is variable and Cl may become concentrated (if $D_i^{v/m} \cdot C_{\text{H}_2\text{O}}^s < 1$) or depleted (if $D_i^{v/m} \cdot C_{\text{H}_2\text{O}}^s > 1$) in the melt during vapour-saturated crystallisation. Even when $D_{\text{Cl}}^{v/m} \cdot C_{\text{H}_2\text{O}}^s < 1$, $D_F^{v/m}$ is generally smaller than $D_{\text{Cl}}^{v/m}$ and F is more strongly enriched in the melt than Cl (Fig. 4.5c).

In the presence of a single supercritical fluid phase, the Cl evolution of a H_2O -saturated melt can be described by:

$$C_{\text{Cl}}^m = C_{\text{Cl}}^0 \cdot \varphi^{[(\hat{D}_{\text{Cl}}^{f/m} \cdot C_{\text{H}_2\text{O}}^s) - 1]} \quad (\text{eq. 4.8})$$

where $\hat{D}_{\text{Cl}}^{f/m}$ is a non-Nernstian apparent partition coefficient, which increases with increasing Cl in the system. Water remains buffered in the melt, as described by equation 4.7 (Fig. 4.5d). As $D_F^{f/m}$ is not affected by fluid salinity (Webster, 1990), F evolution in supercritical hydrosaline fluid-saturated melts is described by equation 4.6 and F becomes concentrated in the melt during crystallisation. In general, $\hat{D}_{\text{Cl}}^{f/m} \cdot C_{\text{H}_2\text{O}}^s > 1$ causing Cl to become depleted in the melt as fractionation continues (Fig. 4.5d). Equations 4.6 and 4.8 imply that, for positive values of $D_{\text{Cl}}^{v/m} \cdot C_{\text{H}_2\text{O}}^s$ and $\hat{D}_{\text{Cl}}^{f/m} \cdot C_{\text{H}_2\text{O}}^s$, Cl will decrease asymptotically in the melt (e.g. Fig. 4.5d) and the salinity of the coexisting fluid would in principle approach infinity at low melt fractions, although in practice this is unfeasible. In

reality, this does not occur because highly saline liquids always undergo vapour-brine immiscibility at high Cl concentrations, even at elevated pressures (Shinohara, 1994).

In H₂O-poor compositions where the first volatile phase to exsolve is a H₂O-bearing brine, Cl will be buffered in the melt as described by equation 4.7 and will remain constant at its solubility limit during progressive crystallisation (Fig. 4.5e). At low H₂O concentrations, brine-melt H₂O partitioning is taken to be Henrian, as is the case for vapour-melt Cl partitioning, and is described by:

$$C_i^m = C_i^0 \cdot \varphi^{[(D_i^{b/m} \cdot C_{Cl}^s) - 1]} \quad (\text{eq. 4.9})$$

where C_{Cl}^s is the concentration of Cl in the melt at saturation, and H₂O is extracted into successive aliquots of the brine phase as crystallisation progresses. As with Cl in H₂O-saturated systems (Fig. 4.3), at higher H₂O concentrations in Cl-saturated supercritical conditions, H₂O partitioning into a supercritical fluid phase is assumed to be non-Henrian and is described by:

$$C_{H_2O}^m = C_{H_2O}^0 \cdot \varphi^{[(\hat{D}_{H_2O}^{f/m} \cdot C_{Cl}^s) - 1]} \quad (\text{eq. 4.10})$$

Thus, during Cl-saturated crystallisation magmatic H₂O concentrations may either increase or decrease, depending on the values of $D_{H_2O}^{b/m}$ or $\hat{D}_{H_2O}^{f/m}$ relative to C_{Cl}^s (Fig. 4.5e). Given the assumption $\hat{D}_{H_2O}^{f/m} > D_{H_2O}^{b/m}$, a decrease in melt H₂O concentration is more likely in H₂O-rich systems under supercritical conditions (Fig. 4.5f). Fluorine does not partition strongly into highly Cl-enriched fluids (Aiuppa et al., 2009a) and its concentration in the melt will increase during Cl-saturated crystallisation, as described by equation 4.9 (Fig. 4.5e).

After brine and vapour saturation under subcritical conditions, both H₂O and Cl are buffered in the melt and are described by equation 4.7. These volatile components

remain constant, at a concentration equivalent to their solubility limit, during further crystallisation (Fig. 4.5g). Fluorine is incorporated into both the vapour and brine phases. Combining equations 4.6 and 4.9, this is described by:

$$C_F^m = C_F^0 \cdot \varphi^{[(D_F^{v/m} \cdot C_{H_2O}^s) + (D_F^{b/m} \cdot C_{Cl}^s) - 1]} \quad (\text{eq. 4.11})$$

As in single-fluid vapour- or brine-saturated systems, F does not partition strongly into the bulk fluid and will become concentrated in the melt as crystallisation continues.

If fluorite is on the liquidus it may buffer magmatic F concentrations. In this case, the F content of the melt remains constant at its saturation concentration, as described by equation 4.7 (Fig. 4.5h). Only trace Cl has been reported in fluorite (Allen, 1952; Eppinger and Closs, 1990), and it is assumed to be nominally anhydrous. Thus, during crystallisation of accessory fluorite, Cl and H₂O concentrations in the melt are described by equation 4.5, with negligible change to $\bar{D}_{Cl}^{c/m}$ and $\bar{D}_{H_2O}^{c/m}$. Under these conditions, magmatic Cl and H₂O concentrations will increase exponentially, as in the volatile-undersaturated case (Fig. 4.5h).

4.5. Modelling the volatile composition of apatite

The second stage of the model calculates the X_F , X_{Cl} and X_{OH} (i.e. the mole fractions of F, Cl and OH respectively) of apatite in equilibrium with the melt at each fractional crystallisation step. This is accomplished using the quasichemical formulation of Candela (1986), which uses an H₂O-O-OH equilibrium constant (i.e. the amount OH, relative to H₂O and O in a melt) of 0.2 (Stolper, 1982) and simplifies the melt to an albitic composition (see original paper for model derivations and discussion). Assuming ideality in the apatite solid solution (i.e. the activity coefficient $[\gamma_i]$ of each component is equal to unity; see Section 4.6.) the activity of apatite phase components equate to their mole

fractions (Korzhinskiy, 1981; Tacker and Stormer, 1989) and equation 4.2 can be used to relate apatite and melt compositions, such that:

$$K_{F-Cl (P,T)} = \frac{C_F^m}{C_{Cl}^m} \cdot \frac{X_{Cl}^{Ap}}{X_F^{Ap}} \quad (\text{eq. 4.12})$$

$$K_{Cl-OH (P,T)} = \frac{C_{OH}^m}{C_{Cl}^m} \cdot \frac{X_{Cl}^{Ap}}{X_{OH}^{Ap}} \quad (\text{eq. 4.13})$$

The equilibrium constants K_{F-Cl} and K_{Cl-OH} (which equate to K_{12} and K_{13} of Candela, 1986, respectively) can be calculated for a given pressure and temperature, if the equilibrium volatile compositions of apatite and the melt are known (see Candela, 1986). For Campi Flegrei, I estimate these exchange coefficients assuming equilibrium between clinopyroxene-hosted apatite and melt inclusions. The most primitive (i.e. highest MgO) melt inclusions measured in Chapter 6 have $C_F^m = C_{Cl}^m = 0.4$ and in Rhyolite-MELTS models the H_2O concentration of the melt at *apatite-in* is ~2.5-3 wt% (starting $H_2O = 2$ wt%; Chapter 5). The compositional evolution of apatite can be assessed through comparison between inclusions that are hosted within phenocrysts that came onto the liquidus at different temperatures (see Chapter 5). In Campi Flegrei, X_F and X_{Cl} are highest in apatite inclusions trapped within early-formed phenocrysts, and progressively decrease in crystals that were in equilibrium with the melt later in magmatic evolution. Thus, the most halogen-enriched clinopyroxene-hosted apatite inclusion measured in Chapter 6 ($X_F^{Ap} = 73.89, X_{Cl}^{Ap} = 17.16, X_{OH}^{Ap} = 10.92$) was used to estimate the apatite composition in equilibrium with primitive clinopyroxene-hosted melt inclusions. These data yield $K_{F-Cl} \approx 0.21$ and $K_{Cl-OH} \approx 4.17 \cdot 10^3$ for Campi Flegrei, which are comparable to those calculated for the Bishop Tuff (0.24 and $6 \cdot 10^3$, respectively; Candela, 1986).

Assuming that K does not vary significantly as a function of magma composition, the calculated exchange coefficients can be used to compute apatite volatile contents at each stage of the fractional crystallisation model by simultaneously solving equations 18-20 of Candela (1986):

$$X_F^{\text{Ap}} + X_{\text{Cl}}^{\text{Ap}} + X_{\text{OH}}^{\text{Ap}} = 1 \quad (\text{eq. 4.14})$$

$$X_{\text{Cl}}^{\text{Ap}} \left(1 + \frac{C_F^{\text{m}}}{K_{\text{F-Cl}} \cdot C_{\text{Cl}}^{\text{m}}} + \frac{N \cdot X_{\text{OH}}^{\text{m}}}{C_{\text{Cl}}^{\text{l}} \cdot K_{\text{Cl-OH}}} \right) = 1 \quad (\text{eq. 4.15})$$

$$X_F^{\text{Ap}} \left(1 + \frac{K_{\text{F-Cl}} \cdot C_{\text{Cl}}^{\text{m}}}{C_F^{\text{m}}} \cdot \frac{N \cdot X_{\text{OH}}^{\text{m}} \cdot K_{\text{F-Cl}}}{C_F^{\text{m}} \cdot K_{\text{Cl-OH}}} \right) = 1 \quad (\text{eq. 4.16})$$

where N is moles O from H_2O plus moles of O from the anhydrous melt component per kg of melt. The values of $K_{\text{F-Cl}}$ and $K_{\text{Cl-OH}}$ do not alter the relative compositional evolution of apatite volatile components during magmatic evolution but dictate their absolute values. Thus, model outputs show the trajectory of apatite compositional evolution during fractionation, even without knowledge of the exchange coefficients (Candela, 1986). In other words, although apatite-melt inclusion pairs are used to quantify $K_{\text{F-Cl}}$ and $K_{\text{Cl-OH}}$ in this study, the model outputs can be used to qualitatively assess magmatic fluid systematics where values of K are unknown.

Based on experimental evidence, the assumption that K remains approximately constant during magmatic evolution appears valid within a limited range of melt compositions (McCubbin *et al.*, 2015a). Other experiments suggest that partitioning (i.e. $D_{\text{Cl}}^{\text{Ap/m}}$ values) may in part be dependent on fluid composition, with the exsolution of a dense brine linked to crystallisation of more Cl-rich apatite (Doherty *et al.*, 2014; Mathez and Webster, 2005; Webster *et al.*, 2009b). This scenario, in which apatite become Cl-

enriched as a result of changing $D_{\text{Cl}}^{\text{Ap/m}}$ values, may occur in near-solidus layered intrusions, where crystals, melts and fluids are trapped and can equilibrate in intercumulus layers (Mathez and Webster, 2005). However, they are unlikely to occur in volcanic systems where crystallisation is insufficient to trap fluids and melts in localised, Cl-rich closed-systems. Consequently, constant K values in the models presented in this chapter (i.e. fractional crystallisation or fractional volatile evolution) are believed to adequately describe volcanic systems. The models may be refined to account for any effect of melt composition on K values with further theoretical and experimental development (Chapter 7).

4.6. Apatite mixing models

At low temperatures (e.g. <500 °C) there is evidence of non-ideality in the apatite solid solution, with non-zero enthalpies of F-OH mixing in OH-rich apatites (Hovis *et al.*, 2014a) and in the F-Cl solid solution (Hovis and Harlov, 2010). However, experimental data show that this is not the case at magmatic temperatures. The Cl-OH solid solution mixes ideally at >500 °C (Tacker and Stormer, 1989) and F-OH and F-Cl apatite series also show ideal mixing behaviours in experiments run at 900 °C (Hovis *et al.*, 2015; Hovis *et al.*, 2014b). Thermodynamic mixing models for apatite ternary solid solutions are currently incomplete (Hovis *et al.*, 2014b) and non-ideality would cause natural and modelled compositional evolution to diverge as $\bar{\gamma}_i \neq 1$ and $\alpha_i^{\text{Ap}} \neq X_i^{\text{Ap}}$. However, given the ideal mixing in binary solid solutions at geologically relevant temperatures, and the lack of evidence for any miscibility gap in natural apatite ternary compositions (Hovis and Harlov, 2010), the assumption of $\bar{\gamma}_i = 1$ appears valid.

4.7. Model outputs: the compositional evolution of apatite as a function of magmatic fluid systematics

The results of the apatite fractional crystallisation modelling detailed above are shown in Figures. 4.4-4.11. These demonstrate the theoretical volatile evolution of apatite during fractional crystallisation in the presence (or absence) of different fluids. Where inputs are unconstrained, models are presented using a wide range of values to show the potential variability of apatite compositional development. In all cases, model outputs are presented in apatite $X_{\text{Cl}}/X_{\text{OH}}$ versus $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{Cl}}/X_{\text{OH}}$ versus $X_{\text{F}}/X_{\text{Cl}}$ space, as these plots best demonstrate the exchange of components within the apatite volatile site, as described in equation 4.2. The ‘families of curves’ produced by these models can be compared directly with natural data sets to determine magmatic fluid systematics at the time of apatite crystallisation, or while apatite-melt volatile equilibrium is maintained; volatile diffusion in apatite is fast (Brenan, 1993) and crystals can therefore rehomogenise with the melt on relatively short timescales once a new fluid-melt equilibrium is established. A summary of the model outputs is given in Section 4.8.

4.7.1. Volatile-undersaturated crystallisation

During crystallisation of apatite (in which $X_{\text{F}} > X_{\text{Cl}} > X_{\text{OH}}$) and minor halogen-poor biotite in Campi Flegrei, $\bar{D}_{\text{F}}^{\text{c/m}} > \bar{D}_{\text{Cl}}^{\text{c/m}} > \bar{D}_{\text{H}_2\text{O}}^{\text{c/m}}$ (see Section 4.3.1.). Furthermore, melt inclusion evidence and Rhyolite-MELTS models show that halogens and H_2O behave incompatibly during crystallisation (Fig. 5.4). $\bar{D}_{\text{I}}^{\text{c/m}}$ values cannot be quantified exactly. However, Figure 4.6. shows the range of potential trajectories of apatite compositional evolution within these qualitative limits and the model outputs discussed below are bound by these empirical constraints.

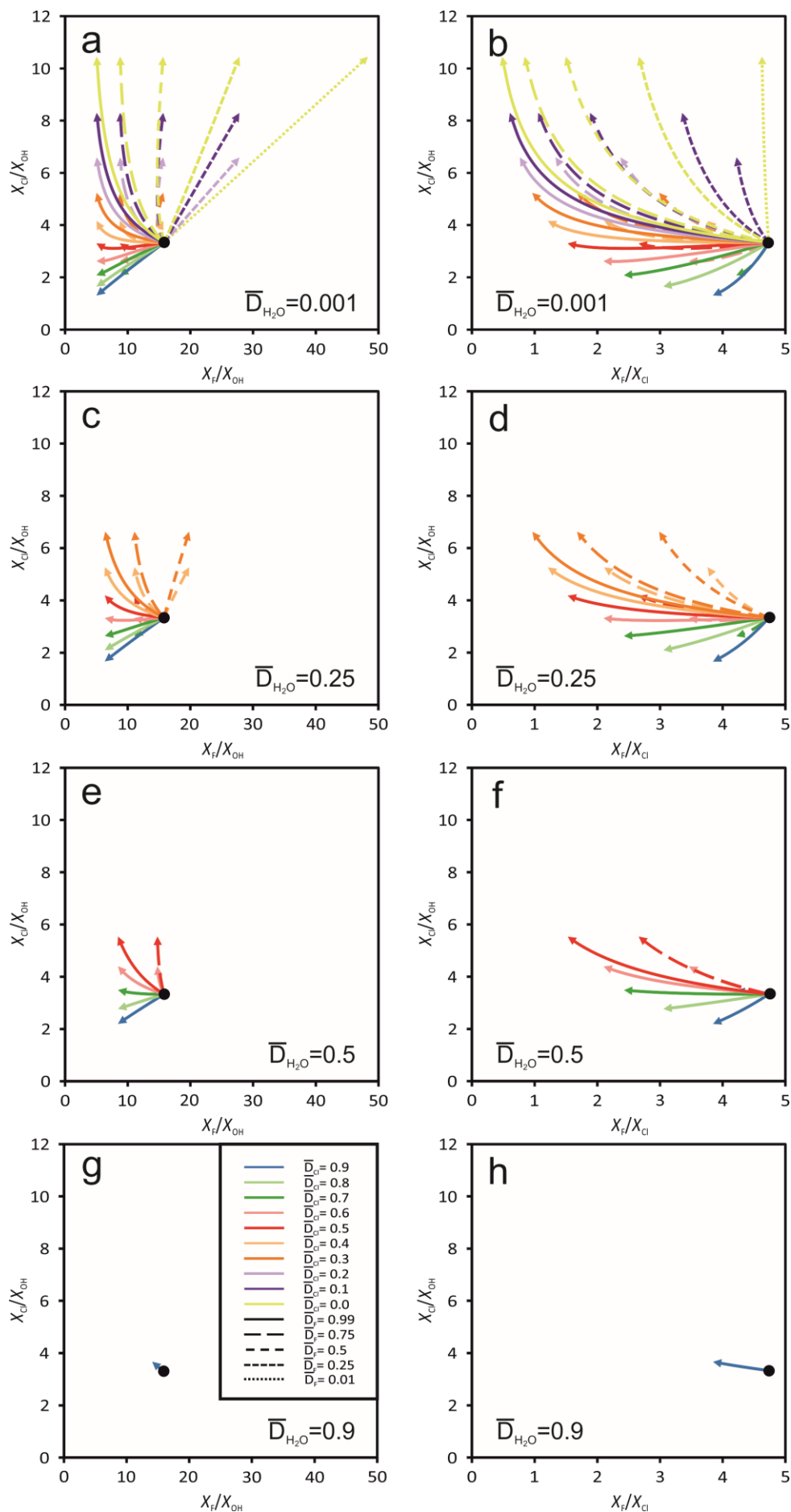


Figure 4.6 | (previous page) Apatite compositional evolution during volatile-undersaturated crystallisation. Arrows show modelled trajectories of apatite compositional evolution in $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{OH}}$ (**a, c, e, g**) and $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{Cl}}$ (**b, d, f, h**) space if $\bar{D}_{\text{F}}^{c/m} \geq \bar{D}_{\text{Cl}}^{c/m} \geq \bar{D}_{\text{H}_2\text{O}}^{c/m}$ and $1 > \bar{D}_{\text{F}}^{c/m} > 0$. In all models, $C_{\text{Cl}}^0 = 0.4$ wt%, $C_{\text{F}}^0 = 0.4$ wt%, $C_{\text{H}_2\text{O}}^0 = 2.5$ wt%, $K_{\text{F-Cl}} = 0.21$ and $K_{\text{Cl-OH}} = 4.17 \cdot 10^3$. Apatite crystallisation begins at the black point and continues until 90% crystallisation. Models are distinguished on the basis of $\bar{D}_{\text{F}}^{c/m}$: Colours represent different values of $\bar{D}_{\text{Cl}}^{c/m}$, dash length represents different values of $\bar{D}_{\text{H}_2\text{O}}^{c/m}$ (see legend). In **a** and **b** $\bar{D}_{\text{H}_2\text{O}}^{c/m} = 0.001$, in **c** and **d** $\bar{D}_{\text{H}_2\text{O}}^{c/m} = 0.25$ in, **e** and **f** $\bar{D}_{\text{H}_2\text{O}}^{c/m} = 0.5$ and in **g** and **h** $\bar{D}_{\text{H}_2\text{O}}^{c/m} = 0.9$.

Varying $\bar{D}_{\text{F}}^{c/m}$ alters the development of apatite $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios during crystallisation. At constant $\bar{D}_{\text{H}_2\text{O}}^{c/m}$, apatite $X_{\text{F}}/X_{\text{OH}}$ ratios may increase during crystallisation at low $\bar{D}_{\text{F}}^{c/m}$ or decrease at higher $\bar{D}_{\text{F}}^{c/m}$ values (Fig. 4.6 a,c). If $X_{\text{F}}/X_{\text{OH}}$ increases, higher $\bar{D}_{\text{F}}^{c/m}$ values reduce the rate of escalation per unit crystallisation for a given value of $\bar{D}_{\text{H}_2\text{O}}^{c/m}$. In contrast, if $X_{\text{F}}/X_{\text{OH}}$ decreases during crystallisation (for example, if large modal amounts of apatite were to crystallise), the rate of decline correlates positively with $\bar{D}_{\text{F}}^{c/m}$ for a set value of $\bar{D}_{\text{H}_2\text{O}}^{c/m}$. Apatite $X_{\text{F}}/X_{\text{Cl}}$ ratios decrease with crystallisation in all models and at constant $\bar{D}_{\text{Cl}}^{c/m}$ the rate of change increases at higher $\bar{D}_{\text{F}}^{c/m}$ values. Changes in $\bar{D}_{\text{F}}^{c/m}$ do not affect apatite $X_{\text{Cl}}/X_{\text{OH}}$ ratios. However, at constant $\bar{D}_{\text{Cl}}^{c/m}$ and $\bar{D}_{\text{H}_2\text{O}}^{c/m}$ the overall effect of increasing $\bar{D}_{\text{F}}^{c/m}$ is to cause a clockwise rotation of modelled trajectories in Figure 4.6 where crystal $X_{\text{Cl}}/X_{\text{OH}}$ ratios decrease during crystallisation, and an anticlockwise rotation where $X_{\text{Cl}}/X_{\text{OH}}$ ratios increase.

Changes in $\bar{D}_{\text{Cl}}^{c/m}$ alter the evolution of apatite $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios during magmatic differentiation. During crystallisation at constant $\bar{D}_{\text{H}_2\text{O}}^{c/m}$, the $X_{\text{Cl}}/X_{\text{OH}}$ content of apatite may either increase at low $\bar{D}_{\text{Cl}}^{c/m}$ values or decrease at higher $\bar{D}_{\text{Cl}}^{c/m}$ (Fig. 4.6 a,c,e).

At constant $\bar{D}_{\text{H}_2\text{O}}^{c/m}$, increasing $\bar{D}_{\text{Cl}}^{c/m}$ either reduces the rate of $X_{\text{Cl}}/X_{\text{OH}}$ escalation or increases the rate of decline per unit crystallisation. Similarly, for a given value of $\bar{D}_{\text{F}}^{c/m}$, increasing $\bar{D}_{\text{Cl}}^{c/m}$ reduces the rate at which apatite $X_{\text{F}}/X_{\text{Cl}}$ decrease during crystallisation. In general, the effect of increasing $\bar{D}_{\text{Cl}}^{c/m}$ at constant $\bar{D}_{\text{F}}^{c/m}$ and $\bar{D}_{\text{H}_2\text{O}}^{c/m}$ is to causes an anticlockwise rotation in the crystal compositional trajectories shown in Figure 4.6. However at low $\bar{D}_{\text{F}}^{c/m}$ and $\bar{D}_{\text{H}_2\text{O}}^{c/m}$ values, where apatite $X_{\text{F}}/X_{\text{OH}}$ ratios increase during crystallisation, increasing $\bar{D}_{\text{Cl}}^{c/m}$ causes a clockwise rotation of modelled apatite compositional trajectories.

Varying $\bar{D}_{\text{H}_2\text{O}}^{c/m}$ in apatite compositional models affects crystal $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{Cl}}/X_{\text{OH}}$ evolution in the opposing sense to $\bar{D}_{\text{F}}^{c/m}$ and $\bar{D}_{\text{Cl}}^{c/m}$; an increase in $\bar{D}_{\text{H}_2\text{O}}^{c/m}$ causes a clockwise rotation in the apatite compositional trajectories shown in Figure 4.6 at constant $\bar{D}_{\text{F}}^{c/m}$ and $\bar{D}_{\text{Cl}}^{c/m}$. Increasing $\bar{D}_{\text{H}_2\text{O}}^{c/m}$ at set $\bar{D}_{\text{Halogen}}^{c/m}$ values can cause a transition from decreasing to increasing apatite $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{Cl}}/X_{\text{OH}}$ ratios during crystallisation. In the case of decreasing apatite $X_{\text{Halogen}}/X_{\text{OH}}$, increasing $\bar{D}_{\text{H}_2\text{O}}^{c/m}$ causes a reduction in the rate of decline per unit crystallisation. Conversely, if apatite $X_{\text{Halogen}}/X_{\text{OH}}$ ratios rise during crystallisation, elevated $\bar{D}_{\text{H}_2\text{O}}^{c/m}$ values increase the rate of change.

Figure 4.7 illustrates the effect of varying C_i^0 in volatile-undersaturated apatite crystallisation models, within a realistic range of starting concentrations (i.e. $C_{\text{F}}^0 = 0.1 - 1$ wt%, $C_{\text{Cl}}^0 = 0.1 - 1$ wt%, $C_{\text{H}_2\text{O}}^0 = 2.5 - 4.5$ wt%). The same arbitrary $\bar{D}_i^{c/m}$ value is used in each panel. Changing C_i^0 alters the model start points (i.e. black dots in Figs 4.6, 4.7) in mole fraction ratio space. However, although changing C_i^0 alters the relative variation of $X_{\text{F}}/X_{\text{OH}}$, $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios per unit crystallisation, the *direction* of crystal compositional evolution (i.e. whether ratios increase or decrease) remains

constant. Thus, the main consequence of varying C_i^0 is to change the magnitude of apatite compositional evolution over a set crystallisation interval.

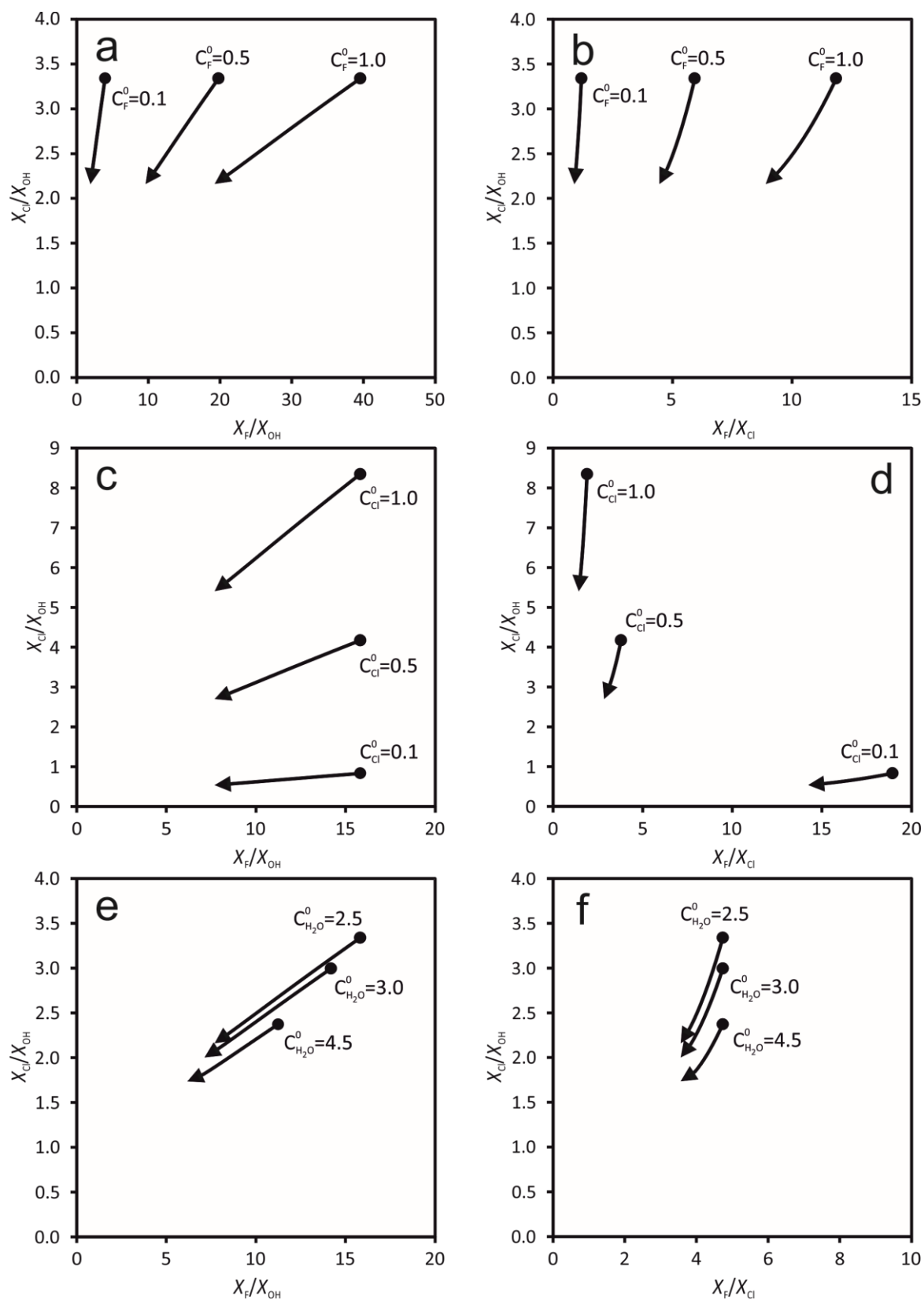


Figure 4.7 | (previous page) The effect of starting composition on apatite compositional evolution during volatile-undersaturated crystallisation. Arrows show modelled trajectories of apatite compositional evolution in $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{OH}}$ (**a, c, e**) and $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{Cl}}$ (**b, d, f**) space, at $\bar{D}_{\text{F}}^{\text{c/m}} = 0.7$, $\bar{D}_{\text{Cl}}^{\text{c/m}} = 0.85$, $\bar{D}_{\text{H}_2\text{O}}^{\text{c/m}} = 0.001$, $K_{\text{F-Cl}} = 0.21$ and $K_{\text{Cl-OH}} = 4.17 \cdot 10^3$, for different values of C_{i}^0 . Unless otherwise stated, $C_{\text{F}}^0 = 0.4$ wt%, $C_{\text{Cl}}^0 = 0.4$ wt% and $C_{\text{H}_2\text{O}}^0 = 2.5$ wt%. **a,b** Apatite compositional trajectories for $C_{\text{F}}^0 = 0.1$ wt%, 0.5 wt% and 1.0 wt%. **c,d** Apatite compositional trajectories for $C_{\text{Cl}}^0 = 0.1$ wt%, 0.5 wt% and 1.0 wt%. **d,e** Apatite compositional trajectories for $C_{\text{H}_2\text{O}}^0 = 2.5$ wt%, 3.0 wt% and 4.5 wt%. Apatite crystallisation begins at the black point and continues until 85% crystallisation in all models.

4.7.2. Water-saturated crystallisation

Apatite $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ increase during H_2O -saturated crystallisation (Fig. 4.8). The compositional change per unit crystallisation is significantly greater than in volatile-undersaturated models and crystals can attain very high $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios over a short crystallisation interval (i.e. $X_{\text{F}}/X_{\text{OH}} = 44$ and $X_{\text{F}}/X_{\text{Cl}} = 4 \cdot 10^5$ after 25% crystallisation following H_2O saturation at $D_{\text{Cl}}^{\text{f/m}} = 100$ in Figure 4.8). This is highlighted in Figure 4.8, in which the black lines, representing 65% volatile-undersaturated crystallisation, are significantly shorter than the coloured lines, which represent only 33% volatile-saturated crystallisation. The degree of $X_{\text{F}}/X_{\text{Cl}}$ enrichment per unit crystallisation correlates positively with $D_{\text{Cl}}^{\text{f/m}}$ because Cl is more strongly depleted in the melt relative to the enrichment in F.

Apatite $X_{\text{Cl}}/X_{\text{OH}}$ ratios can either increase or decrease during volatile-saturated crystallisation, depending on $D_{\text{Cl}}^{\text{f/m}}$ (Fig. 4.8). When $D_{\text{Cl}}^{\text{f/m}} \cdot C_{\text{H}_2\text{O}}^{\text{s}} < 1$ (i.e. where either the melt has a low H_2O solubility or Cl is very weakly partitioned into the fluid, such as at low pressures) Cl is enriched in the melt phase during crystallisation and apatite $X_{\text{Cl}}/X_{\text{OH}}$ ratios increase. Higher values of $D_{\text{Cl}}^{\text{f/m}}$ reduce the degree of melt Cl enrichment and

consequently decrease the rate of apatite $X_{\text{Cl}}/X_{\text{OH}}$ escalation per unit crystallisation. When $D_{\text{Cl}}^{\text{f/m}} \cdot C_{\text{H}_2\text{O}}^{\text{s}} > 1$, (i.e. where Cl is strongly partitioned into the fluid, such as at high pressures) Cl is depleted in the melt phase during H_2O -saturated crystallisation and apatite $X_{\text{Cl}}/X_{\text{OH}}$ decrease. In Figure 4.8, in which $C_{\text{H}_2\text{O}}^{\text{s}} = 7.5 \text{ wt\%}$, this transition occurs at $D_{\text{Cl}}^{\text{f/m}} = 13.3$. Under conditions where apatite $X_{\text{Cl}}/X_{\text{OH}}$ ratios decrease with crystallisation, the rate of decline per unit crystallisation increases at higher $D_{\text{Cl}}^{\text{f/m}}$ values. Low values of $D_{\text{Cl}}^{\text{f/m}}$ (< 25) are typical of Cl-undersaturated vapour-melt partition coefficients ($D_{\text{Cl}}^{\text{v/m}}$; Signorelli and Carroll, 2000). Where Cl is not buffered in the melt, higher values $D_{\text{Cl}}^{\text{f/m}}$ are typical of ‘apparent’ supercritical hydrosaline fluid-melt partition coefficients ($\hat{D}_{\text{Cl}}^{\text{f/m}}$; see Section 4.3.4.) at high Cl concentrations (Signorelli and Carroll, 2000). Importantly, given the non-Nernstian nature of $\hat{D}_{\text{Cl}}^{\text{f/m}}$, under supercritical conditions apatite compositional evolution will not exactly follow any compositional trajectory in Figure 4.8. Rather, it will crosscut these compositional contours in the direction of increasing $D_{\text{Cl}}^{\text{f/m}}$ as the Cl concentration of the system rises and the Cl content of the fluid increases more rapidly than that of the melt (see dashed black line in Fig. 4.8).

As well as changing the amount of crystallisation that occurs before volatile saturation, increasing $C_{\text{H}_2\text{O}}^{\text{s}}$ (i.e. the effect of variations in pressure or melt composition) has a similar effect on the trajectory of apatite compositional evolution as increasing $D_{\text{Cl}}^{\text{f/m}}$ (Fig. 4.9), due to its position in the exponent of equations 4.8 and 4.10. At higher values of $C_{\text{H}_2\text{O}}^{\text{s}}$, the transition between increasing and decreasing apatite $X_{\text{Cl}}/X_{\text{OH}}$ during crystallisation occurs at lower $D_{\text{Cl}}^{\text{f/m}}$, and there is a greater decrease (or smaller increase) in $X_{\text{Cl}}/X_{\text{OH}}$ ratios per unit crystallisation (Fig. 4.9). Elevated $C_{\text{H}_2\text{O}}^{\text{s}}$ values also cause a greater escalation in $X_{\text{F}}/X_{\text{Cl}}$ and a reduced increase in $X_{\text{F}}/X_{\text{OH}}$ per unit crystallisation.

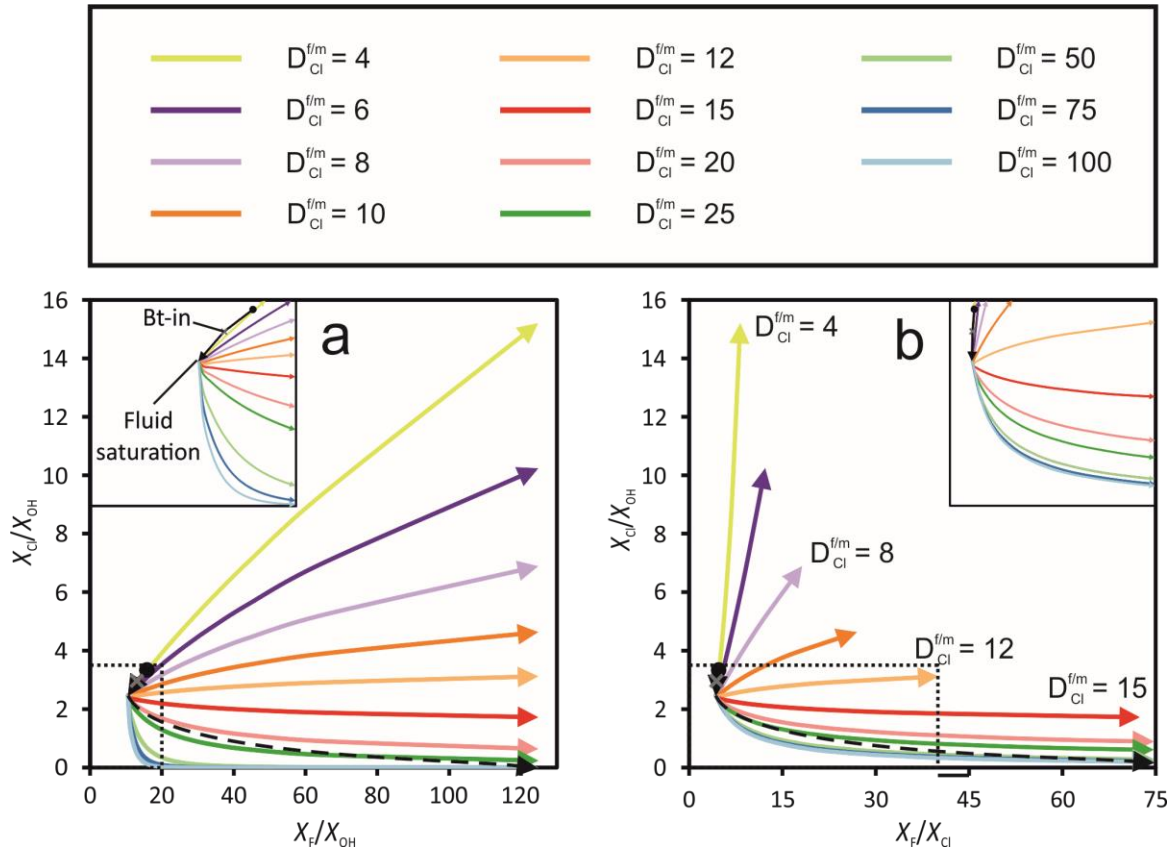


Figure 4.8 | The effect of fluid-melt Cl partitioning on apatite compositional evolution during H₂O-saturated crystallisation. Arrows show modelled trajectories of apatite compositional evolution in $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{OH}}$ (a) and $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{Cl}}$ (b) space. In all models, $K_{\text{F-Cl}} = 0.21$, $K_{\text{Cl-OH}} = 4.17 \cdot 10^3$, $C_{\text{F}}^0 = 0.4$ wt%, $C_{\text{Cl}}^0 = 0.4$ wt% and $C_{\text{H}_2\text{O}}^0 = 2.5$ wt%. The black lines show an arbitrary trajectory of volatile-undersaturated crystallisation: apatite begins crystallising at the black point ($\bar{D}_{\text{F}}^{\text{c/m}} = 0.8$, $\bar{D}_{\text{Cl}}^{\text{c/m}} = 0.65$, $\bar{D}_{\text{H}_2\text{O}}^{\text{c/m}} = 0.001$) and is the only hydrous phase on the liquidus; biotite comes in after 40% crystallisation at the grey cross, slightly altering $\bar{D}_1^{\text{c/m}}$ ($\bar{D}_{\text{F}}^{\text{c/m}} = 0.85$, $\bar{D}_{\text{Cl}}^{\text{c/m}} = 0.8$, $\bar{D}_{\text{H}_2\text{O}}^{\text{c/m}} = 0.01$). Water saturates at 65% crystallisation and all models continue to 98% crystallisation. Models with $D_{\text{Cl}}^{\text{f/m}} \geq 20$ continue to high $X_{\text{F}}/X_{\text{Cl}}$ but are truncated for scaling in b. Insets show expanded regions of the graphs (marked by dotted boxes), around the point of H₂O-saturation. Coloured arrows show the range of apatite compositional trajectories during H₂O-saturated crystallisation. In all models, $C_{\text{H}_2\text{O}}^{\text{s}} = 7.5$ wt% and $D_{\text{F}}^{\text{f/m}} = 0.7$, which are appropriate for phonolitic melts at upper crustal pressures. Models are distinguished on the basis of $D_{\text{Cl}}^{\text{f/m}}$ (see legend). The dashed black line schematically shows the trajectory of non-Nernstian ‘apparent’ fluid-melt partitioning, in which $\hat{D}_{\text{Cl}}^{\text{f/m}}$ increases with total Cl in the system (see discussion in text).

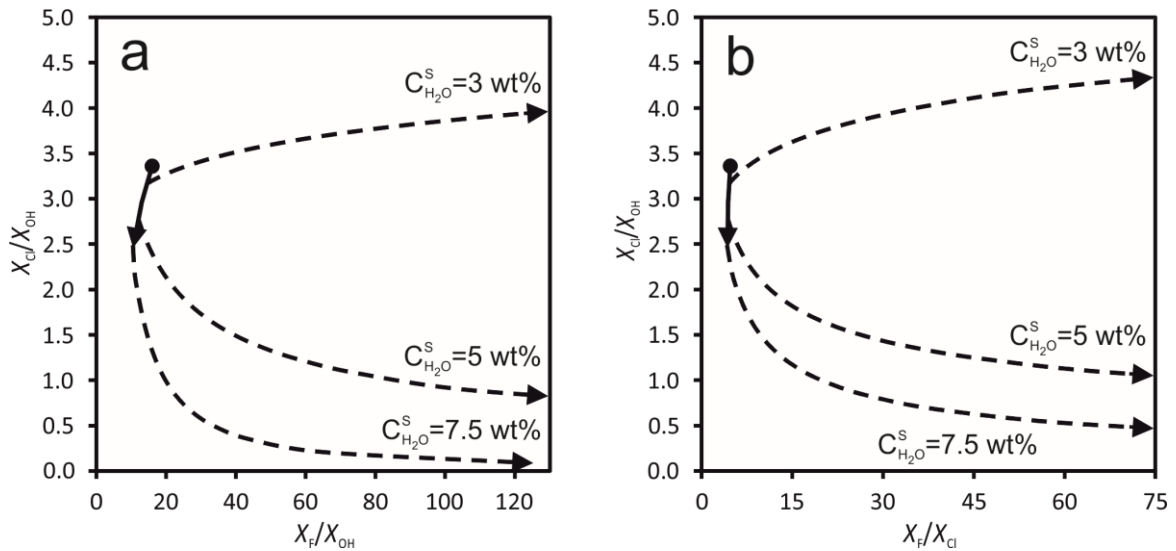


Figure 4.9 | The effect of H₂O solubility on apatite compositional evolution during H₂O-saturated crystallisation. Arrows show modelled trajectories of apatite compositional evolution in X_{Cl}/X_{OH} vs X_F/X_{OH} (a) and X_{Cl}/X_{OH} vs X_F/X_{Cl} (b) space during volatile-undersaturated (solid line) and H₂O-saturated (dashed line) crystallisation. The volatile-undersaturated model parameters, including C_i^0 , are as in Figure 4.8 and volatile-undersaturated fractionation continues to 65% crystallisation. Models of H₂O-saturated apatite evolution are distinguished on the basis of $C_{H_2O}^S$ (see labels). Water saturated crystallisation begins at 15%, 55% and 65% crystallisation in $C_{H_2O}^S = 3 \text{ wt\%}$, $C_{H_2O}^S = 5 \text{ wt\%}$ and $C_{H_2O}^S = 7.5 \text{ wt\%}$ models, respectively. In all models, $D_{Cl}^{f/m} = 30$ and $D_F^{f/m} = 0.7$. Volatile-saturated fractionation continues until 98% crystallisation. For scaling, model end points at high X_F/X_{OH} and X_F/X_{Cl} are truncated in all but the $C_{H_2O}^S = 7.5 \text{ wt\%}$ model in a.

Increasing $D_F^{f/m}$ in H₂O-saturated crystallisation models decreases the rate of apatite X_F/X_{OH} and X_F/X_{Cl} increase per unit crystallisation. However, this effect is negligible in the range $0 < D_F^{f/m} < 1$ (i.e. if F is incompatible in the fluid phase), as defined experimentally in evolved alkali systems (e.g. Webster *et al.*, 2014). As in the volatile-undersaturated case (Fig. 4.7), changing C_i^0 alters the starting composition and the relative magnitude of compositional variations over a set crystallisation interval in volatile-saturated apatite crystallisation models, but it does not change the overall trajectory of compositional evolution.

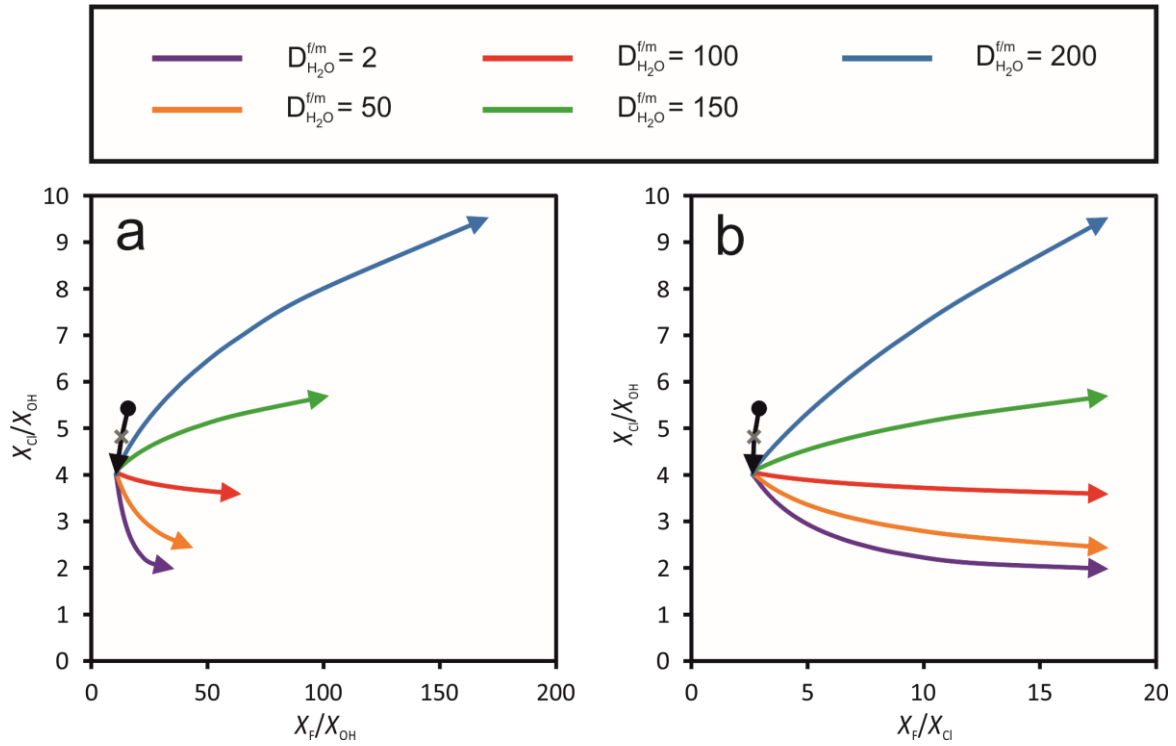


Figure 4.10 | The effect of fluid-melt H₂O partitioning on apatite compositional evolution during Cl-saturated crystallisation. Arrows show modelled trajectories of apatite compositional evolution in $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{OH}}$ (a) and $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{Cl}}$ (b) space. The black lines show the trajectory of volatile-undersaturated crystallisation, with $\bar{D}_i^{c/m}$ and K values as in Figure 4.8. Apatite begins crystallising at the black point and biotite comes in after 40% crystallisation at the grey cross. In all models, $C_{\text{F}}^0 = 0.4$ wt%, $C_{\text{Cl}}^0 = 0.65$ wt% and $C_{\text{H}_2\text{O}}^0 = 2.5$ wt%. Cl saturates at 65% crystallisation and all models continue to 95% crystallisation. The coloured arrows show the range of apatite compositional trajectories during Cl-saturated crystallisation. In all models, $C_{\text{Cl}}^s = 0.9$ wt% and $D_{\text{F}}^{f/m} = 0.7$. Models are distinguished on the basis of $D_{\text{H}_2\text{O}}^{f/m}$ (see legend).

4.7.3. Chlorine-saturated crystallisation

If Cl saturates in the melt before H₂O (i.e. at low H₂O or high Cl concentrations when the first fluid to form would be dense; e.g. liquid C in Fig 4.2), a portion of the magmatic H₂O component will partition into the fluid phase. This may be either a brine or a supercritical hydrosaline fluid (see Section 4.3.4.). Fluid-melt H₂O partition coefficients in Cl-saturated systems (i.e. $D_{\text{H}_2\text{O}}^{b/m}$ and $\hat{D}_{\text{H}_2\text{O}}^{f/m}$) have not been experimentally determined

and are totally unconstrained in nature (future experimental work might address this). However, Figure 4.10 explores the range of apatite compositional trajectories during Cl-saturated crystallisation, varying $D_{\text{H}_2\text{O}}^{\text{f/m}}$ by two orders of magnitude (i.e. $2 < D_{\text{H}_2\text{O}}^{\text{f/m}} < 200$). Modelled compositional trajectories for $0 < D_{\text{H}_2\text{O}}^{\text{f/m}} < 2$, are indistinguishable from $D_{\text{H}_2\text{O}}^{\text{f/m}} = 2$ in Figure 4.10.

In all models, apatite $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios increase during crystallisation in equilibrium with a dense fluid. The degree of $X_{\text{F}}/X_{\text{OH}}$ enrichment per unit crystallisation correlates positively with $D_{\text{H}_2\text{O}}^{\text{f/m}}$ (Fig. 4.10a) and negatively with C_{Cl}^{s} (Fig. 4.11a). The magnitude of $X_{\text{F}}/X_{\text{Cl}}$ variation also correlates negatively with C_{Cl}^{s} (Fig. 4.11b) and reducing C_{Cl}^{s} (i.e. at lower pressures) promotes Cl saturation earlier in volatile-undersaturated magmatic evolution. As in H_2O -saturated models, apatite $X_{\text{Cl}}/X_{\text{OH}}$ ratios may either increase or decrease during Cl-saturated crystallisation (Figs 4.10, 4.11) depending on the value of $D_{\text{H}_2\text{O}}^{\text{f/m}} \cdot C_{\text{Cl}}^{\text{s}}$. A decrease in $X_{\text{Cl}}/X_{\text{OH}}$ occurs if $D_{\text{H}_2\text{O}}^{\text{f/m}} \cdot C_{\text{Cl}}^{\text{s}} < 1$ (where C_{Cl}^{s} is in weight fraction). Under these conditions, water becomes concentrated in the melt during crystallisation and the rate of apatite $X_{\text{Cl}}/X_{\text{OH}}$ decline correlates negatively with $D_{\text{H}_2\text{O}}^{\text{f/m}}$ and C_{Cl}^{s} . Conversely, if $D_{\text{H}_2\text{O}}^{\text{f/m}} \cdot C_{\text{Cl}}^{\text{s}} > 1$, the rate of apatite $X_{\text{Cl}}/X_{\text{OH}}$ escalation per unit crystallisation increases with $D_{\text{H}_2\text{O}}^{\text{b/m}}$ and C_{Cl}^{s} . Thus, increasing $D_{\text{H}_2\text{O}}^{\text{f/m}}$ or C_{Cl}^{s} has the opposite effect on apatite $X_{\text{Cl}}/X_{\text{OH}}$ evolution to increasing $D_{\text{Cl}}^{\text{f/m}}$ or C_{F}^{s} in H_2O -saturated models. Furthermore, as $0 < C_{\text{Cl}}^{\text{s}} \ll C_{\text{H}_2\text{O}}^{\text{s}}$ under upper crustal pressures (Fig. 4.4; Signorelli and Carroll, 2000), during Cl-saturated crystallisation it is not possible to generate the very strong depletion in apatite $X_{\text{Cl}}/X_{\text{OH}}$ ratios observed in H_2O -saturated models at high $D_{\text{Cl}}^{\text{f/m}}$ (Fig. 4.8), where compositional trajectories approach $X_{\text{Cl}}/X_{\text{OH}} = 0$ over a short crystallisation interval following H_2O -saturation. In other words, to generate

strongly $X_{\text{Cl}}/X_{\text{OH}}$ -depleted apatites requires supercritical H_2O -saturated conditions. Under Cl-saturated conditions, apatites may only trend towards very high $X_{\text{F}}/X_{\text{Cl}}$ ratios at low C_{Cl}^{S} values, far below the most Cl-depleted melt inclusions measured in Campi Flegrei (Fig. 6.7).

Increasing $D_{\text{F}}^{\text{f/m}}$ reduces the increase in apatite $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios per unit crystallisation in all Cl-saturated crystallisation models. However, this effect is negligible where F is retained by the melt phase in the presence of a Cl-rich fluid (i.e. in the range $0 < D_{\text{F}}^{\text{f/m}} < 1$; Aiuppa *et al.*, 2009a). As in volatile-undersaturated and H_2O -saturated models, varying C_{Cl}^0 changes the apatite starting composition and the relative variations in

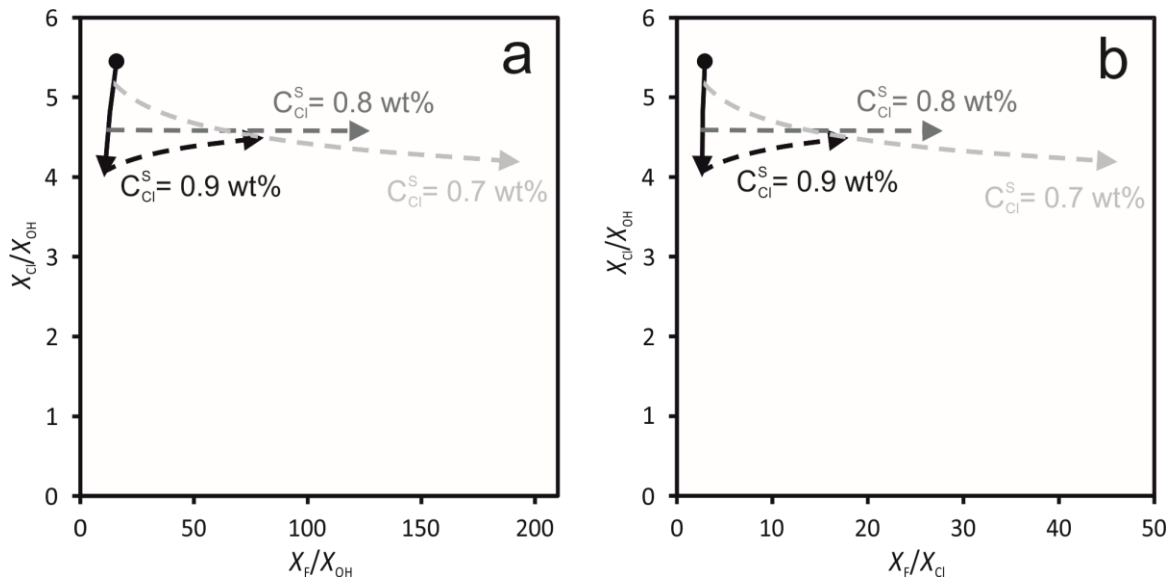


Figure 4.11 | The effect of Cl solubility on apatite compositional evolution during Cl-saturated crystallisation. Arrows show the modelled trajectories of apatite compositional evolution in $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{OH}}$ (a) and $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{Cl}}$ (b) space during volatile-undersaturated (solid line) and Cl-saturated (dashed line) crystallisation. The volatile-undersaturated model parameters, including C_{Cl}^0 , are as in Figure 4.10 and volatile-undersaturated fractionation continues to 65% crystallisation. Models of Cl-saturated apatite evolution are distinguished on the basis of C_{Cl}^{S} (see labels). Chlorine-saturated crystallisation begins at 20%, 50% and 68% crystallisation in $C_{\text{Cl}}^{\text{S}} = 0.7 \text{ wt\%}$, $C_{\text{Cl}}^{\text{S}} = 0.8 \text{ wt\%}$ and $C_{\text{Cl}}^{\text{S}} = 0.9 \text{ wt\%}$ models, respectively. In all models, $D_{\text{F}}^{\text{f/m}} = 0.7$ and $D_{\text{H}_2\text{O}}^{\text{f/m}} = 125$. Volatile-saturated fractionation continues until 95% crystallisation.

volatile mole fraction ratios over a set crystallisation interval, but not the trajectory of crystal compositional evolution.

4.7.4. Vapour + brine-saturated crystallisation

In subcritical volcanic systems, both a vapour and brine may coexist with the silicate melt. During progressive crystallisation under these conditions, H_2O and Cl are buffered in the melt and apatite $X_{\text{Cl}}/X_{\text{OH}}$ ratios remain constant. Fluorine does not partition into either fluid phase and becomes concentrated in the melt, causing both apatite $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios to increase (Fig. 4.12). The rate of $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ enrichment is dependent on C_{Cl}^s and $C_{\text{H}_2\text{O}}^s$, as well as $D_{\text{F}}^{v/m}$ and $D_{\text{F}}^{b/m}$ (i.e. bulk fluid-melt partitioning).

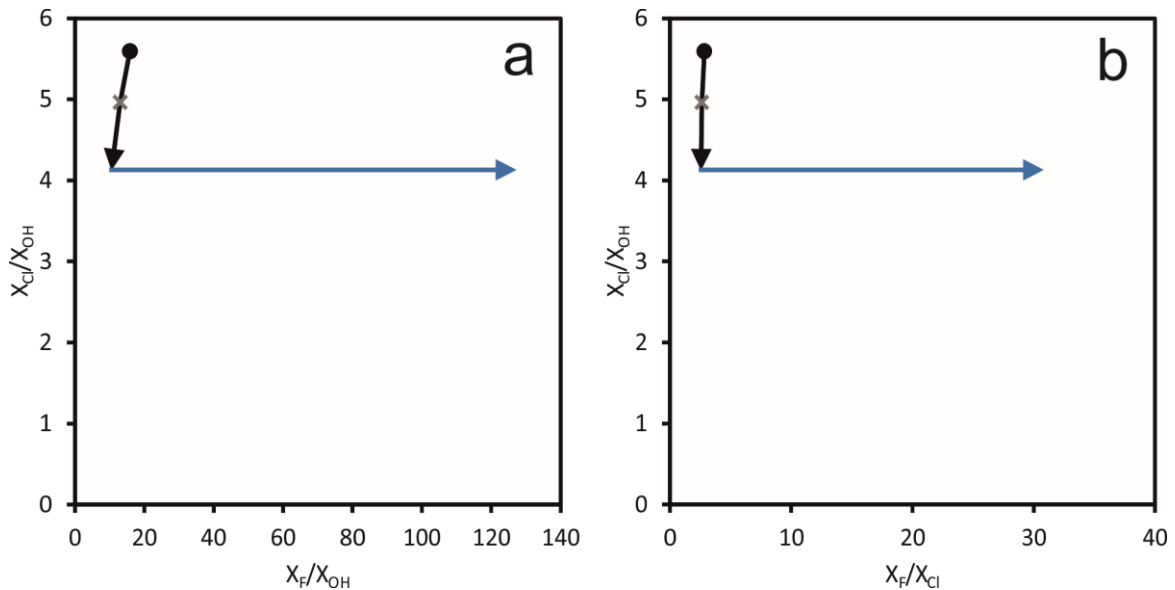


Figure 4.12 | Apatite compositional evolution during vapour + brine-saturated crystallisation. Arrows show the modelled trajectories of apatite compositional evolution in $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{OH}}$ (a) and $X_{\text{Cl}}/X_{\text{OH}}$ vs $X_{\text{F}}/X_{\text{Cl}}$ (b) space. The black lines show the trajectory of volatile-undersaturated crystallisation, with $\bar{D}_{\text{F}}^{c/m}$ and K values as in Figure 4.8. $C_{\text{F}}^0 = 0.4$ wt%, $C_{\text{Cl}}^0 = 0.67$ wt% and $C_{\text{H}_2\text{O}}^0 = 2.5$ wt%. Apatite begins crystallising at the black point and biotite comes in after 40% crystallisation at the grey cross. Both H_2O and Cl saturate at 65% crystallisation and fluid-saturated fractionation continues to 98% crystallisation (blue line). $C_{\text{Cl}}^s = 0.9$ wt%, $C_{\text{H}_2\text{O}}^s = 7.1$ wt%, $D_{\text{F}}^{v/m} = D_{\text{F}}^{b/m} = 0.7$.

However, variability is minor in the range $0 < D_F^{f/m} < 1$ and within a realistic range of H_2O and Cl solubilities (i.e. $5 < C_{H_2O}^s < 7.5$, $0.1 < C_{Cl}^s < 2$). Changing C_{Cl}^s and $C_{H_2O}^s$ alters the timing of vapour + brine saturation during magmatic evolution but has no effect on the overall trajectory of compositional evolution. Similarly, varying C_i^0 changes the model starting compositions and relative variations in X_F/X_{OH} and X_F/X_{Cl} but does not affect the direction of compositional evolution.

4.7.5. Fluorite-saturated crystallisation

Depending on $\mu(CaO)$, crystallisation of magmatic fluorite may buffer F in the melt. Chlorine and H_2O partitioning is unaffected by minor fluorite crystallisation (Section 4.3.3.). After *fluorite-in*, apatite compositional evolution therefore follows a similar trajectory to previous volatile-undersaturated crystallisation (Fig. 4.6), with an inflection reflecting the change in $\bar{D}_F^{c/m}$ (Fig. 4.13). The magnitude of the apatite compositional inflection is proportional to the change in $\bar{D}_F^{c/m}$ at *fluorite-in*. This is maximised when F is buffered in the melt (i.e. in Ca -rich systems), where $\bar{D}_F^{c/m} = 1$. During F -buffered crystallisation, apatite X_F/X_{OH} and X_F/X_{Cl} ratios decrease in all models because Cl and H_2O are not incorporated into fluorite and remain incompatible with the crystallising phase assemblage. Apatite X_{Cl}/X_{OH} ratios may increase or decrease, depending on $\bar{D}_{Cl}^{c/m}$ and $\bar{D}_{H_2O}^{c/m}$.

The effect of buffering F in the melt is to increase the rate of apatite X_F/X_{OH} and X_F/X_{Cl} decline per unit crystallisation, relative to volatile-undersaturated fractionation models at equivalent $\bar{D}_{Cl}^{c/m}$ and $\bar{D}_{H_2O}^{c/m}$ (Fig. 4.13). Following F saturation at constant $\bar{D}_{H_2O}^{c/m}$, the rate of apatite X_F/X_{Cl} decline is greater at higher $\bar{D}_{Cl}^{c/m}$ values. At constant $\bar{D}_{Cl}^{c/m}$, the

rate of X_F/X_{Cl} decline is greater at lower $\bar{D}_{H_2O}^{c/m}$ values. Fluorite saturation has no effect on apatite X_{Cl}/X_{OH} evolution.

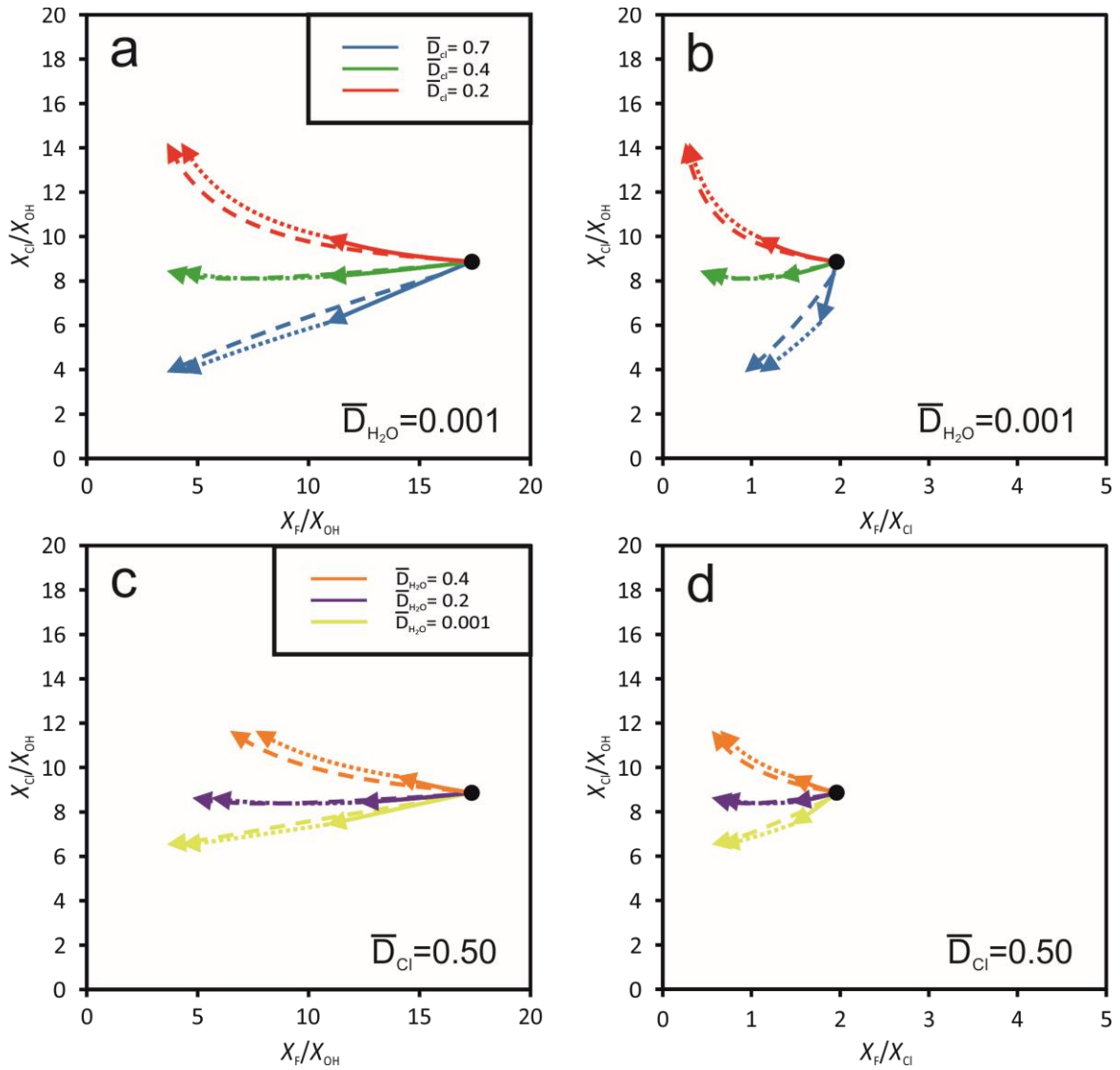


Figure 4.13 | Apatite compositional evolution during F-saturated crystallisation.

Arrows show the modelled trajectories of apatite compositional evolution in X_{Cl}/X_{OH} vs X_F/X_{OH} (a,c) and X_{Cl}/X_{OH} vs X_F/X_{Cl} (b,d) space during volatile-undersaturated (solid line) and fluorite-saturated (dashed/dotted line) crystallisation. In all models, $C_{Cl}^0 = 0.4$ wt%, $C_F^0 = 0.165$ wt%, $C_{H_2O}^0 = 0.57$ wt%, $\bar{D}_F^{c/m} = 0.8$, $K_{F-Cl} = 0.21$ and $K_{Cl-OH} = 4.17 \cdot 10^3$. Apatite-only fractionation begins at the black point and continues until 63% crystallisation. F-saturated crystallisation begins at 15% and 63% crystallisation in $C_F^s = 0.17$ wt% (dashed line) and $C_F^s = 0.2$ wt% (dotted line) models, respectively. Colours denote different values of $\bar{D}_{Cl}^{c/m}$ (a,b) and $\bar{D}_{H_2O}^{c/m}$ (c,d) (see legends). In a and b, $\bar{D}_{H_2O}^{c/m} = 0.001$. In c and d, $\bar{D}_{Cl}^{c/m} = 0.5$. F-saturated fractionation continues to 95% crystallisation in all models.

When F is buffered in the melt, the rate of X_F/X_{OH} and X_F/X_{Cl} decline per unit crystallisation is greatest at high C_F^S values (Fig. 4.13). However, if F is saturated in Campi Flegrei melts, measured glass F concentrations (generally <0.2 wt%; see Chapter 6) constrain C_F^S to low values and thus variability in apatite compositional trajectories as a result of changing C_F^S would be minimal. As in Sections 4.7.1-4.7.4., varying C_i^0 in F-saturated models alters model start points and the relative variations in apatite volatile ratios but does not change the overall direction of crustal compositional evolution.

4.8. Summary and application to natural magmatic systems

In this chapter, I have developed new thermodynamic models of apatite compositional evolution during fractional crystallisation in the presence of different magmatic fluids. This builds on early work by Candela (1986), improving volatile-undersaturated crystallisation models to account for the variable comparability of volatiles species during hydrous mineral precipitation, and deriving new sets of equations that describe the range of volatile-saturated crystallisation scenarios (with respect to H_2O , Cl and F) that can occur in natural magmatic systems. Some experiments have been undertaken to investigate apatite compositional evolution during fractional crystallisation or fractional volatile evolution (e.g. Ustunisik *et al.*, 2011; Ustunisik *et al.*, 2015). These show good agreement with the model outputs, providing validation for the thermodynamic approach outlined in this chapter.

I have identified the range of model input parameters that can be expected in natural systems (focussing on Campi Flegrei) and by systematically varying input parameters within these limits, I have explored the range of apatite compositional space that can be accessed by invoking different magmatic fluid scenarios. This method creates

‘families of curves’ that are defined by the thermodynamics of fluid-melt volatile exchange in each fluid ‘scenario’. These are summarised as follows:

- **Volatile-undersaturated crystallisation** (Fig. 4.6): Apatite X_F/X_{Cl} ratios always decrease. X_{Cl}/X_{OH} ratios may increase or decrease, with declining X_{Cl}/X_{OH} at low $\bar{D}_{Cl}^{c/m}$ or very high $\bar{D}_{H_2O}^{c/m}$. Apatite X_F/X_{OH} ratios generally decrease but can increase, accompanied by increasing X_{Cl}/X_{OH} , at low $\bar{D}_F^{c/m}$ values. This agrees with the experiments of Ustunisik *et al.* (2015), which show an evolution towards more OH-rich apatite compositions during volatile-undersaturated fractional crystallisation.
- **Water-saturated crystallisation** (i.e. low-density fluid present; Fig. 4.8): Characterised by a large increase in apatite X_F/X_{OH} and X_F/X_{Cl} ratios per unit crystallisation. X_{Cl}/X_{OH} ratios strongly decrease during H₂O-saturated crystallisation at high $D_{Cl}^{f/m}$ values. At lower $D_{Cl}^{f/m}$, apatite X_{Cl}/X_{OH} ratios either decrease slowly or increase with progressive crystallisation. This agrees with the experiments of Ustunisik *et al.* (2011), which show a decrease in apatite Cl contents and an evolutionary trajectory towards more F-rich compositions during fractional volatile evolution and degassing.
- **Chlorine-saturated crystallisation** (i.e. dense fluid present; Fig. 4.10): Apatite X_F/X_{OH} and X_F/X_{Cl} ratios always increase but the magnitude of X_F/X_{Cl} escalation is considerably lower than in H₂O-saturated models over a given crystallisation interval. X_{Cl}/X_{OH} ratios increase at high $D_{H_2O}^{f/m}$ values and decrease at lower $D_{Cl}^{f/m}$ but it is not possible to generate the sharply declining in X_{Cl}/X_{OH} trajectories observed in H₂O-saturated models.

- **Vapour + brine-saturated crystallisation** (Fig. 4.12): Apatite crystallisation under conditions of subcritical two-fluid stability is distinguished by increasing X_F/X_{OH} and X_F/X_{Cl} at constant X_{Cl}/X_{OH} .
- **F-buffered (fluorite saturated) crystallisation** (Fig. 4.13): Apatite compositional evolution will continue along a similar compositional trajectory to volatile-undersaturated crystallisation at equivalent $\bar{D}_{Cl}^{c/m}$ and $\bar{D}_{H_2O}^{c/m}$. However, there will be an inflection at *fluorite-in*, reflecting an increase in the rate of X_F/X_{OH} and X_F/X_{Cl} decline per unit crystallisation.

Combined with an understanding of the effects of pressure and temperature on apatite compositional evolution (Section 5.4.3.), these modelled ‘families of curves’ can be compared with natural apatite analyses to interpret magmatic fluid systematics during crystallisation. Comparisons can be made between different apatite populations or between crystals within a single population. However, full interpretation is aided by knowledge of apatite volatile diffusion rates and the timescales of crystal compositional re-equilibration.

In Chapter 5, the models developed in this chapter are used to interpret a compositional trend identified between apatite inclusions hosted within different phenocryst phases from a single eruption of Campi Flegrei. This provides a temporal record of magmatic volatile systematics in the build-up to eruption. In Chapter 6, the models are used to understand compositional trends observed in apatite microphenocrysts from multiple Campi Flegrei eruptions, elucidating magmatic volatile behaviours on short pre-eruptive timescales. Furthermore, in Chapter 6, the new thermodynamic constraints on apatite volatile evolution are used to understand systematic differences in crystal volatile compositions between different eruptions at Campi Flegrei.

Chapter 5

Temporal evolution of magmatic volatile contents in the build-up to eruption

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Late-stage volatile saturation as a potential trigger for explosive volcanic eruptions.

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The saturation, exsolution and expansion of volatile elements provides the driving force for volcanic eruptions. Models of magma chamber evolution commonly assume relatively slow, incremental assembly under volatile-saturated conditions, with eruptions triggered by an injection of new volatile-rich melt or overpressure generated through protracted crystallisation. However, there is little or no empirical evidence for the temporal evolution of dissolved volatiles prior to eruption. Here, I use texturally constrained apatite and melt inclusions to examine the evolution of magmatic volatiles through time in the lead-up to an explosive eruption of the Campi Flegrei caldera, Italy. I demonstrate that the magma chamber

*The Supplementary Discussion accompanying this paper is presented in Section 5.4. of this thesis.

remained persistently H₂O-undersaturated throughout its evolution, and show that volatile saturation and final ‘priming’ of magmatic systems may only occur on very short timescales, days before eruption. This late-stage volatile saturation likely acted to trigger eruption. Furthermore, I conclude that in Campi Flegrei and other similar magmatic systems, magma recharge may both increase repose times and reduce the likelihood of eruption.

5.1. Introduction

Volcanic gases (principally H₂O and CO₂) dissolved in silicate melts exert a first-order control on the eruptive behaviour of many volcanoes (Huppert and Woods, 2002; Roggensack *et al.*, 1997; Wilson, 1980). Vapour saturation in magmas may be reached during ascent (Roggensack *et al.*, 1997; Woods and Koyaguchi, 1994) or through progressive crystallisation (Blake, 1984; Tait *et al.*, 1989). After volatile saturation, continued growth of vapour bubbles during crystallisation (Blake, 1984; Tait *et al.*, 1989) or replenishment (Folch and Martí, 1998; Sparks *et al.*, 1977) will pressurise the magma reservoir, and may eventually trigger eruption. Constraining pre-eruptive volatile concentrations and the timing of volatile saturation is therefore critical to our understanding of volcanic eruptions. Although many models assume that saturation occurs early in magmatic evolution (e.g. Arienzo *et al.*, 2010; Humphreys *et al.*, 2008; Isaia *et al.*, 2004; Roggensack *et al.*, 1997), it is not known whether this is generally the case; or whether, instead, melts can remain undersaturated on long timescales during crustal storage. Developing ways to constrain variations in dissolved magmatic volatile contents through time, in the build-up to an explosive eruption, would be invaluable for the assessment of volcanic hazards, as past eruptions provide clues to the future behaviour of the system.

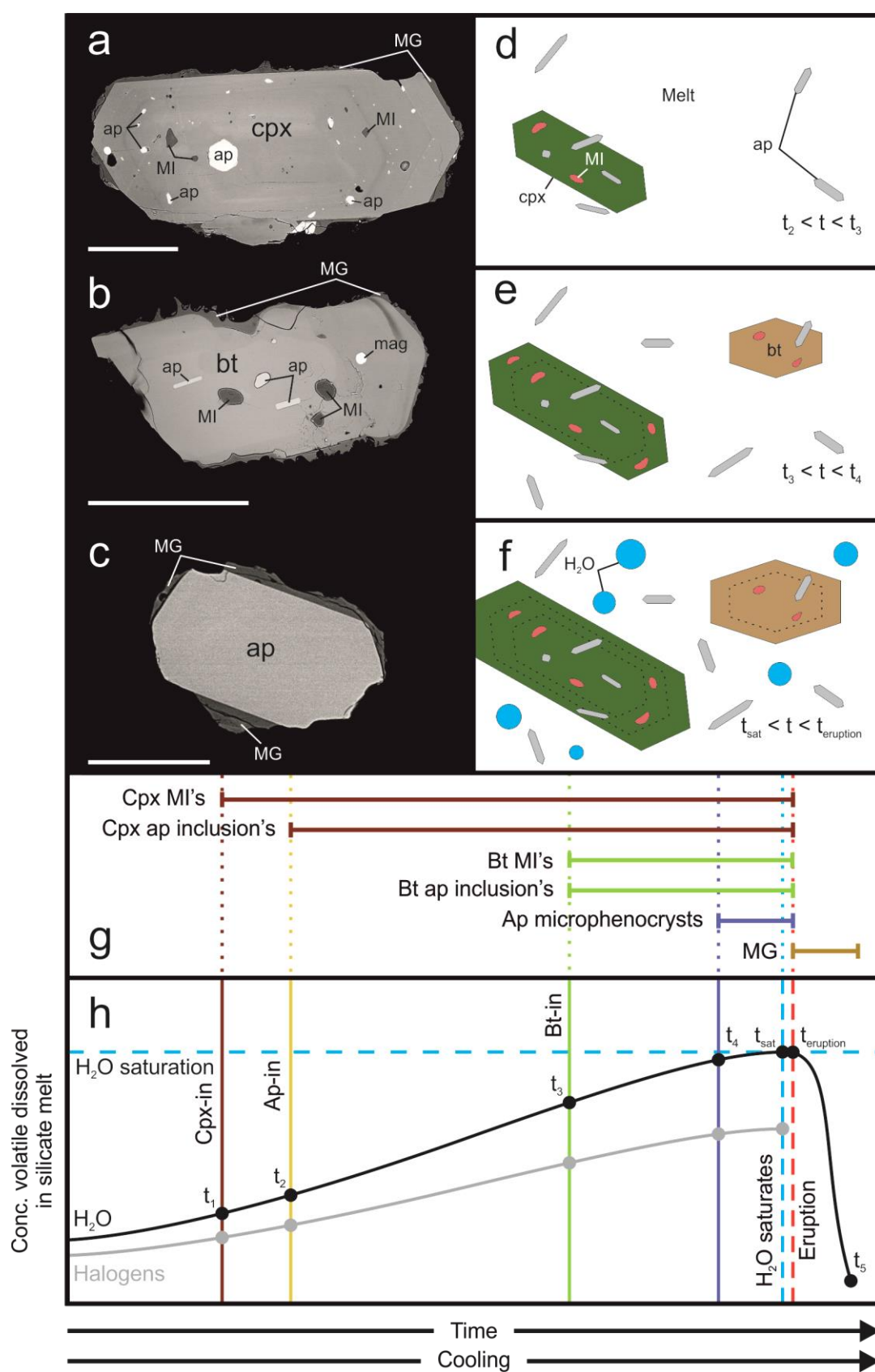


Figure 5.1 | (previous page) Textural relationships of different hydrous phases in the Astroni 1 magma and the preservation of a temporally constrained magmatic volatile record. a,b, Backscattered-electron (BSE) images showing apatite and melt inclusions hosted within **(a)** a clinopyroxene and **(b)** a biotite phenocryst. **c,** BSE image of an apatite microphenocryst, rimmed by silicate glass, demonstrating the potential for diffusive apatite-melt exchange until the matrix was quenched on eruption. **d-f,** Sketches summarising the model by which hydrous phases obtain and retain the volatile composition of the silicate melt during fractionation. Apatite crystals and melt inclusions are progressively trapped within pyroxene and biotite phenocrysts and are subsequently considered closed to diffusive exchange with the melt (except for H₂O in melt inclusions; see discussion in text). Apatite microphenocrysts continue to grow and equilibrate with the melt on timescales controlled by individual species diffusivities (Brenan, 1993). Volatile saturation occurs before eruption **(f)**. **g,** The relative timescales over which texturally constrained hydrous phases preserve a record of melt volatile contents. **h,** Schematic graph showing the hypothetical volatile-undersaturated evolution of H₂O (black line) and halogens (grey line) in a silicate melt during isobaric cooling and crystallisation, followed by H₂O saturation and ascent. The concentration of H₂O in the melt would be buffered during crystallisation if vapour saturation occurred significantly before eruption. After vapour saturation under equilibrium conditions, the F/Cl ratio in the melt will increase. However, equilibration may be kinetically inhibited during rapid ascent, causing halogen concentrations in the melt to remain approximately constant despite the presence of a vapour phase (see text for details). Vertical lines show the relative timing of mineral precipitation and microphenocryst equilibration. t_1 - t_5 refer to the relative timing of events shown in panel **h**. t_4 represents the time after which apatite microphenocryst compositions are preserved on eruption; before this they are reset by diffusional re-equilibration. t_{eruption} and t_{sat} denote the relative onset of ascent and H₂O saturation, respectively. Scale bars are 250 μm in **a**, 500 μm in **b** and 100 μm in **c**. ap= apatite, cpx= clinopyroxene, bt= biotite, mag= magnetite, MI= melt inclusion, MG= matrix glass.

Apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$, is a common accessory phase in igneous rocks that takes all major magmatic volatiles (OH, C, S, Cl, F) into its crystal structure. It has recently been used to elucidate the volatile contents of silicate melts in terrestrial (Boyce and Hervig, 2008; Piccoli and Candela, 1994; Scott *et al.*, 2015) and extraterrestrial (Boyce *et al.*, 2014; McCubbin *et al.*, 2011) environments. Apatite offers several

important benefits for the determination of pre-eruptive magmatic volatile contents compared to the widely used ‘melt inclusion’ approach. In particular, apatites are less susceptible to post-entrapment volatile leakage, or to modification by post-entrapment crystallisation or bubble growth (Lowenstern, 1995). Here, I present analyses of apatites and melt inclusions that are hosted in phenocryst phases (clinopyroxene and biotite) and were trapped and isolated from the melt at different times during the crystallisation history of an evolving magma. I also analysed apatite microphenocrysts that remained in contact with the melt until shortly before eruption; and matrix glasses, which quenched during eruption. Combined with thermodynamic models, these ‘texturally constrained’ hydrous phases reveal how magmatic volatiles evolved (Fig. 5.1) in the build-up to the phonolitic Astroni 1 eruption, 4.3–4.1 kyr ago (Smith *et al.*, 2011; sample description in Section 5.4.1.). The Astroni 1 eruption marked the beginning of the most recent phase of prolonged explosive volcanism at Campi Flegrei, one of the most hazardous volcanoes in Europe (Smith *et al.*, 2011). My approach is distinct from previous studies, which have assessed apatite growth zoning (Boyce and Hervig, 2008) or texturally unconstrained analyses (Piccoli and Candela, 1994). Although I focus on a single event, my approach can be applied widely to determine the temporal evolution of pre-eruptive volatiles in other volcanic systems.

5.2. Results

5.2.1. Volatile variations in apatite

The volatile composition of apatite relates to that of its host liquid by a set of exchange reactions between F, Cl and OH, for example:

$$K_{(P,T)} = \frac{f_{\text{H}_2\text{O}}^{\text{l}}}{f_{\text{HF}}^{\text{l}}} \cdot \frac{X_{\text{F}}^{\text{Ap}}}{X_{\text{OH}}^{\text{Ap}}} \quad (\text{eq. 5.1})$$

where exchange coefficients, K , are constant at a given pressure (P) and temperature (T ; Piccoli and Candela, 1994), f is fugacity, X is mole fraction and superscripts l and Ap denote the liquid and apatite phases, respectively. I measured F, Cl and OH directly using secondary ion mass spectrometry and electron microprobe analysis (see Chapter 2). I neglect sulphur, because S diffusion in apatite is inhibited by a coupled substitution (Peng *et al.*, 1997), and equilibrium is not maintained on short timescales. Apatite compositions from Astroni 1 show a negative correlation between X_{F} and X_{OH} and a weaker negative correlation between X_{Cl} and X_{OH} (where X_{F} , X_{Cl} and X_{OH} are the mole fractions of F, Cl and OH, respectively; Appendix 3), demonstrating this exchange of components within the crystal volatile site. Some crystals are slightly non-stoichiometric, within the range reported in other studies (Nadeau *et al.*, 1999). I focus on mole fraction ratios as these relate to liquid composition, pressure and temperature through relationships such as equation 5.1. Data show a positive correlation between $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{OH}}$ (Fig. 5.2a), with one low- X_{Cl} , high- X_{F} outlier. In general, $X_{\text{F}}/X_{\text{Cl}}$ is constant within error, except in the outlier which has high $X_{\text{F}}/X_{\text{Cl}}$ (Fig. 5.2b). Clinopyroxene-hosted apatite inclusions extend to higher $X_{\text{Halogen}}/X_{\text{OH}}$ ratios than biotite-hosted apatite inclusions. Both clinopyroxene- and biotite-hosted inclusions extend to higher $X_{\text{Halogen}}/X_{\text{OH}}$ ratios than apatite microphenocrysts that were in contact with melt until eruption. The overall $X_{\text{Halogen}}/X_{\text{OH}}$ trend is apparently linear, suggesting that there was no significant relative change in F or Cl compatibility during apatite crystallisation.

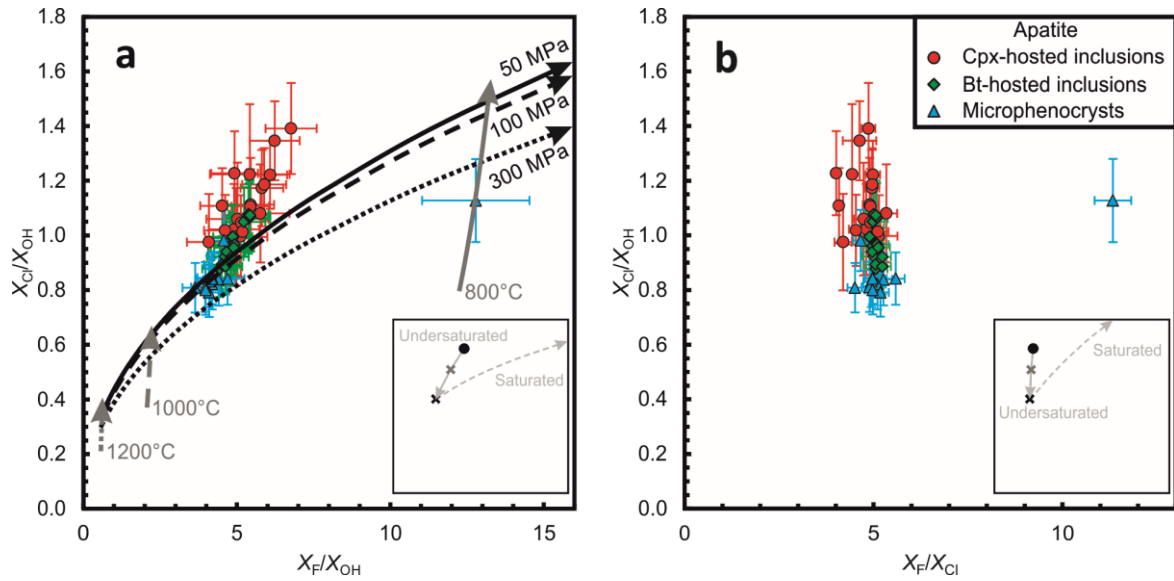


Figure 5.2 | The volatile compositions of Astroni 1 apatites. **a**, Apatite volatile compositions in $X_{\text{F}}/X_{\text{OH}}$ versus $X_{\text{Cl}}/X_{\text{OH}}$ space. Black arrows show the modelled trajectory of apatite compositional evolution with decreasing temperature (1200-700 °C), at a constant melt volatile composition and at pressures of 50 MPa (solid line), 100 MPa (dashed line) and 300 MPa (dotted line). Dark grey arrows show the modelled trajectory of apatite compositional evolution with decreasing pressure (1000-0 MPa), at a constant melt volatile composition and at temperatures of 800 °C (solid line), 1000 °C (dashed line) and 1200 °C (dotted line). This modelling was undertaken using the equations of Piccoli and Candela (1994) (see Section 5.4.3. for details). **b**, Apatite volatile compositions in $X_{\text{F}}/X_{\text{Cl}}$ versus $X_{\text{Cl}}/X_{\text{OH}}$ space. Insets show the trajectory of apatite compositions during volatile-undersaturated (solid light grey line) and volatile-saturated (dashed light grey line) crystallisation, calculated using an adaptation of the model in Candela (1986) to account for differences in the relative compatibility of volatile species during hydrous mineral precipitation (see Section 5.4.4. for details). Apatite crystallisation begins at the black point, *biotite-in* is after 40% crystallisation (grey cross) and volatile saturation occurs after 73% crystallisation (black cross). If vapour saturation occurred in Astroni 1, apatites would move to high $X_{\text{Cl}}/X_{\text{OH}}$ ratios, progressing towards fluorapatite end-member compositions (case 2 of Candela, 1986) due to the high H_2O solubility (Webster *et al.*, 2014) and vapour-melt Cl partition coefficient (Signorelli and Carroll, 2000). The general measured trend of decreasing $X_{\text{Halogen}}/X_{\text{OH}}$ is incongruent with the modelled compositional trend caused by cooling or depressurisation, or with equilibrium with a H_2O -saturated melt. All elements were measured by SIMS. Errors bars represent precision with a 90% confidence interval, as detailed in the Chapter 2. Data are distinguished on the basis of phenocryst host and textural association (see legend).

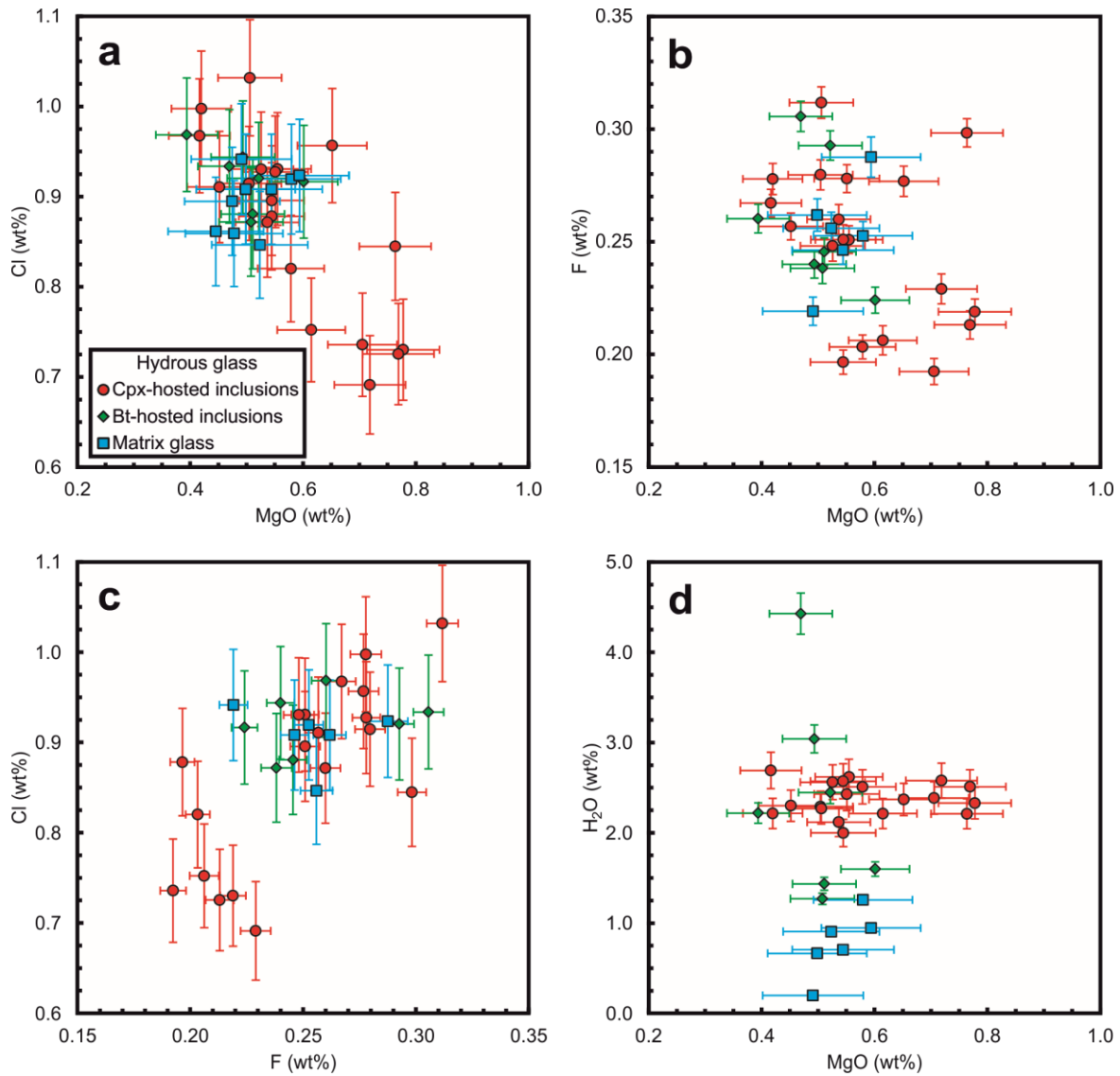


Figure 5.3 | The volatile contents of Astroni 1 hydrous glasses. a, b, MgO versus Cl and F respectively. **c,** F versus Cl. **d,** MgO versus H₂O. MgO and Cl were measured by EPMA. F and H₂O were measured by SIMS. Error bars represent precision with ± 1 s.d. (EPMA data) and a 90% confidence interval (SIMS data), as detailed in Chapter 2. Data are distinguished on the basis of their phenocryst host or textural association (see legend).

5.2.2. Volatile variations in hydrous glasses

Melt inclusions are typically phonolitic, with an average molar $\text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O})$ of 0.44 and $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ of 0.87, similar to Vesuvian melt compositions (Webster *et al.*, 2014). MgO and FeO concentrations are <0.78 wt% and <4.20 wt%,

respectively (Appendix 3). Fluorine and Cl contents of clinopyroxene- and biotite-hosted melt inclusions correlate negatively with MgO (Fig. 5.3a,b), reflecting halogen incompatibility in the silicate melt during fractionation. Water is constant within error in clinopyroxene-hosted melt inclusions (~2 wt%), but is highly variable in biotite-hosted inclusions (1.3–4.5 wt%), with no correlation between melt inclusion H₂O and MgO (Fig. 5.3d). All melt inclusions contain very low CO₂ contents, typically <250 ppm (Appendix 3), similar to concentrations observed in other Campi Flegrei magmas (Arienzo *et al.*, 2010; Marianelli *et al.*, 2006).

Matrix glasses have MgO contents similar to the most evolved melt inclusions. Fluorine and Cl contents are similar to those of biotite-hosted melt inclusions and the most evolved clinopyroxene-hosted inclusions (Fig. 5.3a-c). However, matrix glasses have low H₂O contents relative to both clinopyroxene- and biotite-hosted melt inclusions, typically <1 wt% (Fig. 5.3d).

5.2.3. Modelling fractionation and volatile saturation

I model magma evolution in the Campi Flegrei system using the Rhyolite-MELTS thermodynamic software (details in Section 5.4.2.; Bohrsen *et al.*, 2006; Cannatelli, 2012; Fowler *et al.*, 2007; Gualda *et al.*, 2012). Because major and trace element trends between different eruptions of Campi Flegrei can be related by fractional crystallisation of a single parental magma (Civetta *et al.*, 1991), I use the most primitive olivine-hosted melt inclusion reported from the past 15 kyr (Mi1-C1-o5-M1 of Cannatelli *et al.*, 2007) as the starting composition. Models were run over the pressure range 50–300 MPa, at an oxygen fugacity 1 log unit above the Quartz-Fayalite-Magnetite buffer ($f_{\text{O}_2} = \text{QFM} + 1$) and with liquidus H₂O concentrations ($L_{\text{H}_2\text{O}}$) of 2–3 wt%, to simulate the entire range of conditions identified in previous phase equilibria and petrological studies as best reproducing the stable phase assemblages observed in Campi Flegrei eruptions (Bohrson *et al.*, 2006;

Cannatelli, 2012; Fowler *et al.*, 2007). Because Rhyolite-MELTS uses a pure-H₂O solubility model that is not appropriate for alkali melts (see Section 5.4.2.), I repressed fluid exsolution in my models and instead used recent experimental data as a guide to volatile saturation in Campi Flegrei magmas (Fig. 5.4).

The model results confirm the crystallisation sequence: olivine (~1,330 °C) + clinopyroxene (~1,080 °C) + apatite (~1,020 °C) + biotite (~910 °C) + K-feldspar (~790 °C) at 150 MPa, $L_{H_2O} = 3$ wt% (Fig. 5.4). This matches the observed phase assemblage in Astroni 1 products, except that olivine is absent in natural samples and fluorite occurs as a late microphenocryst phase. Within the modelled range, L_{H_2O} has no effect on the order of crystallisation, but clinopyroxene and apatite both arrive on the liquidus at slightly higher temperatures at lower L_{H_2O} conditions ($\Delta T \sim 20$ °C and ~ 30 °C, respectively). During fractionation, modelled melt MgO contents decrease from ~3.8 wt% at *clinopyroxene-in* to ~0.2 wt% at *K-feldspar-in*; dissolved H₂O contents increase from 3.7 wt% to 6.2 wt% over the same interval. Pressure has little effect on the modelled down-temperature MgO and H₂O evolution of the system before volatile saturation is achieved, but would change L_{H_2O} if volatile saturation occurred before *olivine-in* (Fig. 5.4).

Magma storage pressures can be constrained independently from geophysical observations. Seismic reflection data suggest that the main melt zone beneath Campi Flegrei is at ~7–7.5 km (De Siena *et al.*, 2010; Zollo *et al.*, 2008), with ephemeral sills and intrusions extending to ~3 km (De Siena *et al.*, 2010; Woo and Kilburn, 2010). This equates to pressures of 170–180 MPa for the main reservoir, assuming a melt density of 2,440 kg m⁻³. The H₂O solubility of phonolitic melts is >7.5 wt% at 900–950 °C, 200 MPa (Webster *et al.*, 2014), falling to ~6.33 wt% H₂O at 870 °C, 150 MPa and <3 wt% H₂O at <50 MPa (Carroll and Blank, 1997). On the basis of these experimental

data, H₂O saturation in my model runs is achieved at 750–785 °C at 200 MPa and 775–805 °C at 150 MPa, within the range L_{H₂O} = 2–3 wt% (Fig. 5.4). In both cases this is significantly later than *apatite-in*.

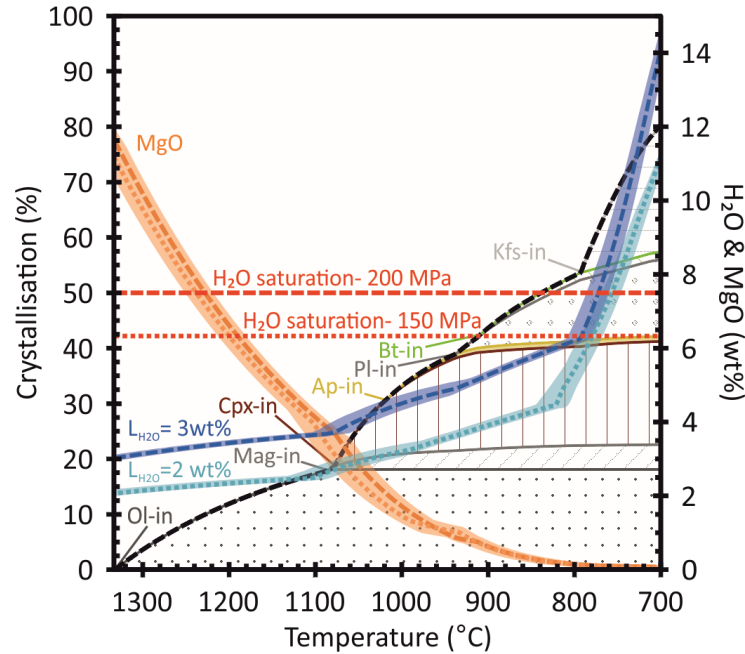


Figure 5.4 | Rhyolite-MELTS thermodynamic modelling of the Astroni 1 system.

The dashed black line shows total solids and solid lines show modelled phase proportions at 150 MPa and L_{H₂O} = 3 wt%. This is similar to observed phase assemblage in Astroni 1, except that olivine is absent as a phenocryst phase in natural samples (see Section 5.4). The light and dark blue dashed lines show the modelled H₂O concentration dissolved in the silicate melt at 150 MPa, L_{H₂O} = 2 wt% and 3 wt% respectively. The blue fields show the range of dissolved H₂O contents modelled for these L_{H₂O} concentrations within the pressure range 50–300 MPa. The light and dark orange dashed lines show the modelled MgO concentration of the melt at 150 MPa and L_{H₂O} = 2 wt% and 3 wt%, respectively. The orange field shows the range of melt MgO concentrations within the pressure range 50–300 MPa and L_{H₂O} = 2–3 wt%. The dashed red line shows the H₂O concentration at volatile saturation for a low-CO₂ phonolite at 910–944 °C, 200 MPa, based on experiments in Webster *et al.* (2014). The dotted red line shows the saturation H₂O concentration for a CO₂-free phonolite at 870 °C, 150 MPa, based on experiments in Carroll and Blank (1997). The starting composition in this model is melt inclusion Mi1-C1-o5-M1 of Cannatelli *et al.* (2007). Within a realistic pressure and L_{H₂O} range, the Astroni 1 magma chamber is likely to reach H₂O saturation at T ≈ 800 °C. Ol = olivine (dots); mag = magnetite (diagonal lines); cpx = clinopyroxene (vertical lines); ap = apatite; Pl = plagioclase (spots); bi = biotite (diagonal lines); Kfs = K-feldspar (horizontal lines).

5.3. Discussion

5.3.1. Progressive temporal trends in melt volatile contents

The modelled crystallisation sequence provides the context for me to interpret progressive changes in melt and apatite volatile compositions, from clinopyroxene-hosted melt or apatite inclusions, to biotite-hosted inclusions, to microphenocrysts and matrix glasses.

Apatite–liquid exchange coefficients (equation 5.1) have been constrained experimentally for the system apatite–fluid as a function of pressure and temperature (Piccoli and Candela, 1994 and references therein). At constant liquid volatile composition, decreasing temperature causes a strong increase in apatite $X_{\text{Halogen}}/X_{\text{OH}}$ ratios (Fig. 5.2a). However, the pressure dependence is small and almost exclusively affects $X_{\text{Cl}}/X_{\text{OH}}$ (Piccoli and Candela, 1994). The trend of decreasing $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{OH}}$ during magmatic evolution revealed by my data set is inconsistent with changing K due to cooling or depressurisation (Fig. 5.2a; see Section 5.4.3. for model details). Although magma mixing may cause temporary heating, interpretations involving significant long-term heating or pressurisation are not geologically realistic during the protracted magmatic fractionation required to produce the Astroni 1 phenocryst assemblage (Fig. 5.4). Instead, the observed trend in apatite compositions reflects a progressive change in the melt volatile composition through time, during magma evolution.

Within the limits of analytical precision, melt inclusions show that melt halogen concentrations increased during magma evolution (Fig. 5.3a–c). Assuming that K_D (equation 1) does not vary significantly with evolving melt composition, the decreasing apatite $X_{\text{Halogen}}/X_{\text{OH}}$ ratios (Fig. 5.2) must reflect a comparative increase in dissolved melt H_2O contents during crystallisation: that is, H_2O -undersaturated behaviour. This concurs with my Rhyolite-MELTS modelling. When compared with phonolite solubility

experiments (Carroll and Blank, 1997; Webster *et al.*, 2014), models predict late, low-temperature H₂O saturation, with melt H₂O concentrations increasing throughout magmatic evolution, at pressures consistent with independent estimates of magma storage depths (that is, $P > 150$ MPa; Fig. 5.4).

Trends in apatite compositions observed in Astroni 1 can be reproduced using models based on volatile-undersaturated fractionation (Chapter 4; Candela, 1986), assuming that F, Cl and H₂O are moderately incompatible during crystallisation of apatite and biotite (insets Fig. 5.2 and Section 5.4.4.). The effect of biotite precipitation on apatite compositional evolution is minor (Candela, 1986), whereas the effect of late-stage vapour saturation on the compositional evolution of apatite is orders of magnitude more significant (Chapter 4; Candela, 1986). This is because vapour-melt Cl partition coefficients in H₂O-saturated phonolites are >1 (Signorelli and Carroll, 2000); whereas F is retained within the silicate liquid (Webster *et al.*, 2014). The effect of this is to increase the F/Cl ratio in the melt. After vapour saturation, apatite will move towards a F–Cl binary composition, progressing towards endmember fluorapatite (case 2 of Candela, 1986; insets Fig. 5.2). I do not see this trend in my data set (Fig. 5.2), and infer that the system remained volatile-undersaturated while the apatite microphenocrysts were in equilibrium with the melt.

If the melt inclusions were trapped in the presence of a hydrosaline brine, I would expect to see constant melt Cl instead of the observed negative correlation between Cl and MgO (Fig. 5.3a). Experimental data show that in the presence of a vapour phase, Cl-solubility in phonolitic magmas is pressure dependent (Signorelli and Carroll, 2000). The highest Cl concentrations measured in Astroni 1 melt inclusions (>1 wt%) require unreasonably low entrapment pressures (<25 MPa) under vapour-saturated conditions (Signorelli and Carroll, 2000). Instead, my data are consistent with crystallisation in the

absence of a free fluid, in agreement with experimental constraints (Webster and De Vivo, 2002).

Melt inclusion halogen concentrations show a negative correlation with MgO (Fig. 5.3a,b), which is consistent with incompatible behaviour during crystallisation. However, the lack of correlation between H₂O and MgO in melt inclusions (Fig. 5.3d) cannot be reconciled either with apatite compositions (Fig. 5.2) or crystallisation models (Fig. 5.4). Instead, I suggest that H₂O contents of melt inclusions have been modified by diffusion after entrapment, whereas halogen concentrations record primary magmatic processes. Hydrogen diffuses rapidly through pyroxene, even at 800 °C (Woods *et al.*, 2000), and this is widely implicated in post-entrapment modification of melt inclusion volatile contents (Danyushevsky *et al.*, 2002). From published H diffusivity data, the H₂O concentrations of clinopyroxene-hosted melt inclusions in the centre of mm-scale phenocrysts will change on timescales of hours (Woods *et al.*, 2000). Thus, short-term stalling of magma at shallow depths after volatile saturation provides a mechanism to reset the H₂O contents of melt inclusions with varying MgO concentrations. No data exist for H diffusivity in biotite, although the strong cleavage would presumably reduce its competency as a melt inclusion host. High H₂O concentrations in some biotite-hosted inclusions (Fig. 5.3d) suggest that melt H₂O contents could have reached >4.5 wt% during biotite crystallisation. Biotite-hosted melt inclusions with H₂O contents that approach the concentrations measured in matrix glass have probably leaked. The low H₂O content of matrix glass is consistent with efficient syn-eruptive degassing during magma ascent. Under equilibrium conditions at depth, Cl would partition preferentially into the vapour phase (Signorelli and Carroll, 2000). However, halogens diffuse significantly more slowly than H₂O in silicate melts (Baker *et al.*, 2005), inhibiting vapour-melt equilibration and inducing disequilibrium on short timescales during ascent. Thus, degassed matrix glasses

may retain Cl concentrations similar to evolved melt inclusions (Fig. 5.3). At low pressure, vapour-melt Cl partition coefficients approach unity (Signorelli and Carroll, 2000).

5.3.2. Timescales of volatile undersaturation

If the magma became volatile-saturated before eruption this should result in disequilibrium between the melt and pre-existing apatite microphenocrysts. However, apatite volatile data show no evidence for partial re-equilibration towards strongly Cl-poor, F-rich (volatile-saturated) compositions as predicted by volatile-saturated

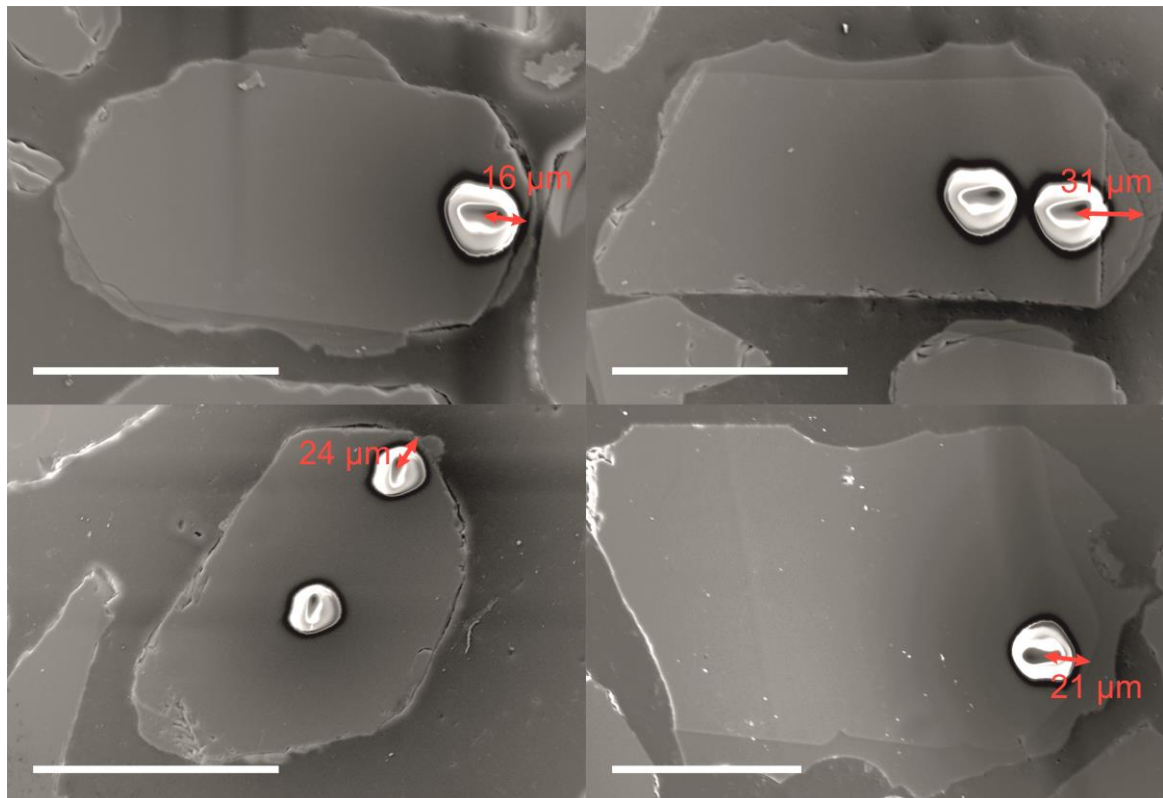


Figure 5.5 | Secondary-electron images of apatite microphenocrysts. Images show the positions of analyses close to the rims of apatite microphenocrysts used in the calculation of diffusion timescales. Distances were measured by SEM post-analysis. Scale bars in all images are 100 μm . Crystals used in this modelling are oriented c-axis parallel to the sample surface, with terminations indicating that they were not broken during or after eruption. All analyses are indistinguishable from microphenocryst cores and show no evidence of re-equilibration with a volatile-saturated melt.

thermodynamic crystallisation models (Chapter 4; Candela, 1986; Fig. 5.2), even within 16 μm of the crystal rims (Fig. 5.5). I use diffusion constraints (Brenan, 1993) to estimate the maximum time between volatile saturation and eruption. At 800 °C and 1 GPa, the characteristic timescale for halogen diffusion over $\sim 16 \mu\text{m}$ is ~ 10 days. At 1 atm this time would be ~ 3 yr. This suggests that the maximum time delay between volatile saturation and eruption in Astroni 1 was of the order of $10\text{--}10^3$ days. Hence, the magma chamber remained persistently H_2O -undersaturated until only shortly before eruption. Similarly, the lack of evidence for syn-eruptive volatile loss from apatite microphenocrysts is due to the diffusive re-equilibration time exceeding realistic eruptive timescales.

5.3.3. Pre-eruptive volatile undersaturation at Campi Flegrei

In combination, analysis of apatites and melt inclusions offers great potential as a forensic petrological tool, providing new information about the temporal evolution of pre-eruptive volatile contents in volcanic systems. Using this method, I have demonstrated that the Astroni 1 magma chamber remained H_2O -undersaturated until shortly before eruption. This interpretation is consistent with thermodynamic modelling of magma evolution (Fig. 5.4), and with interpretations of ongoing patterns of degassing and deformation in Campi Flegrei, which can be explained by local volatile saturation at the roof of a largely H_2O -undersaturated magma chamber (Bodnar *et al.*, 2007). I observe a measurable decrease in apatite $X_{\text{Halogen}}/X_{\text{OH}}$ between biotite-hosted inclusions and microphenocrysts, indicating continued crystallisation and an increase in melt H_2O concentration after *biotite-in*. Because H_2O saturation is predicted at temperatures only slightly lower than *biotite-in* (Fig. 5.4), but microphenocrysts have not re-equilibrated with a volatile-saturated melt, I suggest that the melt became H_2O -saturated just before eruption. In Astroni 1, only a small amount of additional crystallisation is required to significantly increase the

abundance of the aqueous vapour phase (Fig. 5.4), generating overpressures that would exceed the fracture criterion, inducing eruption (Fig. 5.6; Tait *et al.*, 1989). I cannot discount the possibility that the pre-eruptive melt remained H₂O-undersaturated, and eruption was initiated by an external trigger; however, in the absence of any evidence for an external trigger, I suggest that progressive concentration of dissolved H₂O in the silicate melt triggered eruption after saturation was eventually achieved.

Because H₂O concentrations increase during crystallisation, I infer that fresh batches of mafic melt arriving from depth would probably be more volatile-undersaturated than the evolved melts within an upper crustal reservoir. Although Astroni 1 shows no evidence of pre-eruptive magma mixing (Smith *et al.*, 2011; Tonarini *et al.*, 2009), mingling is reported in other Campi Flegrei eruptions, including later eruptions from the Astroni vent (Isaia *et al.*, 2004; Smith *et al.*, 2011; Tonarini *et al.*, 2009). The solubility of H₂O in phonolite is not significantly affected by temperature (Schmidt and Behrens, 2008), so pre-eruptive magma replenishment and mixing would ‘dilute’ the dissolved volatile content of the silicate melt, returning the system to a more undersaturated state. In this case, I expect the repose period between eruptions to reflect the balance between timescales of magma storage and crystallisation (driving the system towards volatile saturation), and the recharge rate (driving it away). Volatile-undersaturated recharge would require greater crustal deformation than volatile-saturated mixing to accommodate new melt without exceeding the fracture criterion (Blake, 1981). Such deformation may be responsible for observed large-scale inter-eruptive bradyseismicity at Campi Flegrei (Chiodini *et al.*, 2015; Guidoboni and Ciuccarelli, 2011), with recharge events inducing significant magma chamber dilation during repose periods.

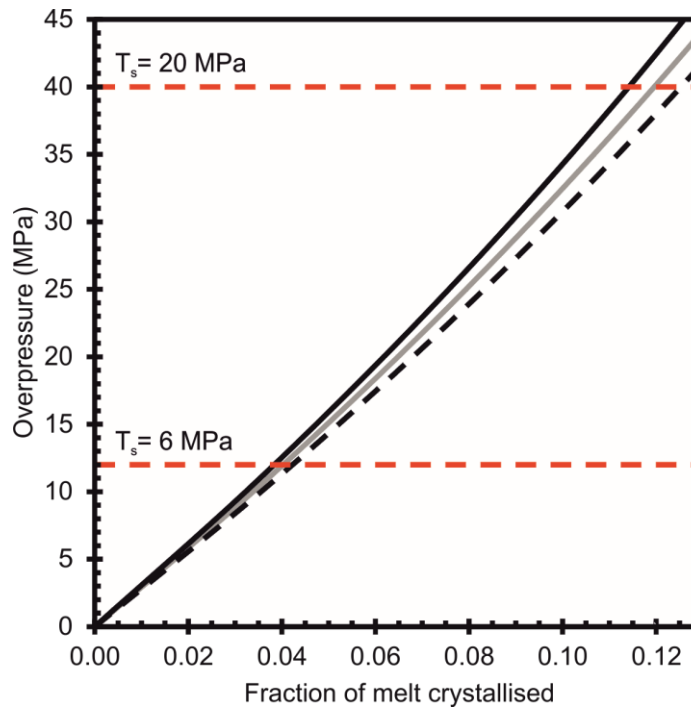


Figure 5.6 | The pressure history of the Astroni 1 magma chamber following volatile saturation. Calculated using the model of Tait *et al.* (1989). In this model, the initial pressure is taken as 170 MPa, equating to a magma chamber depth of ~7 km (Zollo *et al.*, 2008; see Section 5.2.3. for details). The melt density is 2442 kgm^{-3} , calculated using the method of Lange and Carmichael (1990) and the bulk modulus of the phonolitic melt is 10.95 GPa, calculated using the equation of Seifert *et al.* (2013). The rigidity of the crust surrounding the Astroni 1 magma chamber is 5 GPa, as in Woo and Kilburn (2010). As Campi Flegrei melts contain very low CO_2 concentrations, I assume that there was no initial gas present in the magma chamber. I also assume that the effect of crystallisation contraction was negligible, given that feldspar is the dominant crystallising phase at the time of H_2O saturation and this has a similar density to the phonolitic melt (Fig. 5.4). Phonolite H_2O solubility laws were obtained by regressing experimental solubility data for a natural Montaña Blanca phonolite at 800-900°C (Carroll and Blank, 1997; dashed black line) and synthetic phonolitic melts, based on compositions from Montaña Blanca (solid black line) and Laacher See (solid grey line) at 845-900°C (Schmidt and Behrens, 2008). The phonolite solubility laws are sufficiently similar that there is little effect on the model output. The magma chamber will fracture, permitting melt to ascend, when the overpressure generated by H_2O exsolution exceeds twice the tensile strength (T_s) of the surrounding rock (red dashed lines; Tait *et al.*, 1989). For crustal rocks, T_s is typically <6 MPa (Trasatti *et al.*, 2005). However, in a volcanic edifice, such as Campi Flegrei T_s may be as high as ~20 MPa (Gottsmann *et al.*, 2006). The model therefore predicts that the fracture criterion will be achieved with 4-13% additional crystallisation, after H_2O saturation. On the basis of my Rhyolite-MELTS modelling (Fig. 5.4), this equates to only ~15-45°C additional cooling.

5.3.4. Volcanological implications

My data show that the sub-volcanic feeding systems for explosive eruptions can remain volatile-undersaturated until late in their evolution. This implies that the depths of magma stalling and storage are not controlled by changes in melt rheology resulting from degassing-induced crystallisation (Annen *et al.*, 2006), but may instead reflect local crustal discontinuities in density or rigidity (Chaussard and Amelung, 2014). Furthermore, melt inclusion H_2O – CO_2 data give only a minimum estimate of crystallisation pressures.

The potential for persistent magmatic volatile undersaturation has significant implications for the monitoring of restless volcanoes. Although magma chamber assembly can occur on decadal timescales (Druitt *et al.*, 2012), there is a growing number of examples where deformation pulses are not immediately followed by eruption; and others, including the only historic eruption of Campi Flegrei (Guidoboni and Ciuccarelli, 2011), where explosive eruptions begin with little or no early geodetic ‘warning’ (Biggs *et al.*, 2014; Parks *et al.*, 2012). This suggests that the final pre-eruptive ‘priming’ of the system may occur on timescales far shorter than timescales of assembly; perhaps as short as days to months. Because ground-deformation and seismic evidence for unrest may accompany the long-term processes of subterranean magma recharge and chamber assembly, and not simply pre-eruptive activity, this poses a challenge for agencies engaged in volcano monitoring. This is not a ubiquitous triggering mechanism. However, in persistently volatile-undersaturated systems, the onset of volatile saturation might provide some pre-eruptive chemical indicators, such as accompanying the leakage of magmatic volatiles into the surrounding edifice, or hydrothermal system, and an increased magmatic component in fumarolic gases at the surface. Successful monitoring of these

systems will demand high temporal resolution chemical and isotopic analysis of fluid and gas emissions (Chiodini *et al.*, 2015).

5.4. Supplementary discussion

5.4.1. Samples

A representative bulk sample was taken from all levels of the Astroni 1 pyroclastic deposit at Contrada Romano, Naples (sample CF69; Smith *et al.*, 2011). The deposit was ash-rich, with some pumiceous lapilli beds. After sampling, lapilli-sized material was crushed and sieved to a <500 μm size fraction and efficiently mixed with the ash, to avoid any bias in crystal separation. Astroni 1 samples have up to 12 vol.% crystals, with a phase assemblage of K-feldspar + plagioclase + clinopyroxene + biotite + apatite + magnetite + fluorite. A detailed petrographic description of erupted products from the Astroni volcano is given by Isaia *et al.* (2004).

5.4.2. Rhyolite-MELTS fractionation modelling

Thermodynamic fractionation models were run across a reasonable range of storage conditions to investigate the theoretical evolution of the magmatic system and to identify whether the empirically determined volatile evolution can be reconciled with theoretical models.

Isobaric fractional crystallisation models were run using Rhyolite-MELTS (Gualda *et al.*, 2012) to constrain the conditions of magma storage. Only phases observed in natural Campi Flegrei samples were permitted to precipitate in the models (i.e. olivine $\pm$ clinopyroxene $\pm$ rhombohedral oxides $\pm$ apatite $\pm$ feldspar $\pm$ biotite $\pm$ leucite). Due to a paucity of experimental data, Rhyolite-MELTS currently incorporates a single-component H_2O solubility model (Ghiorso and Sack, 1995; Gualda and Ghiorso, 2014; Gualda *et al.*,

2012) that experimental evidence suggests is not appropriate for alkali systems (Iacovino *et al.*, 2013; Ni and Keppler, 2013; Papale *et al.*, 2006; Vetere *et al.*, 2011). I therefore repressed any potential fluid phase in my models and instead used appropriate experimental studies (Carroll and Blank, 1997; Webster *et al.*, 2014) retrospectively to interpret volatile saturation conditions. This allowed comparison between the dissolved H₂O concentrations predicted by Rhyolite-MELTS and a range of different H₂O solubility models. The red lines in Figure 5.4 show phonolite H₂O solubility at 910-944 °C, 200 MPa (dashed line; Webster *et al.*, 2014), and at 870 °C, 150 MPa (dotted line; Carroll and Blank, 1997). Phonolite H₂O solubility is almost invariant with temperature (Schmidt and Behrens, 2008). Given the low CO₂-contents of Astroni 1 melt inclusions (Appendix 3), my results are compared with low-CO₂ or CO₂-free solubility experiments. In CO₂-rich systems, H₂O saturation would occur at higher pressures or with less crystallisation. Permitting vapour saturation in the Rhyolite-MELTS models makes no difference to the liquid line of descent before vapour saturation. For non-volatile elements, the main consequence of vapour saturation is a change in the behaviour of TiO₂, due to a predicted increase in magnetite compatibility, and a minor change in liquid Na₂O and CaO evolution, due to a variation in feldspar compositions and a small change in the modal abundance of apatite. Despite the limited applicability of Rhyolite-MELTS in alkali systems, when a vapour phase is permitted, models predict low-temperature H₂O saturation, within ~180 °C of that predicted through comparison with phonolite solubility experiments.

I used the most mafic olivine-hosted melt inclusion reported in the Campi Flegrei system from the last 15 ka as the starting composition for my Rhyolite-MELTS models (inclusion Mi1-C1-o5-M1 of Cannatelli *et al.*, 2007), as distinguished by its high MgO and low incompatible element concentrations. This is an approximation for the primitive

melt composition feeding the Campi Flegrei system as major and trace element trends between different eruptions can be related by fractional crystallisation of a single parental magma (Civetta *et al.*, 1991; Pappalardo *et al.*, 2002)

Previous modelling has shown that it is not possible to reproduce the phase assemblages or compositional trends in minerals and melt inclusions from Campi Flegrei eruptions with L_{H_2O} outside the range 2-3 wt% (Bohrson *et al.*, 2006; Cannatelli, 2012; Fowler *et al.*, 2007). Similarly, oxygen fugacity is constrained to $\sim QFM + 1$ in order to reconcile natural and modelled phase equilibria and compositional trends (Bohrson *et al.*, 2006; Cannatelli, 2012; Fowler *et al.*, 2007). However, varying fO_2 within the range $QFM + 1 < fO_2 < NNO + 1.5$ has no effect on liquid MgO or H_2O concentrations.

Following previous studies (Bohrson *et al.*, 2006; Cannatelli, 2012; Fowler *et al.*, 2007), I ran my models over the pressure range 50-300 MPa, to account for the possible range of Campi Flegrei magma storage depths. This includes the pressure (170-180 MPa) estimated for the current melt storage zone at Campi Flegrei, which is believed to be at ~ 7 km, based on geophysical observations (De Siena *et al.*, 2010; Zollo *et al.*, 2008).

5.4.3. Apatite *PT* compositional model

Apatite-melt exchange coefficients (K ; defined in equation 5.1) are pressure and temperature dependent. A null hypothesis is that observed compositional variations between texturally constrained apatite populations reflect changes in these intensive parameters. To model the apatite compositional evolution that would be predicted to occur through cooling or decompression, I followed the approach outlined in Piccoli and Candela (2002), whereby the equations of Piccoli and Candela (1994) are used to calculate changes in apatite-aqueous phase exchange coefficients under different *PT*

conditions, assuming all F in the fluid exists as HF and all Cl exists as HCl. Rearranging the equations of Piccoli and Candela (1994):

$$\frac{X_{\text{Cl}}^{\text{Ap}}}{X_{\text{OH}}^{\text{Ap}}} = \frac{f_{\text{HCl}}^{\text{aq}}}{f_{\text{H}_2\text{O}}^{\text{aq}}} \cdot 10^{[0.04661 + \frac{2535.8}{T} - \frac{0.0303(P-1)}{T}]} \quad (\text{eq. 5.2})$$

$$\frac{X_{\text{F}}^{\text{Ap}}}{X_{\text{OH}}^{\text{Ap}}} = \frac{f_{\text{HF}}^{\text{aq}}}{f_{\text{H}_2\text{O}}^{\text{aq}}} \cdot 10^{[0.18219 + \frac{5301.1}{T} - \frac{0.00360(P-1)}{T}]} \quad (\text{eq. 5.3})$$

where $f_{\text{H}_2\text{O}}^{\text{aq}}$, $f_{\text{HCl}}^{\text{aq}}$ and $f_{\text{HF}}^{\text{aq}}$ are the fugacities of H_2O , HCl and HF components in the aqueous phase respectively and X_{F}^{Ap} , $X_{\text{Cl}}^{\text{Ap}}$ and $X_{\text{OH}}^{\text{Ap}}$ are the mole fractions of fluorapatite, chlorapatite and hydroxyapatite components in the apatite phase. T is temperature in Kelvin and P is pressure in bars. The constants in these equations were calibrated from experimentally determined thermodynamic data (Robie *et al.*, 1978; Stull and Prophet, 1971; Zhu and Sverjensky, 1992). Unfortunately, a lack of available experimental data currently precludes a similar calculation of exchange coefficients between apatite and silicate melt. Instead, I used these calculations to provide a reference frame to outline the effects of physical processes such as cooling and decompression on apatite compositions in $X_{\text{Halogen}}/X_{\text{OH}}$ space; the modelled results are not quantitatively robust.

To generate the set of curves shown in Figure 5.2a I used $\frac{f_{\text{HCl}}^{\text{aq}}}{f_{\text{H}_2\text{O}}^{\text{aq}}}$ and $\frac{f_{\text{HF}}^{\text{aq}}}{f_{\text{H}_2\text{O}}^{\text{aq}}}$ of 0.0001 and 0.006, respectively. Equations 5.2 and 5.3 were then solved simultaneously for temperatures decreasing from 1200 °C to 700 °C at pressures of 50, 100 and 300 MPa and for pressures decreasing from 1000 MPa to 0 MPa at temperatures of 800, 1000 and 1200 °C.

5.4.4. Modelling apatite compositional variability during magmatic evolution

As outlined in Chapter 4, I calculated the compositional evolution of apatite as a function of magmatic fractionation, following a similar approach to that of Candela (1986), in which F, Cl and H₂O were considered perfectly incompatible. In Astroni 1, when apatite is a liquidus phase, F and Cl must be more compatible than H₂O. Using exchange coefficients calculated by means of the method outlined by Candela (1986) and adapting the model to account for the differences in the relative compatibilities of volatile species during volatile-undersaturated apatite and biotite crystallisation predicts decreasing $X_{\text{Halogen}}/X_{\text{OH}}$ ratios, in agreement with observations from Astroni 1 (inset Fig. 5.2). The models in this chapter use bulk crystal-melt partition coefficients ($\bar{D}_i^{c/m}$) of $\bar{D}_F^{c/m} = 0.8$, $\bar{D}_{\text{Cl}}^{c/m} = 0.7$, $\bar{D}_{\text{H}_2\text{O}}^{c/m} = 0.001$ during biotite-absent apatite crystallisation and $\bar{D}_F^{c/m} = 0.85$, $\bar{D}_{\text{Cl}}^{c/m} = 0.8$, $\bar{D}_{\text{H}_2\text{O}}^{c/m} = 0.01$ after *biotite-in*, on the basis of measured Campi Flegrei biotite compositions (Appendix 2; Fabbrizio *et al.*, 2009).

Once vapour saturation is achieved, H₂O is buffered in the melt and remains constant during subsequent isobaric crystallisation; F is concentrated in the melt; and Cl may either become concentrated in the melt or depleted as it partitions into the vapour phase (Section 4.4; Candela, 1986). The vapour-saturated models in this chapter use a water solubility ($C_{\text{H}_2\text{O}}^s$) of 7.5 wt% (Webster *et al.*, 2014), a vapour-melt F partition coefficient ($D_F^{v/m}$) of 0.7 (Borodulin *et al.*, 2009) and a vapour-melt Cl partition coefficient ($D_{\text{Cl}}^{v/m}$) of 9 (Signorelli and Carroll, 2000), which were determined experimentally for evolved alkaline systems at 100-200 MPa and 650-850 °C.

Chapter 6

Inter-eruption variability in magmatic volatile contents at Campi Flegrei

A version of this chapter is in preparation for publication as:

Stock M.J., Humphreys M.C.S., Smith V.C., Pyle D.M. and Isaia R., in prep. The volatile history of past eruptions at Campi Flegrei (Italy): Evidence from hydrous minerals and glass. *Journal of Petrology*.

6.1. Introduction

Long-lived volcanic systems display spatial and temporal variability in magma compositions, reflecting changes in the mechanisms of mantle melt generation (i.e. petrogenesis; Ballmer *et al.*, 2011; Bryant *et al.*, 1999; Crisci *et al.*, 1991; Hildreth and Moorbath, 1988; Plank and Langmuir, 1993; Straub *et al.*, 2015; Straub and Zellmer, 2012) and/or in crustal processes (Gamble *et al.*, 1999; Hawkesworth *et al.*, 2004; Raia *et al.*, 2000; Smith *et al.*, 2005). These trends in space and time are typically identified through stratigraphically-constrained major element, trace element and isotopic analysis of minerals and glasses (e.g. Clocchiatti *et al.*, 2004; Devine *et al.*, 1998; Peate *et al.*, 2008; Smith *et al.*, 2005; Tepley *et al.*, 2000). In many cases, progressive changes in pre-

eruptive processes or the compositions of primitive melts feeding a volcanic system correlate with the composition, style, timing or spatial distribution of eruptive activity at the Earth's surface (e.g. Ballmer *et al.*, 2011; Gamble *et al.*, 1999; Gertisser and Keller, 2003; Straub *et al.*, 2015). Understanding the temporal development of magmatic and mantle processes is therefore essential for determining the current state of a volcanic system and the nature of any future volcanic hazards.

Phenocryst-hosted melt inclusions in erupted products may record systematic variability in pre-eruptive magma volatile concentrations, during the long-term development of a volcanic system, or at different eruptive centres within a single volcanic district (Wallace, 2005). These spatial and temporal trends in magmatic volatile budgets have been interpreted as resulting from changes in crustal storage depths (Bégué *et al.*, 2015) or the volatile contents of primitive melts entering the crust (Cervantes and Wallace, 2003; Portnyagin *et al.*, 2007; Wallace, 2005). Primitive melt H₂O contents have been proposed as a primary control on erupted magma compositions (Kinzler *et al.*, 2000; Zimmer *et al.*, 2010). Furthermore, in some cases, variability in pre-eruptive magmatic volatile contents has been linked with changes in the style of volcanic activity at the Earth's surface (e.g. Raia *et al.*, 2000; Roggensack *et al.*, 1997).

However, constraining the nature of the magmatic fluid phase and the concentrations of volatile elements dissolved within silicate melts remains a challenge. Despite our ability to identify subtle spatiotemporal changes in mantle and crustal processes (Ballmer *et al.*, 2011; Gamble *et al.*, 1999; Gertisser and Keller, 2003; Gómez-Tuena *et al.*, 2003; Nakada and Kamata, 1991; Smith *et al.*, 2005; Straub *et al.*, 2015), the impact of these on pre-eruptive volatile concentrations remains largely unconstrained. Magmas depressurise on ascent, becoming H₂O-saturated and degassing as the solubility of H₂O falls (Collins *et al.*, 2009; Newman and Lowenstern, 2002). Hence, petrologic

volatile records (e.g. melt inclusions; Chapter 1) trapped during magma ascent may only preserve a history of syn-eruptive processes (e.g. Collins *et al.*, 2009; Métrich *et al.*, 2004; Wade *et al.*, 2006), and only records trapped prior to volatile saturation stand any chance of preserving an unmodified account of primitive or pre-eruptive magmatic volatile concentrations or fluid phase systematics. Additionally, due to the short timescales of H diffusion in common mineral phases under magmatic conditions (Gaetani *et al.*, 2012; Ingrin and Blanchard, 2006; Ingrin *et al.*, 1995; Portnyagin *et al.*, 2008; Woods *et al.*, 2000), melt inclusions may rehomogenise after entrapment, overwriting any previous volatile record with a late-stage or syn-eruptive signature (e.g. Plank *et al.*, 2013; Zellmer *et al.*, 2015). In Chapter 5, syn-eruptive rehomogenisation was identified as the cause of disparity between apatite and melt inclusion volatile records; apatite inclusions preserve a temporal record of pre-eruptive volatile-undersaturated crystallisation, whereas melt inclusions have approximately constant H₂O concentrations that do not correlate with a fractionation index (i.e. MgO), which implies that they were reset during ascent.

This chapter draws together different components of my thesis, using the techniques of apatite analysis established in Chapter 3 and the thermodynamic framework developed in Chapter 4, to investigate magmatic volatile systematics in multiple eruptions in the past 15 kyr of activity at the Campi Flegrei caldera. The approach of coupled apatite and glass analysis developed in Chapter 5 avoids the common problem of syn-eruptive melt inclusion H₂O rehomogenisation, and gives an alternative means to assess pre-eruptive volatile contents. Applying this method to multiple eruptions has two objectives: first, to identify variability in the timing of volatile saturation and composition of magmatic fluids prior to eruption. This will determine whether the late-stage volatile saturation identified in Astroni 1 (Chapter 5) is a general process at Campi Flegrei, or whether melts more typically saturate in volatiles early in crystallisation, as is frequently

inferred from melt inclusion evidence (e.g. Arienzo *et al.*, 2016; Mangiacapra *et al.*, 2008). Second, this chapter aims to establish whether there is any systematic spatiotemporal variability in the pre-eruptive volatile budgets of Campi Flegrei eruptions, and whether they correlate with the style of volcanic activity. These objectives will improve our fundamental understanding of magmatic processes at Campi Flegrei and help to advance monitoring of this hazardous system.

6.1.1. Spatial and temporal evolution of the Campi Flegrei system

Previous studies have identified spatial and temporal variability in the major element, trace element and isotopic compositions of erupted material at Campi Flegrei, through matrix glass, melt inclusion and bulk rock analysis. This work is summarised below to provide a framework for interpretation of pre-eruptive volatile contents from apatite and glass analyses in this chapter.

The most mafic magmas identified at Campi Flegrei are shoshonitic-trachybasaltic in composition, and are assumed to be representative of the mantle melts feeding the system (Cannatelli *et al.*, 2007; Mangiacapra *et al.*, 2008; Vetere *et al.*, 2011; Webster *et al.*, 2003). Existing major and trace element studies of Campi Flegrei glasses show an evolutionary trend extending from these mafic compositions to evolved trachytes-phonolites (Civetta *et al.*, 1991; D'Antonio *et al.*, 2007; Pappalardo *et al.*, 2002; Smith *et al.*, 2011). This is consistent with fractional crystallisation dominantly controlling the composition of erupted products (D'Antonio *et al.*, 1999b; Pappalardo *et al.*, 2002; Section 6.4.1.), punctuated by periodic recharge events (D'Antonio *et al.*, 1999b; Di Renzo *et al.*, 2011; Smith *et al.*, 2011). Modelling shows that the entire compositional diversity at Campi Flegrei can be achieved through variable degrees of fractionation of a single shoshonitic parental magma (Civetta *et al.*, 1991; Villemant, 1988). Samples

erupted in the past 15 kyr show a larger compositional range than those preceding the Neapolitan Yellow Tuff (NYT) eruption, which cover only the evolved end of the compositional spectrum (Pappalardo *et al.*, 2002). In the past 15 kyr, Smith *et al.* (2011) show that the most primitive matrix glasses were erupted in Epoch 1, immediately following the NYT event. Epoch 2 and Epoch 3 glasses are generally more evolved, with indistinguishable major element compositions. Matrix glasses from the post-Epoch 3, 1538 AD Monte Nuovo event are unlike previous eruptions, with anomalously high Na_2O concentrations (Fig. 6.1.; Smith *et al.*, 2011).

The isotopic evolution of Campi Flegrei is more complex and requires processes beyond fractional crystallisation to account for the compositional diversity (D'Antonio *et al.*, 1999b; Di Renzo *et al.*, 2011; Pappalardo *et al.*, 2002). On the basis of combined Sr-Nd-Pb-B isotopic evidence, Campi Flegrei melts can be broadly divided into two groups, temporally divided by the Campanian Ignimbrite (CI) eruption (at 39 kyr; D'Antonio *et*

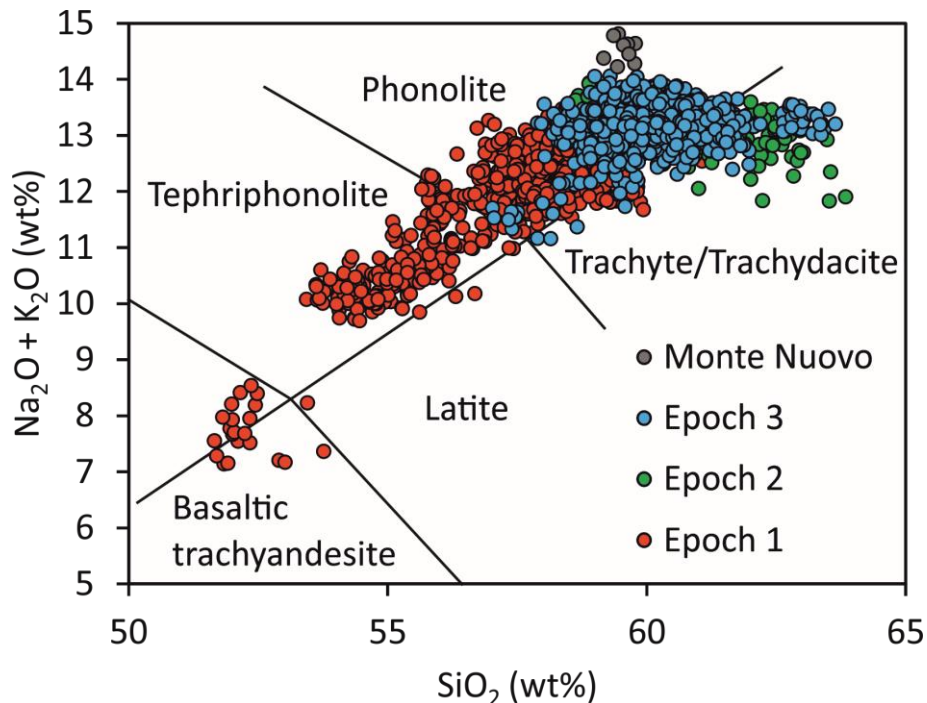


Figure 6.1 | Total alkalis - silica diagram with matrix glass compositions of Campi Flegrei eruptions in the past 15 kyr, adapted from Smith *et al.* (2011). Data are distinguished on the basis of the epoch in which they were erupted (see legend).

al., 2007). Pre-CI primitive melts are characterised by a dominantly mid-ocean ridge basalt (MORB)-type asthenospheric mantle wedge signature, variably contaminated by subducted sediment and slab-derived fluids (D'Antonio *et al.*, 2007; Tonarini *et al.*, 2004). Post-CI melts are affected by country rock assimilation (Di Renzo *et al.*, 2011; Pappalardo *et al.*, 2002) but the degree of assimilation must be small (only 1-2%), both to explain the isotopic range (D'Antonio *et al.*, 2007; Tonarini *et al.*, 2009) and the unaffected major and trace element fraction trends (D'Antonio *et al.*, 2007; Fowler *et al.*, 2007).

Boron isotopes in magmas are not affected by crustal contamination, instead reflecting mantle heterogeneity (D'Antonio *et al.*, 2007; Tonarini *et al.*, 2009). At Campi Flegrei, $\delta^{11}\text{B}$ enrichment may reflect a more metasomatised mantle source caused by a higher slab-derived fluid input to the sub-volcanic asthenosphere (D'Antonio *et al.*, 2007) and/or a lower subducted sediment input to the mantle wedge (Di Renzo *et al.*, 2011; Tonarini *et al.*, 2004). Strontium, Nd and Pb isotopes track the degree of magma contamination by continental crust, with low $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ and high $^{87}\text{Sr}/^{86}\text{Sr}$ reflecting greater crustal interaction (D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2011).

The isotopic diversity of Campi Flegrei melts in the past 15 kyr reflects variable mixing between at least three distinct end-member components (D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2011; Tonarini *et al.*, 2004). Di Renzo *et al.* (2011) suggest that the prevalence of these end-members correlates with the periods of volcanic activity: Epoch 1 and Epoch 2 are characterised by mixing between an 'NYT end-member' ($^{87}\text{Sr}/^{86}\text{Sr}$: 0.70750–0.70753, $^{143}\text{Nd}/^{144}\text{Nd}$: 0.51246, $^{206}\text{Pb}/^{204}\text{Pb}$: 19.04, $\delta^{11}\text{B}$: –7.9‰) and 'Minopoli 2 end-member' ($^{87}\text{Sr}/^{86}\text{Sr}$: ~0.70860, $^{143}\text{Nd}/^{144}\text{Nd}$: ~0.51236, $^{206}\text{Pb}/^{204}\text{Pb}$: ~18.90, $\delta^{11}\text{B}$: –7.32‰), whereas Epoch 3 involves mixing between the 'NYT end-member' and 'Astroni

6 end-member' ($^{87}\text{Sr}/^{86}\text{Sr}$: ~ 0.70726 , $^{143}\text{Nd}/^{144}\text{Nd}$: ~ 0.51250 , $^{206}\text{Pb}/^{204}\text{Pb}$: ~ 19.08 , $\delta^{11}\text{B}$: -9.8‰). Post-Epoch 3 Monte Nuovo melts show the same mixing trend as Epoch 3, but are near 'Astroni 6 end-member' compositions (Di Renzo *et al.*, 2011). The isotopic signatures of Epochs 1 and 2 reflect greater crustal contamination, plus a high slab derived fluid and/or low subducted sediment input to the mantle wedge (i.e. the 'Minopoli 2 end-member' signature; D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2011; Tonarini *et al.*, 2004). Conversely, Epoch 3 and Monte Nuovo isotopic signatures exhibit less crustal interaction, plus a reduced slab derived fluid and/or high subducted sediment input to the asthenosphere (i.e. the 'Astroni 6 end-member' signature; D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2011; Tonarini *et al.*, 2004).

There has been a corresponding variation in the spatial distribution of Campi Flegrei volcanism in the past 15 kyr (Fig. 6.2.; Orsi *et al.*, 1996): with the exception of the La Pietra and Rione Terra events (Di Vito *et al.*, 1999), Epoch 1 eruptions generally exploited faults along the rim of the NYT caldera (D'Antonio *et al.*, 1999b; Di Vito *et al.*, 1999; Smith *et al.*, 2011). Following Epoch 1, vent locations generally became more centralised within the NYT caldera depression (Smith *et al.*, 2011). Epoch 2 eruptions predominantly occurred in the eastern sector of the caldera, with the exception of Fondi di Baia, which is located on the western caldera boundary (D'Antonio *et al.*, 1999b; Di Renzo *et al.*, 2011; Smith *et al.*, 2011). Epoch 3 vents are generally aligned along faults associated with the northeastern end of the La Starza block (D'Antonio *et al.*, 1999b; Di Renzo *et al.*, 2011), which formed due to bradyseismic uplift during volcanic resurgence within the NYT caldera (Orsi *et al.*, 1996). The only Epoch 3 eruptions from the western side of the caldera were from the Averno vent (Averno 1 and Averno 2; D'Antonio *et al.*, 1999b; Di Renzo *et al.*, 2011). The post-Epoch 3 Monte Nuovo vent is also located in the

western sector of the NYT caldera (D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2011; Orsi *et al.*, 1996; Smith *et al.*, 2011).

To date, there have been no systematic studies of spatiotemporal variability in magmatic volatile contents at Campi Flegrei, either in primitive melts feeding the system or on short pre-eruptive timescales. However, attempts have been made to constrain primitive melt volatile concentrations for individual eruptions. Based on olivine-hosted melt inclusions from the Minopoli 2 eruption, Mangiacapra *et al.* (2008) suggested that magmas feeding the Campi Flegrei system were CO₂-rich (<1100 ppm). However,

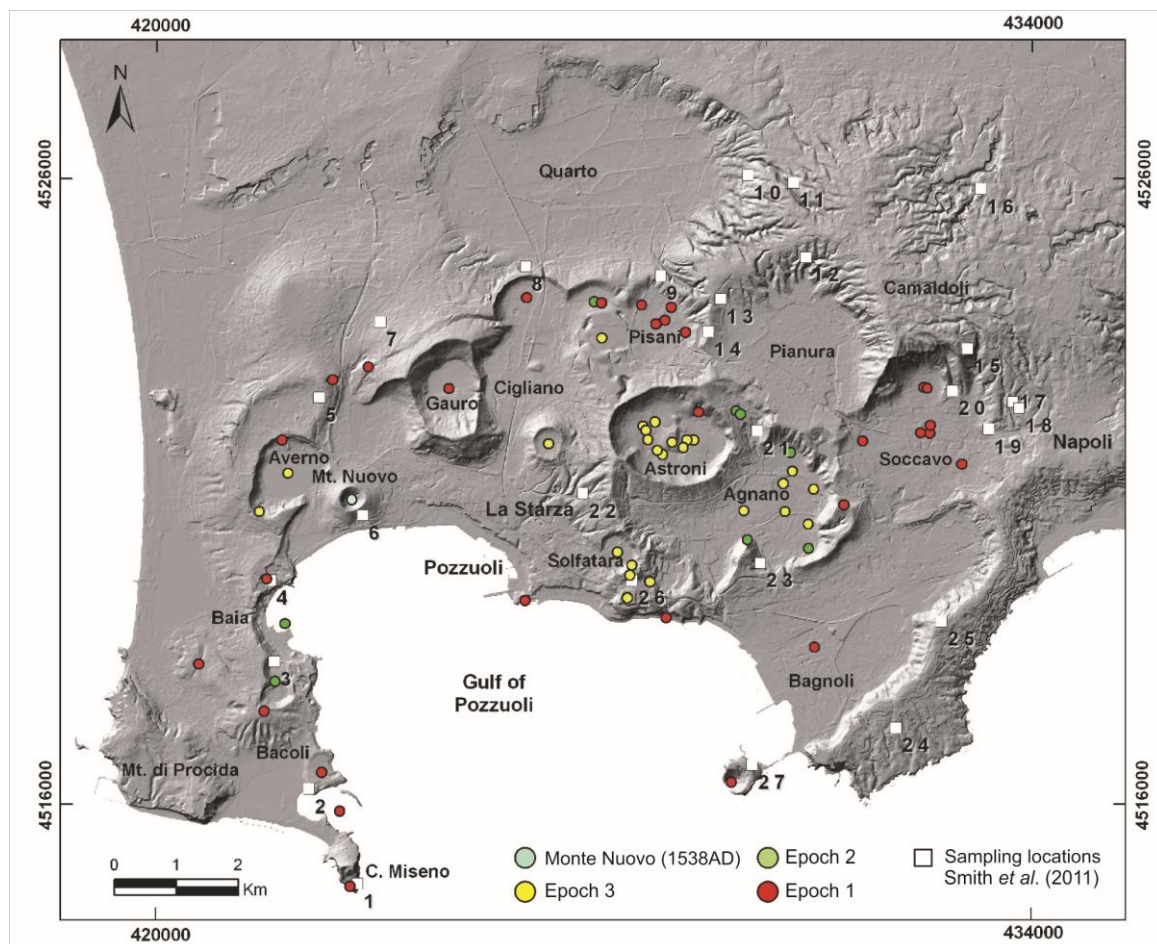


Figure 6.2 | Shaded relief map of Campi Flegrei, showing vent locations of the eruptions in the past 15 kyr (Smith *et al.*, 2011). The location of the La Sarza block is taken from (Di Renzo *et al.*, 2011). Vent locations are distinguished on the basis of the epoch in which they were active (see legend).

following re-processing of their data, the inferred CO₂-contents of these inclusions were revised down (Vetere *et al.*, 2011), bringing them into line with the low CO₂ concentrations (typically <250 ppm) measured in more evolved melt inclusions from other eruptions (Arienzo *et al.*, 2010; Marianelli *et al.*, 2006; Appendix 3). The concentrations of H₂O and CO₂ in these melt inclusions either imply very shallow primitive melt crystallisation depths under volatile-saturated conditions (<1.5 km; Vetere *et al.*, 2011), volatile-undersaturated melt inclusion entrapment, or volatile re-equilibration at low pressures.

6.1.2. Eruptions studied

The eruptions investigated in this study were chosen to cover the range of melt compositions and eruptive styles produced at Campi Flegrei in the past 15 kyr (Table 6.1.). They include: Minopoli 1, Pomici Principali (PP) and Pisani 1 from Epoch 1; Fondi di Baia from Epoch 2; Mt Olibano, Accademia and Astroni 1 from Epoch 3; and the post-Epoch 3 Monte Nuovo eruption (Fig. 1.4; see Smith *et al.*, 2011 for full stratigraphy). With the exception of Monte Nuovo, these eruptions show no evidence of pre-eruptive magma mingling (Smith *et al.*, 2011), thus permitting investigation of processes during magmatic evolution, without complications arising from late-stage alteration of magma compositions or xenocryst incorporation.

The ages, compositions and volumes of material expelled in the studied eruptions are summarised in Table 6.1. Minopoli 1 was an explosive, mafic eruption that produced only <0.1 km³ of material (dense rock equivalent [DRE]; Smith *et al.*, 2011) at 10.3-11.5 kyr (Cannatelli *et al.*, 2007). Pomici Principali is the largest Plinian eruption in Epoch 1 (Di Vito *et al.*, 1999) and erupted 0.85 km³ DRE of material at 11.9-12.1 kyr (Smith *et al.*, 2011). Pisani 1 was a slightly larger explosive mafic eruption than Minopoli 1, and

produced 0.1-0.3 km³ DRE of material towards the end of Epoch 1 (Smith *et al.*, 2011). Fondi di Baia was the first eruption of Epoch 2, at 9.6-9.1 kyr (Pompilio *et al.*, 2015). It was highly evolved and explosively erupted only 0.04 km³ DRE of material (Smith *et al.*, 2011). Mt Olibano was a latitic eruption that formed an effusive lava dome in the central Campi Flegrei caldera at 3.9 kyr (Isaia *et al.*, 2009; Pappalardo and Mastrolorenzo, 2012). The Accademia eruption was also effusive and produced a more evolved, trachytic lava dome in the central caldera. This also occurred at ~3.9 kyr but is stratigraphically younger than Mt Olibano (Di Girolamo *et al.*, 1984; Isaia *et al.*, 2009; Melluso *et al.*, 2012). Astroni 1 was a medium-sized explosive event that erupted 0.06 km³ DRE of material at 4.1-4.3 kyr (Smith *et al.*, 2011). The most recent eruption from the volcanic centre was the historic Monte Nuovo eruption. It produced some of the most chemically evolved melts in the Campi Flegrei system but only erupted 0.03 km³ DRE of material (Smith *et al.*, 2011).

6.2. Samples

Many of the samples analysed in this chapter were collected by V.C. Smith and R. Isaia for another study (Smith *et al.*, 2011). However, two fieldtrips were undertaken in the Phlegrean Volcanic District (Campanian region, Italy), near Naples, in March 2013 and September 2014. The aim of these trips was: to observe the eruption deposits and their vents; to get an idea of the spatial distribution and scale of the volcanism at Campi Flegrei; to increase the sample volume from the eruption deposits selected for apatite separation; and to collect material from previously un-sampled units or eruptions (principally lava domes).

Eruptions analysed							
Epoch	Eruption	Sample number	Age (yr) [*]	Deposit type	Erupted volume (km ³) [*]	Average matrix glass composition	Vent location [*] UTM X UTM Y
Post-Epoch 3	Monte Nuovo	CF195	478	Pyroclastic flow deposit	0.03	Phonolite	423095 4520870
Epoch 3	Astroni 1	CF69	4153-4345	Ash fall with some lapilli layers	0.06	Phonolite	427999 4522122
	Accademia	CF163	4181-4509 ^a	Lava dome	<0.01	Trachyte ^e	427551 4519282
	Mt Olibano	CF200	4382-4509 ^b	Lava dome	<0.01	Latite ^f	427625 4519806
Epoch 2	Fondi di Baia	CF88	9525-9695	Pumice fall	0.04	Trachyte	421855 4517930
Epoch 1	Pisani 1	CF25	10516-12158 ^c	Scoria fall	0.1-0.3	Tephri-phonolite – trachy-andesite	428260 4523970
	Pomici Principali	CF69	11915-12158	Plinian fall (B3 unit)	0.85	Tephri-phonolite – phonolite	428698 4522284
	Minopoli 1	CF13	11915-12721 ^d	Scoria fall	<0.1	Phono-tephrite – tephri-phonolite	432400 4522670

Table 6.1 | (previous page) Summary of eruption deposits analysed in Chapter 6.

Note: Sample numbers correspond with those used in Smith *et al.* (2011).

* Data (including age constraints below) from Smith *et al.* (2011).

^a Eruption not dated precisely but is stratigraphically older than Solfatara eruption at 4181-4386 yr and younger than San Maria delle Grazie eruption at 4382-4509 yr.

^b Eruption not dated precisely but appears approximately contemporaneous with San Maria delle Grazie at 4382-4509 yr based on field constraints.

^c Eruption not dated precisely but is stratigraphically older than Pisani 3 eruption at 10516-10755 yr and younger than PP eruption at 11915-12158 yr.

^d Eruption not dated precisely but is stratigraphically older than PP eruption at 11915-12158 yr and younger than Archiaverno eruption at 12555-12721 yr.

^e Bulk rock composition from Melluso *et al.* (2012).

^f Bulk rock composition from Pappalardo and Mastrolorenzo (2012).

All samples were collected from proximal deposits within the CI caldera (see sampling locations in Fig. 1.4). Minopoli 1, PP, Pisani 1, Fondi di Baia and Astroni 1 samples are CF13, CF6, CF25, CF88 and CF69 of Smith *et al.* (2011), respectively. The Astroni 1 sample (i.e. CF69) is the same as that used in Chapter 5. The Monte Nuovo sample (CF195) is from the upper, light coloured pyroclastic flow unit (Unit II; Piochi *et al.*, 2005) and was collected outside of Oasis Monte Nuovo (X UTM: 423277, Y UTM: 4520614). Mt Olibano (CF200) and Accademia (CF163) samples were collected from the central caldera, at exposures near to the Solfatara crater.

Where exposure permitted, samples were collected vertically through the volcanoclastic units from each eruption and included both lapilli- and ash-sized material. The PP sample represents only the B3 Plinian phase of the eruption (Smith *et al.*, 2011) and the Fondi di Baia sample only comprises the basal units. There is no reported vertical chemical zonation in deposits from these eruptions (Smith *et al.*, 2011) and I therefore assume that these samples are representative of the bulk erupted material.

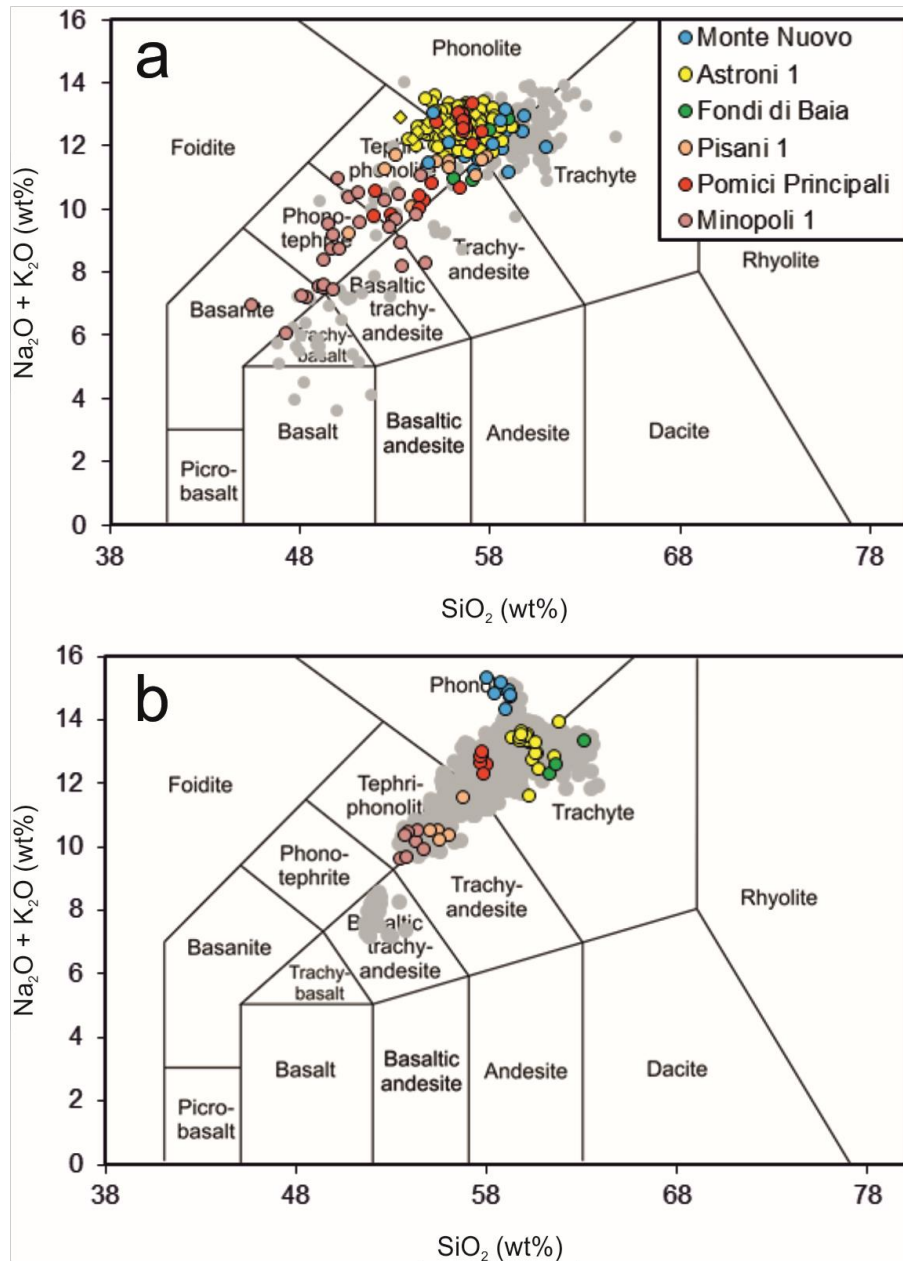


Figure 6.3 | Total alkalis - silica diagrams showing the classification of glasses from Campi Flegrei. **a**, Clinopyroxene- (circles) and biotite- (diamonds) hosted melt inclusion compositions, measured by EPMA. Biotite-hosted inclusions were measured in Astroni 1 only. **b**, Matrix glass compositions (EPMA data normalised to 100% for comparison with literature data). Data are distinguished by eruption (see legend). Grey points show a compilation of literature data: literature clinopyroxene- and olivine-hosted melt inclusion compositions in **a** are from Signorelli et al. (1999), Signorelli et al. (2001), Webster et al. (2003), Bohrsen et al. (2006), Marianelli et al. (2006), Cannatelli et al. (2007), Mangiacapra et al. (2008), Arienzo et al. (2010) and Fourmentraux et al. (2012); literature matrix glass compositions in **b** are from Smith *et al.* (2011).

All samples have the phase assemblage: K-feldspar + plagioclase + clinopyroxene + biotite + apatite + magnetite, with accessory fluorite $\pm$ sulphides $\pm$ sodalite $\pm$ leucite. Olivine is reported in mafic eruptions from Campi Flegrei, including Minopoli 1 (Cannatelli et al., 2007; D'Antonio et al., 1999b) but was not observed in this study. Crystal contents are typically <5-30% (from qualitative observations in this study and in Isaia *et al.*, 2004; Mastrolorenzo and Pappalardo, 2006; Piochi *et al.*, 2005) but are lower in the Fondi di Baia sample ($\ll$ 1%; Mastrolorenzo and Pappalardo, 2006). In Monte Nuovo, two pyroxene populations can be identified in hand specimen, one black and one green. These can be distinguished chemically by their FeO, MgO and TiO₂ contents (Smith et al., in prep). As apatite and melt inclusions show no systematic difference between these pyroxene populations they are not separated in the following discussion.

6.3. Results

In the following section, the compositions of clinopyroxene-hosted melt inclusions, clinopyroxene- and biotite-hosted apatite inclusions, apatite microphenocrysts and matrix glasses from the eight Campi Flegrei eruptions are reported. Data for Astroni 1, presented in Chapter 5, is also included with additional glass and apatite analyses obtained post-publication. I have collected a large dataset of melt inclusion analyses from these Campi Flegrei eruptions. Variations in the major and trace element compositions of melt inclusions and matrix glasses are summarised here, in order to contextualise the glass volatile data. Complete datasets of glass and apatite analyses collected in this study are given in Appendix 4 and Appendix 5, respectively.

Analytical methods are detailed in Chapter 2. Electron microprobe analysis (EPMA) was used to obtain apatite and glass (matrix and melt inclusion) data; the beam size (5-10 μ m) permits analysis of small inclusions. Secondary ion mass spectrometry (SIMS) was used to measure a subset of glasses and apatites for H₂O and halogens with

lower analytical uncertainties. Glass compositions could not be obtained from lava dome eruptions, due to melt inclusion devitrification and abundant groundmass microlites. Furthermore, biotites are partially (Mt Olibano) or fully (Accademia) broken down, and pyroxene phenocrysts are heavily fractured in lava eruptions. All apatite inclusions identified in these samples are either touching major cracks or are incompletely enclosed by their host phenocrysts. They are excluded from the following discussion, as they were not isolated from the melt prior to eruption. It was not possible to analyse melt inclusions from Fondi di Baia by SIMS as they are too small (typically $<20\text{ }\mu\text{m}$). Glass data are unnormalised in the discussion and figures that follow, unless otherwise stated.

6.3.1. Major and trace element chemistry of Campi Flegrei glasses

6.3.1.1. Melt inclusions

Melt inclusions cover a wide compositional range from trachy-basalts and basanites to phonolites and trachytes (Fig. 6.3a; Appendix 4). In all cases, the melts are Na_2O and K_2O enriched, following an alkali fractionation trend. The samples in this study cover almost the entire compositional range of Campi Flegrei melts reported in the literature (Fig. 6.3), although more alkali-depleted basaltic and trachybasaltic melt inclusions have been reported in clinopyroxene- and olivine-hosted melt inclusions from the Minopoli 1 and Fondo Riccio eruptions (Cannatelli *et al.*, 2007) and more SiO_2 -enriched trachytic melt inclusions are present in some units from the CI (Marianelli *et al.*, 2006). Of the eruptions analysed here, Minopoli 1 has the most mafic melt inclusions, covering the largest compositional range, from 45 to 55 wt% SiO_2 . Pisani 1 includes the next most mafic melt inclusions, with SiO_2 concentrations as low as 51 wt%. Melt inclusions from other eruptions are predominantly phonolitic-trachytic, except PP that has inclusions covering a compositional range from 52 to 58 wt% SiO_2 and includes tephri-phonolitic compositions (Fig. 6.3a). After total alkalis - silica content, the aluminium saturation index (A/CNK;

molar $\text{Al}_2\text{O}_3/[(\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})]$) is a second-order classification of igneous rocks, which has been reported to correlate with apatite solubility (Piccoli and Candela, 2002). Melt inclusions from all eight eruptions have metaluminous or peraluminous compositions, with A/CNK of 0.8 to 1.1, within the range reported for Campi Flegrei glasses in previous studies (Fig. 6.4a). Pyroxene-hosted melt inclusions with lower A/CNK ratios have been reported in Minopoli 1 (Cannatelli *et al.*, 2007) and higher A/CNK compositions have been reported in melt inclusions from the Fondo Riccio and Minopoli 2 eruptions (Mangiacapra *et al.*, 2008). Typically, apatite solubility is higher in more peraluminous melts (Piccoli and Candela, 2002) but experiments show that this variability occurs only at $\text{A/CNK} > 1.1$ (Wolf and London, 1994).

Harker diagrams (Figs 6.5, 6.6) show the liquid line of descent for Campi Flegrei melts, using MgO as a fractionation index. For all elements, glasses in this study plot within the range of literature data, following the same compositional trajectories (Fig. 6.5). Literature analyses generally show more scatter than those in this study, likely due to variable data quality and analytical uncertainties. Melt inclusion SiO_2 , Na_2O and K_2O concentrations typically increase strongly with decreasing MgO. However, K_2O decreases at low MgO contents (≤ 0.5 wt% MgO). Low-MgO melt inclusions from Fondi di Baia, Astroni 1 and Monte Nuovo are particularly K_2O -depleted and Na_2O -rich (Fig. 6.5). Melt inclusion CaO, FeO and TiO concentrations correlate positively with MgO. However, literature data suggest that FeO and TiO_2 are constant at high MgO concentrations (> 5 wt% MgO), in more mafic inclusions than those analysed here. Al_2O_3 is approximately constant in the melt inclusions measured in this study but sit on a trend of decreasing Al_2O_3 with increasing MgO that is observed in the literature data. Melt inclusions from most eruptions have very low P_2O_5 concentrations. However, Minopoli 1 melt inclusions clearly define the positive correlation between P_2O_5 and MgO.

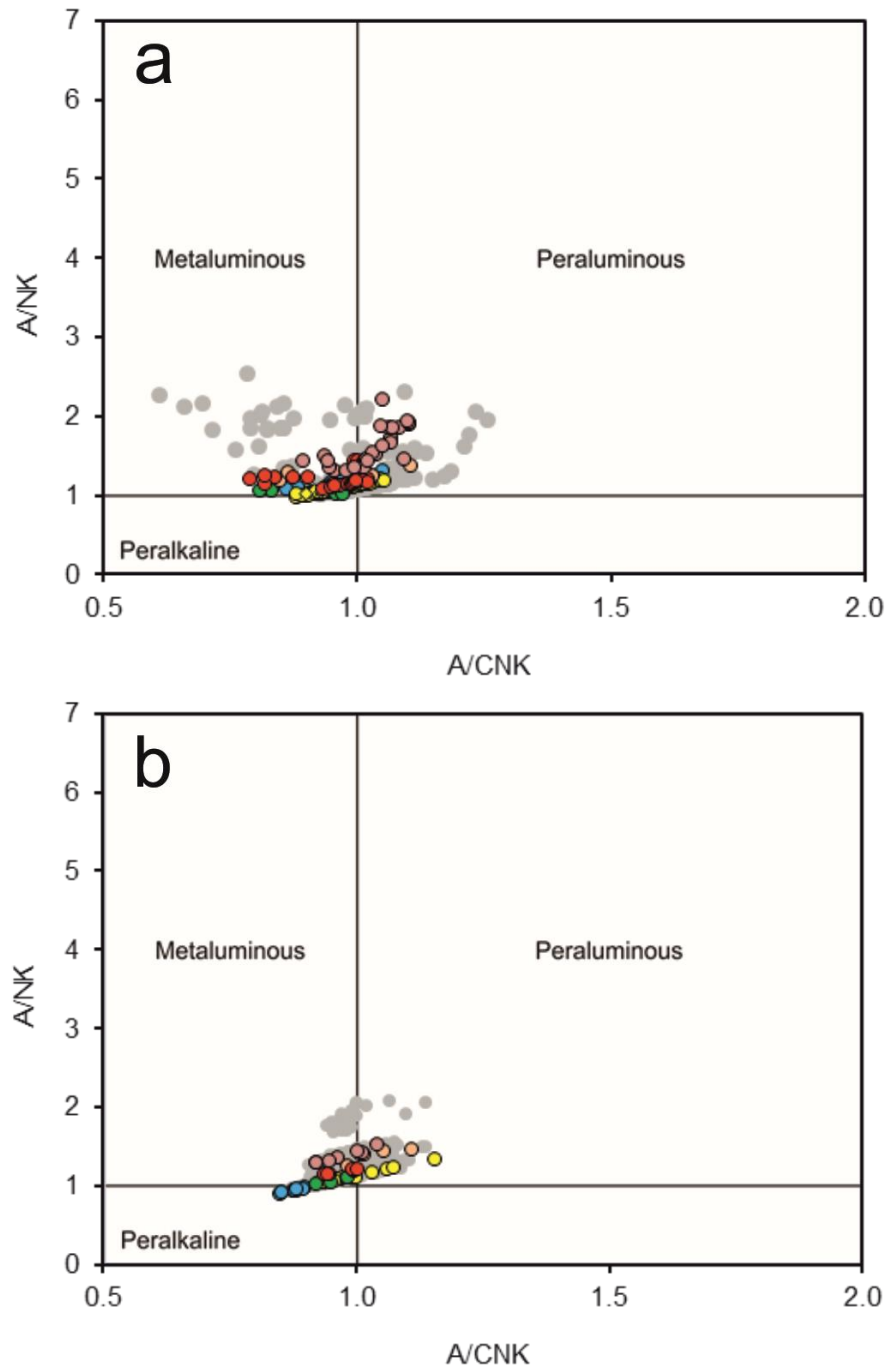


Figure 6.4 | A/CNK versus A/NK diagram showing the classification of glasses from Campi Flegrei. a, Clinopyroxene- (circles) and biotite- (diamonds) hosted melt inclusion compositions. Biotite-hosted inclusions were measured in Astroni 1 only. **b,** Matrix glass compositions. All data were measured by EPMA. Data are distinguished by eruption and grey points show literature clinopyroxene- and olivine-hosted melt inclusion compositions. Legend and data sources are as in Figure 6.3.

6.3.1.2. Matrix glasses

In general, matrix glasses are more evolved than melt inclusions from the same eruption, with higher SiO_2 (typically >53 wt%) and higher alkali element concentrations (Fig. 6.3; Appendix 4). Monte Nuovo matrix glasses have total alkali concentrations that are

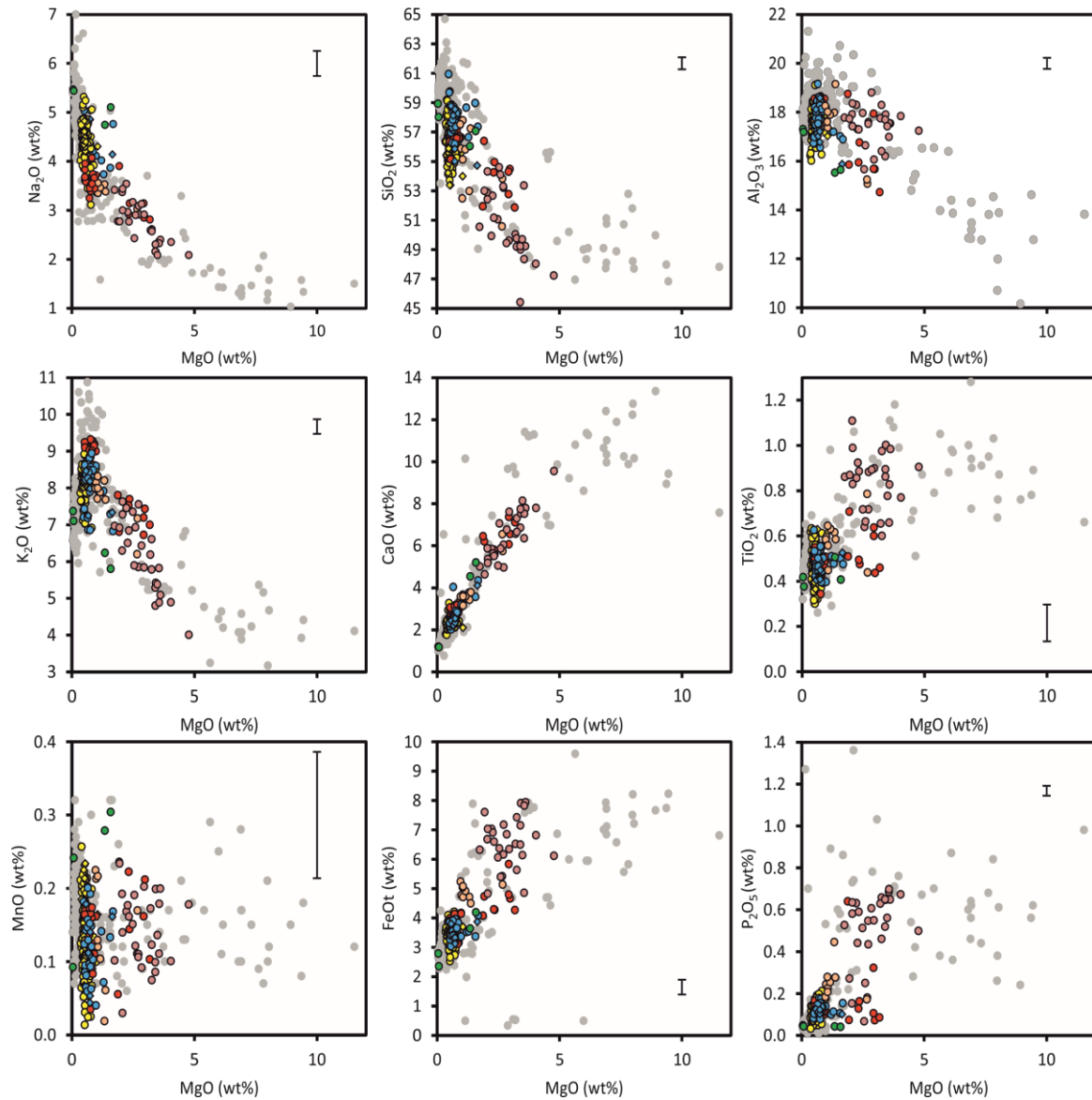


Figure 6.5 | Harker diagrams showing the range of Campi Flegrei melt inclusion compositions. Clinopyroxene- (circles) and biotite- (diamonds) hosted melt inclusions are both shown but biotite-hosted inclusions were measured in Astroni 1 only. All data were measured by EPMA. Where shown, error bars represent average precision with ± 1 s.d.; otherwise uncertainties are less than the size of the data points. Data are distinguished by eruption and grey points show literature clinopyroxene- and olivine-hosted melt inclusion compositions. Legend and data sources are as in Figure 6.3.

notably enriched relative to glasses from other eruptions (Fig. 6.3b). Matrix glasses are generally metaluminous-peraluminous and have a comparable A/CNK range to melt inclusions (0.9 to 1.2). However, the A/NK (molar $\text{Al}_2\text{O}_3/[\text{Na}_2\text{O}+\text{K}_2\text{O}]$) range is much smaller in matrix glasses. In Monte Nuovo, matrix glass A/NK ratios are <1 and the melts are therefore slightly peralkaline (Fig. 6.4b). The liquid lines of descent defined by matrix glass analyses are the same as in melt inclusions (Fig. 6.6), with more evolved (i.e. lower MgO) compositions. The only difference is that in very low MgO matrix glasses SiO_2 starts to decrease, with decreasing K_2O (Fig. 6.6) but increasing total alkalis (Fig. 6.3). This may reflect low temperature stabilisation of quartz (not observed in this study), which is reported in the literature (e.g. Smith *et al.*, 2011).

6.3.2. Volatile element compositions of Campi Flegrei glasses

6.3.2.1. Melt inclusions

At very high MgO concentrations (>5 wt%) the Cl contents of previously published Campi Flegrei melt inclusions are approximately constant at 0.3-0.5 wt% (Cannatelli *et al.*, 2007). At lower MgO concentrations, glass Cl shows a strong negative correlation with MgO (Fig. 6.7a), except in the CI where melt inclusions have anomalously low Cl concentrations (Marianelli *et al.*, 2006; Signorelli *et al.*, 1999). Minopoli 1 melt inclusions have the lowest Cl concentrations measured in this study, within the range 0.3 to 0.8 wt%. Pisani 1 and PP deposits also include low-Cl melt inclusions, ranging 0.6 to 0.9 wt%. Melt inclusions from other eruptions have high Cl concentrations, extending up to 1.1 wt%.

Melt inclusion F concentrations in mafic glasses (i.e. >1.5 wt% MgO) show a lot of scatter, both in this study (by SIMS and EPMA) and in the literature (Fig. 6.7b). Minopoli 1 melt inclusion F concentrations range from <0.2 to 0.4 wt% in SIMS data.

However, some Minopoli 1 melt inclusions measured by EPMA have compositions that extend to lower F concentrations (<0.09 wt%, below EPMA detection limit; inset Fig. 6.7b), suggesting that the subset of inclusions analysed by SIMS may not be representative. This range is similar to that identified in the literature. In more evolved melt inclusions (i.e. <1.5 wt% MgO) F correlates negatively with MgO. This is particularly clear in literature data, which include lower MgO melt inclusions than were

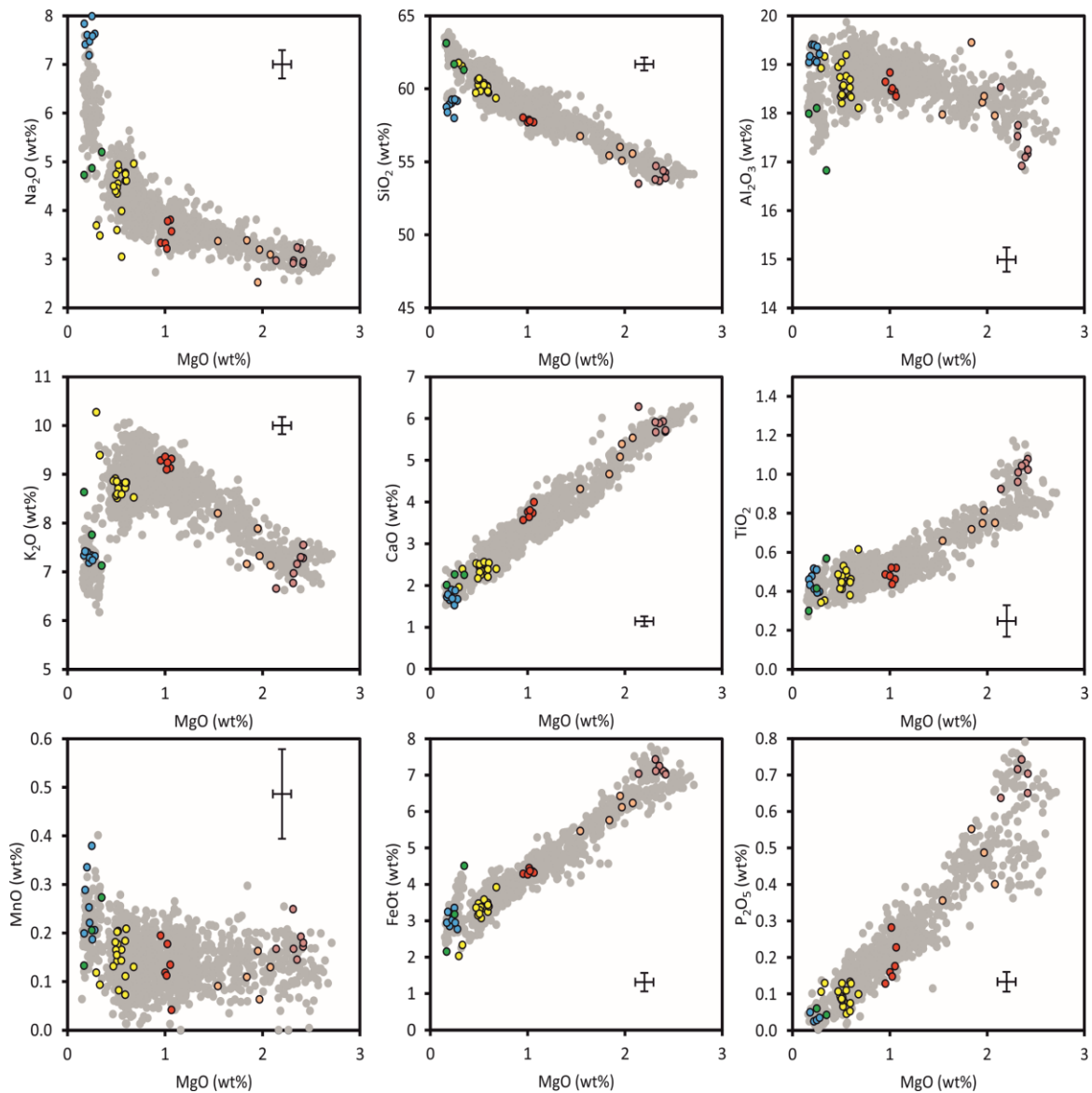


Figure 6.6 | Harker diagrams showing the range of Campi Flegrei matrix glass compositions. Compositions were measured by EPMA and are normalised to 100% to facilitate comparison with literature data. Error bars represent average precision with ± 1 s.d. Data are distinguished by eruption and grey points show literature matrix glass compositions from Smith *et al.* (2011).

analysed this study, extending to ~0.6 wt% F. The most F-rich melt inclusion analysed in this study is from Fondi di Baia and contains 0.4 wt% F (inset Fig. 6.7b).

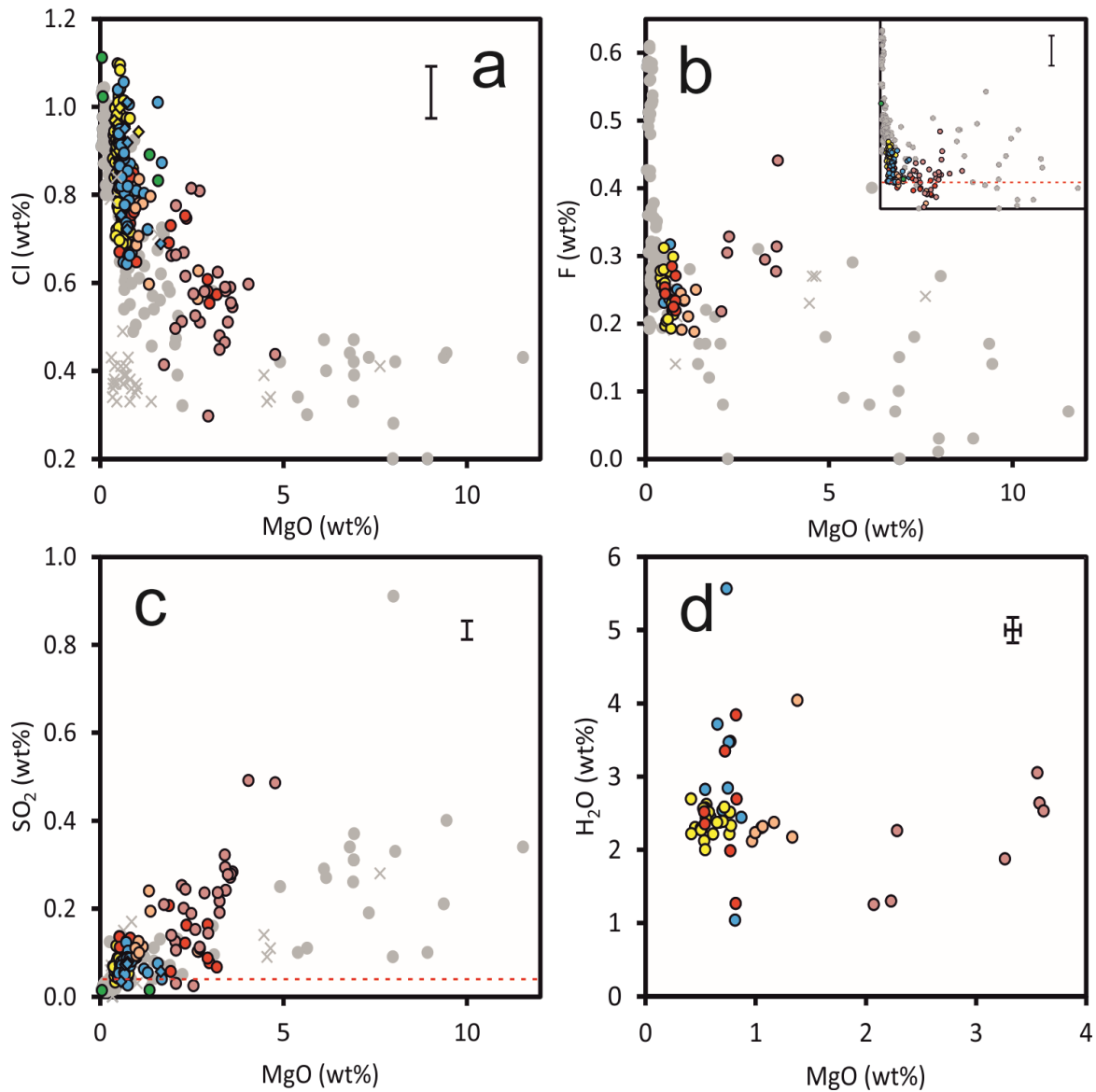


Figure 6.7 | The volatile compositions of Campi Flegrei melt inclusions. a, MgO versus Cl. **b,** MgO versus F. **c,** SO₂ versus MgO. **d,** H₂O versus MgO. In the main panels, MgO, SO₂ and Cl are measured by EPMA, H₂O and F are measured by SIMS. The inset in **b** shows MgO versus F measured by EPMA. The red dashed lines show EPMA detection limits. Clinopyroxene- (circles) and biotite-hosted (diamonds) melt inclusions are both shown but biotite-hosted inclusions were measured in Astroni 1 only. Where shown, error bars represent average precision with ±1 s.d. (EPMA) or a 95% confidence interval (SIMS); otherwise uncertainties are less than the size of the data points. Data are distinguished by eruption and grey points show literature clinopyroxene- and olivine-hosted melt inclusion compositions from the past 15 kyr (circles) and the CI eruption (crosses). Legend and data sources are as in Figure 6.3.

The SO₂ concentrations of melt inclusions analysed in this study show a weak positive correlation with MgO (Fig. 6.7c). Minopoli 1 melt inclusions have SO₂ concentrations up to 0.5 wt%, within the range previously reported for mafic Campi Flegrei eruptions. The lowest melt inclusion SO₂ concentrations, from Fondi di Baia, are below EPMA detection limits (i.e. <0.02 wt%).

Water concentrations in clinopyroxene-hosted melt inclusions from explosive Campi Flegrei eruptions (Table 6.1) average ~2-3 wt% and show no correlation with MgO (Fig. 6.7d). The generally restricted range of melt inclusion H₂O concentrations from Campi Flegrei has been noted previously (Arienzo *et al.*, 2016). A number of inclusions have lower H₂O concentrations (1-2 wt%) and may be degassed. The largest variability in melt inclusion H₂O contents is observed at low MgO concentrations (<1.5 wt%), where H₂O concentrations extend to 5.6 wt%. The data collected in this study plot within the range of literature data (Arienzo *et al.*, 2010; Cannatelli *et al.*, 2007; Fourmentraux *et al.*, 2012; Mangiacapra *et al.*, 2008; Marianelli *et al.*, 2006; Webster *et al.*, 2003) but literature data are not shown in Figure 6.7d, as data quality is variable and cannot be verified. High H₂O concentrations (>3 wt% H₂O) are reported in mafic (>5 wt% MgO) melt inclusions from the Fondo Riccio and Minopoli 1 eruptions (Cannatelli *et al.*, 2007) but the authors later discounted these as erroneous primitive melt compositions (Cannatelli, 2012), potentially highlighting a data quality issue.

6.3.2.2. Matrix glasses

In general, matrix glass Cl concentrations correlate negatively with MgO, reaching 1.2 wt% in Monte Nuovo and Fondi di Baia (Fig. 6.8a). The Cl concentrations of the most mafic matrix glasses from Minopoli 1 and Pisani 1 are between 0.5 wt% and 0.8 wt%. In general, matrix glass Cl concentrations are similar to those measured in the most evolved melt inclusions from each eruption. At low MgO (≤ 0.5 wt% MgO) some matrix glasses

from Astroni 1 and Fondi di Baia plot with low matrix glass Cl contents (<0.6 wt% Cl; Fig. 6.8a).

Fluorine concentrations are approximately constant in Campi Flegrei matrix glasses, but show a slight positive correlation with MgO in SIMS data until ≤ 0.5 wt% MgO (Fig. 6.8b). Typically, matrix glass F concentrations are 0.1 to 0.3 wt%. However,

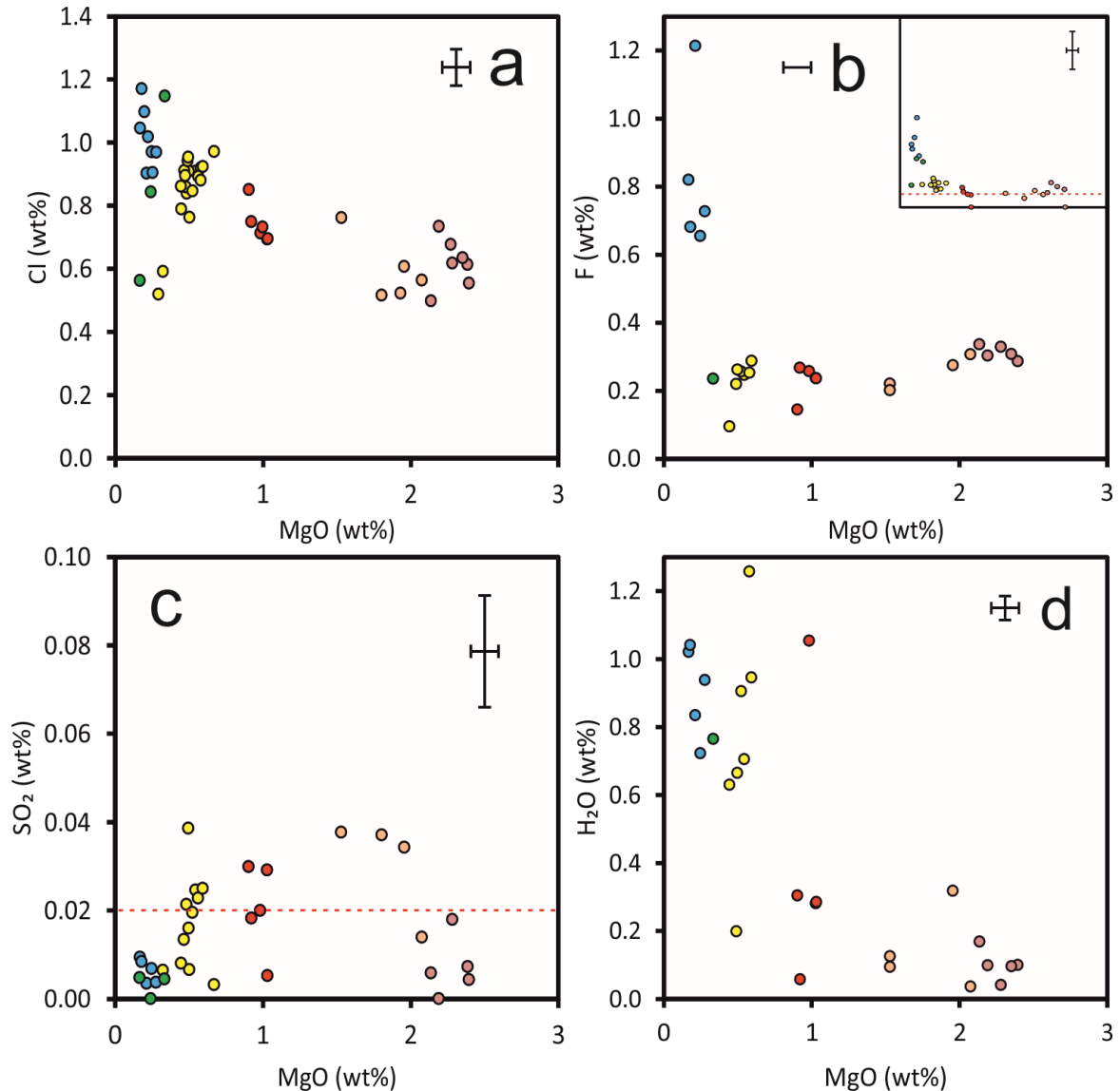


Figure 6.8 | The volatile compositions of Campi Flegrei matrix glasses. a, MgO versus Cl. **b,** MgO versus F. **c,** SO₂ versus MgO. **d,** H₂O versus MgO. In the main panels, MgO, SO₂ and Cl are measured by EPMA, H₂O and F are measured by SIMS. The inset in **b** shows MgO versus F measured by EPMA. The red dashed lines show EPMA detection limits. Where shown, error bars represent average precision with ± 1 s.d. (EPMA) or a 95% confidence interval (SIMS); otherwise uncertainties are less than the size of the data points. Data are distinguished by eruption (see legend in Figure 6.3).

they are significantly enriched in low MgO (i.e. ≤ 0.5 wt% MgO) matrix glasses from Monte Nuovo and Fondi di Baia (generally 0.7 to 0.8 wt% F), with a single analysis reaching a concentration 1.2 wt% F.

Most matrix glass SO₂ analyses are below EPMA detection limit (i.e. < 0.02 wt%; Fig. 6.8c). A few analyses have higher SO₂ concentrations, up to 0.04 wt%. There is no correlation between the matrix glass SO₂ and MgO outside of uncertainty. In all eruptions, matrix glasses are SO₂-depleted relative to melt inclusions, consistent with efficient syn-eruptive degassing.

The H₂O contents of matrix glasses are lower than those in melt inclusions, ranging from < 0.05 to ~ 1.3 wt% (Fig. 6.8d). Matrix glasses from Minopoli 1 and Pisani 1 consistently have H₂O concentrations < 0.4 wt% but more variability is observed in lower MgO analyses. Concentrations reach up to > 1 wt% H₂O in PP, Astroni 1 and Monte Nuovo. There is a clear negative correlation between matrix glass H₂O and MgO, becoming more significant after ~ 1 wt% MgO (Fig. 6.8d).

6.3.3. Volatile compositions of Campi Flegrei apatites

Apatite crystals from all eight Campi Flegrei eruptions are F-rich, with minor Cl and OH (Fig. 6.9; Appendix 5). Fluorine concentrations vary between 1.7 wt% and > 4 wt%. However, the maximum stoichiometric F that can be incorporated in to the apatite crystal structure is 3.76 wt% (Spear and Pyle, 2002), assuming negligible CO₃²⁻ (Fleet *et al.*, 2004; Tacker, 2008). Fluorine analyses considerably above 3.76 wt% (up to ~ 4.5 wt%) were only measured by EPMA and likely result from electron beam-induced halogen migration in near end-member fluorapatites (FAp; Goldoff *et al.*, 2012; Chapter 3). In SIMS data, measured F concentrations of up to ~ 3.9 wt% are stoichiometric within analytical uncertainty. All eruptions show a wide range of F concentrations but end-member FAp is only observed from the Mt Olibano and Accademia lava dome eruptions

(Fig. 6.9). Maximum apatite OH concentrations in Campi Flegrei apatites are 1.2 wt% and Cl concentrations vary from <0.1 wt% to 1.5 wt%.

Electron probe analysis of ~600 crystals demonstrates that Campi Flegrei apatites can be sub-divided into three groups, primarily based on their Cl concentrations (Figs 6.9, 6.10). The Cl concentrations of ‘high-Cl’ apatites are >0.8 wt%, ‘medium-Cl’ apatites are within the range 0.8 wt% to 0.4 wt% and ‘low-Cl’ apatites are <0.4 wt% (Fig. 6.10). In some cases, these groups are indistinct and definite boundaries cannot be identified; this is particularly true at high F concentrations and in the Fondi di Baia eruption where there

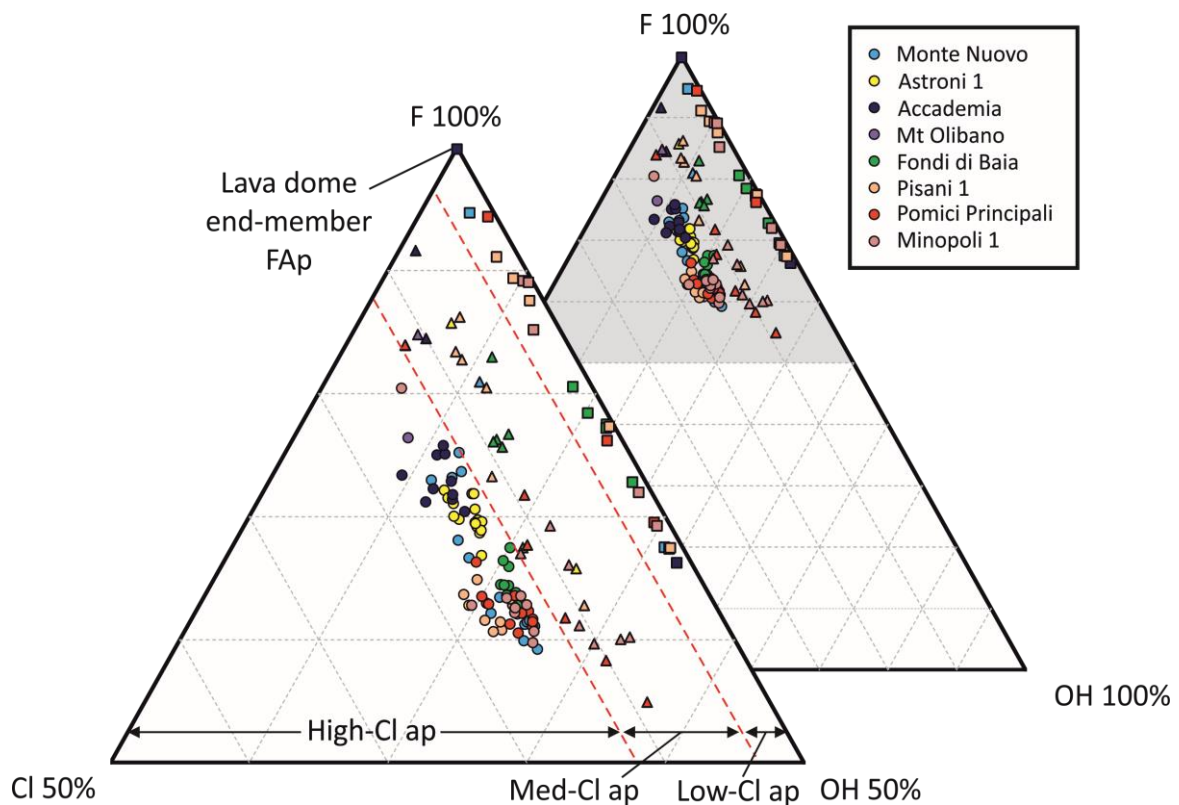


Figure 6.9 | F-Cl-OH ternary diagrams showing the volatile compositions of Campi Flegrei apatite microphenocrysts. All data were measured by SIMS. The back graph shows the entire range of ternary space and the overlain graph shows an expanded region in the top corner, with Cl and OH <50% (shaded grey). Dashed red lines show the boundaries between high-Cl (circles), medium-Cl (triangles) and low-Cl (squares) apatite populations. Crystals measured in lava domes with >3.76 wt% F are stoichiometric within uncertainty and are plotted as end-member FAp (i.e. F = 100%; see annotation). Data are distinguished by eruption (see legend).

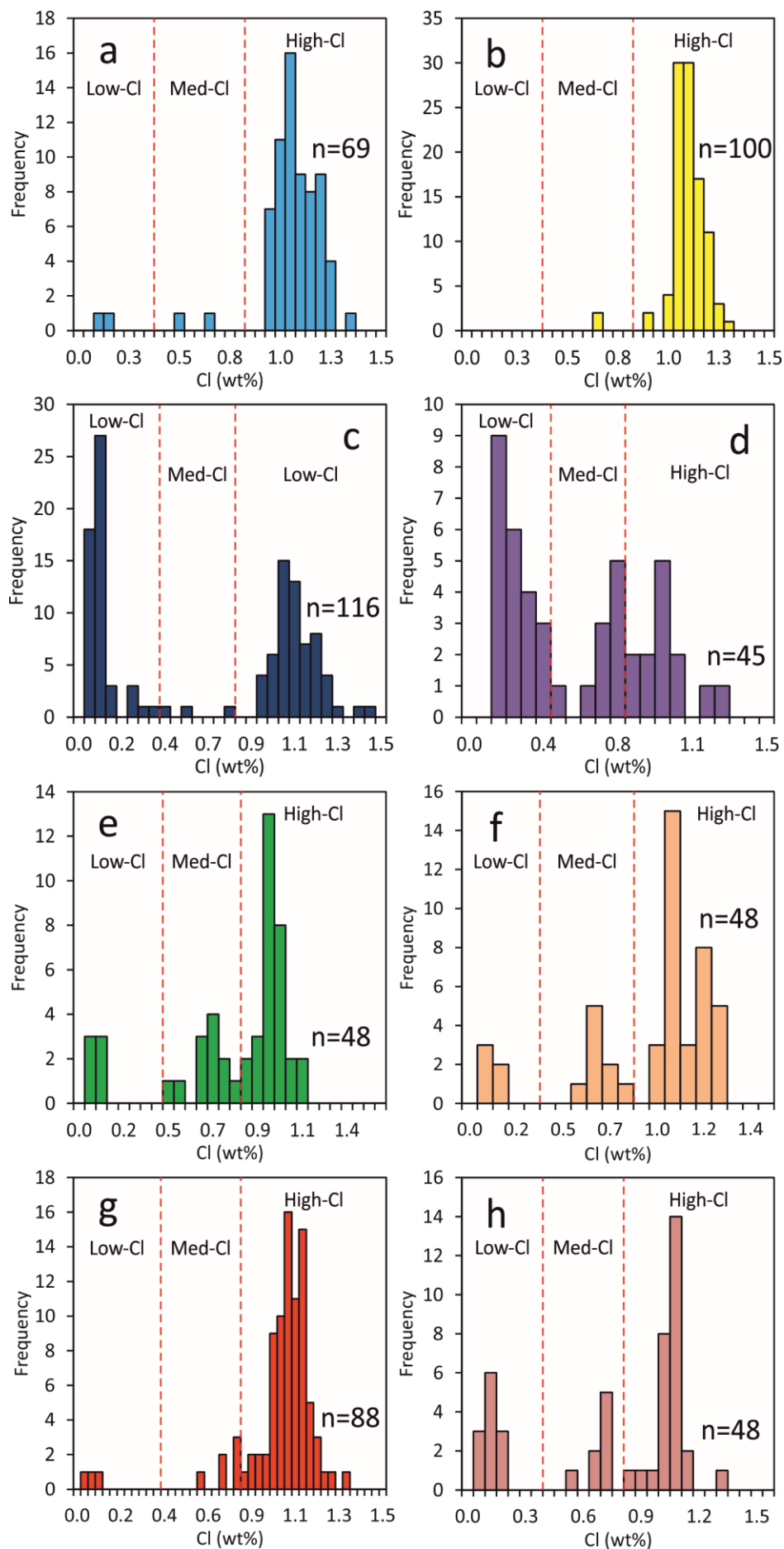


Figure 6.10 | (previous page) Frequency histograms showing the Cl concentrations of Campi Flegrei apatite microphenocrysts. All data were measured by EPMA. **a**, Monte Nuovo, **b**, Astroni 1, **c**, Accademia, **d**, Mt Olibano, **e**, Fondi di Baia, **f**, Pisani 1, **g**, Pomici Principali and **h**, Minopoli 1. Red lines show the divisions between high-, medium- and low-Cl apatite populations. n= total number of analyses collected for each eruption.

is no clear boundary between high- and medium-Cl apatite populations. All eruptions contain apatite microphenocrysts from all three populations, except Astroni 1 where only two medium-Cl apatites and no low-Cl apatites were identified in a survey of 100 crystals (Fig. 6.10).

The rapidity and relative ease of EPMA analysis, relative to SIMS, permits large numbers of apatite crystals to be screened for identification of the different populations (Fig. 6.10). Compositional trends in each apatite population are the same in SIMS and EPMA datasets, confirming that the smaller sub-set of crystals measured by SIMS is representative of the broader populations (Fig. 6.11; Appendix Fig. A5.2). However, the OH component must be calculated ‘by difference’ in EPMA analyses. Electron-beam induced halogen migration will cause a greater overestimation of apatite F concentrations in more F-rich crystals, resulting in a greater underestimation of OH (Chapter 3) and introducing a systematic, composition-dependent uncertainty into EPMA analyses. The following discussion is therefore focussed on SIMS data. The full EPMA dataset is presented in Appendix 5, demonstrating the correlation between the observed trends in SIMS and EPMA data.

6.3.3.1. Apatite inclusion F-Cl-OH compositions

Clinopyroxene-hosted apatite inclusions typically have X_F/X_{OH} ratios in the range 2.0 to 7.4, X_{Cl}/X_{OH} ratios between 0.5 and 1.4 and X_F/X_{Cl} ratios of 3.9 to 6.2, plotting within the high-Cl population (Figs 6.11a, b). Fondi di Baia is an exception, as clinopyroxene-hosted

apatite inclusions have low $X_{\text{Cl}}/X_{\text{OH}}$ (~ 0.3) and high $X_{\text{F}}/X_{\text{Cl}}$ (7.3 to 12.7) ratios relative to other eruptions and plot within the medium-Cl population. Although there is significant overlap between eruptions, clinopyroxene-hosted apatite inclusions from Astroni 1 extend to the highest $X_{\text{Cl}}/X_{\text{OH}}$ ratios, followed by Monte Nuovo. Minopoli 1, Pisani 1 and PP have lower $X_{\text{Cl}}/X_{\text{OH}}$ ratios. Clinopyroxene-hosted apatite inclusions from Astroni 1 and

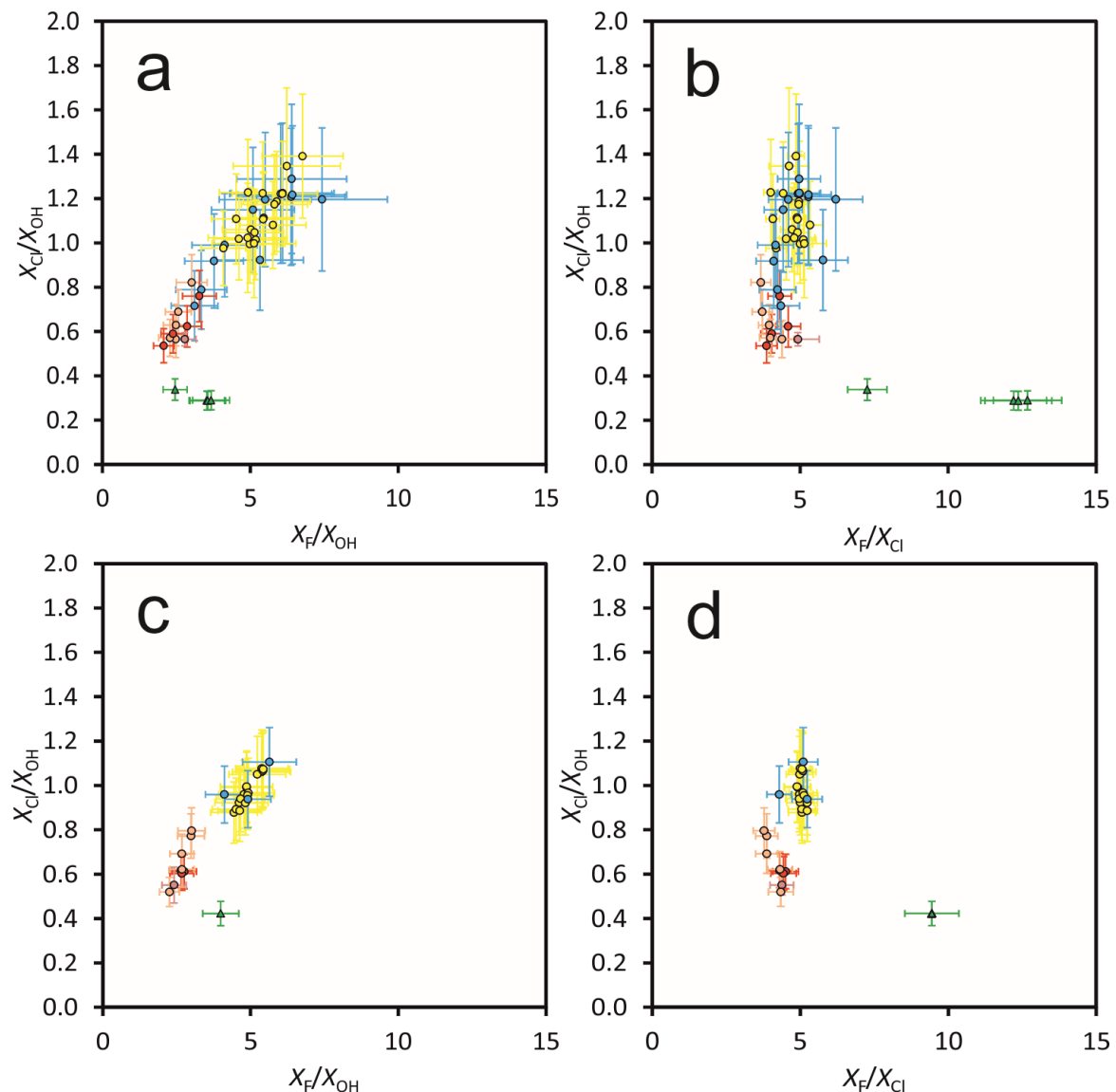


Figure 6.11 | The volatile compositions of Campi Flegrei apatite inclusions. a,b, Clinopyroxene-hosted apatite inclusions. **c,d,** Biotite-hosted apatite inclusions. Apatite volatile compositions are shown in $X_{\text{Cl}}/X_{\text{OH}}$ versus $X_{\text{F}}/X_{\text{OH}}$ (**a,c**) and $X_{\text{Cl}}/X_{\text{OH}}$ versus $X_{\text{F}}/X_{\text{Cl}}$ (**b,d**) space. All data were measured by SIMS. Errors bars represent precision with a 95% confidence interval. Data are distinguished by eruption (see legend in Figure 6.9) and include both high-Cl (circles) and medium-Cl (triangles) apatite populations.

Monte Nuovo also generally have higher X_F/X_{OH} ratios than other eruptions (Fig. 6.11a). The X_F/X_{Cl} ratios of clinopyroxene-hosted apatite inclusions show a slight positive correlation with X_{Cl}/X_{OH} within analytical uncertainty (except in Fondi di Baia; Fig. 6.11b).

Biotite-hosted apatite inclusions fall within a more limited compositional range than clinopyroxene-hosted inclusions but the sample size is smaller ($n=29$). All biotite-hosted apatite inclusions, except those from Fondi di Baia, plot within the high-Cl apatite population, with X_F/X_{OH} ratios of 2.3 to 5.6, X_{Cl}/X_{OH} of 0.5 to 1.1 and X_F/X_{Cl} between 3.8 and 5.2 (Fig. 6.11c,d). A single biotite-hosted apatite analysis from Fondi di Baia is transitional between the medium- and low-Cl populations ($X_{Cl}/X_{OH} = 0.4$, $X_F/X_{OH} = 4.0$, $X_F/X_{Cl} = 9.4$). Astroni 1 and Monte Nuovo biotite-hosted apatite inclusions have the higher X_{Cl}/X_{OH} and X_F/X_{OH} ratios than those from Minopoli 1, Pisani 1 and PP (Fig. 6.11c). As in clinopyroxene-hosted inclusions, biotite-hosted apatite inclusion X_F/X_{Cl} ratios overlap considerably between eruptions (except in Fondi di Baia), but show a slight positive correlation with X_{Cl}/X_{OH} (Fig. 6.11d).

6.3.3.2. Apatite microphenocryst F-Cl-OH compositions

Apatite microphenocrysts have a large compositional range. High-Cl microphenocryst X_F/X_{OH} ratios typically range from 2.3 to 9.3, with X_{Cl}/X_{OH} of 0.6 to 1.9 and X_F/X_{Cl} in the range 6.1 to 3.5. In general, high-Cl microphenocrysts from the Mt Olibano and Accademia lava dome eruptions have the highest $X_{Halogen}/X_{OH}$ and X_F/X_{Cl} ratios, followed by Monte Nuovo and Astroni 1 (Fig. 6.12). The high-Cl microphenocrysts with the lowest $X_{Halogen}/X_{OH}$ and X_F/X_{Cl} ratios are from Pisani 1, Minopoli 1 and PP. A single outlier from Minopoli 1 has elevated X_F/X_{OH} (13.9) and X_{Cl}/X_{OH} (2.4) ratios, relative to other eruptions. High-Cl microphenocrysts from most eruptions plot within a limited compositional range, but those from Monte Nuovo cover almost the entire compositional diversity. The high-Cl

microphenocryst population shows a positive correlation between $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{OH}}$ and between $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ outside of uncertainty (Fig. 6.12).

Medium-Cl microphenocryst $X_{\text{F}}/X_{\text{OH}}$ ratios are in the range 1.5 to 19.5, $X_{\text{Cl}}/X_{\text{OH}}$ are 0.2 to 2.7 and $X_{\text{F}}/X_{\text{Cl}}$ are 5.5 to 13.8 (Fig. 6.12). The lowest $X_{\text{F}}/X_{\text{OH}}$, $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ medium-Cl apatite microphenocrysts are typically from PP, except one very high $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{OH}}$ outlier, which is transitional between the high- and medium-Cl populations. Medium-Cl microphenocrysts from lava dome eruptions also have high $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{Cl}}/X_{\text{OH}}$ ratios and plot close to the PP outlier. Medium-Cl apatites show a positive correlation between $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{OH}}$ and between $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ outside of uncertainty, albeit with a shallower gradient than the high-Cl population (Fig. 6.12).

Low-Cl apatite microphenocrysts from explosive eruptions consistently have

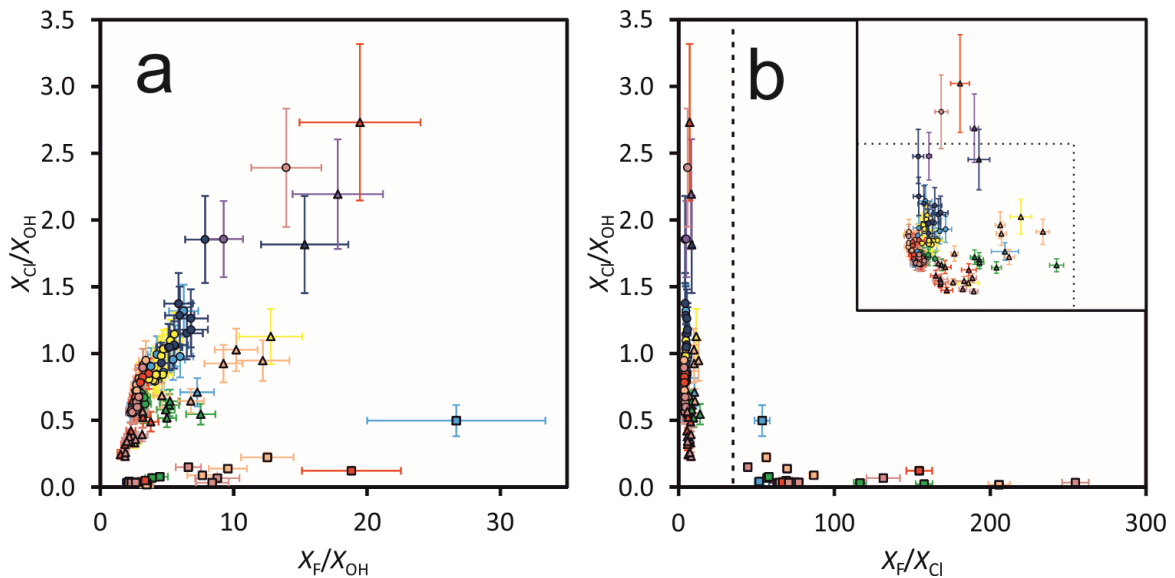


Figure 6.12 | The volatile compositions of Campi Flegrei apatite microphenocrysts. Apatite volatile compositions are shown in $X_{\text{Cl}}/X_{\text{OH}}$ versus $X_{\text{F}}/X_{\text{OH}}$ space (a) and $X_{\text{Cl}}/X_{\text{OH}}$ versus $X_{\text{F}}/X_{\text{Cl}}$ space (b). The inset in b shows an expansion of the area marked by the black dashed line in the main panel. The dotted box in the inset shows the scale of Figures 6.11b and 6.11d. All data were measured by SIMS. Errors bars represent precision with a 95% confidence interval. Data are distinguished by eruption (see legend in Figure 6.9) and include high-Cl (circles), medium-Cl (triangles) and low-Cl (squares) apatite populations. End-member FAp microphenocrysts from lava dome eruptions are not shown, as $X_{\text{Cl}} \approx X_{\text{OH}} \approx 0$ within uncertainty and mole fraction ratios can therefore not be calculated.

$X_{\text{Cl}}/X_{\text{OH}}$ ratios <0.5 . $X_{\text{F}}/X_{\text{OH}}$ ratios vary between 2.1 and 26.7 and $X_{\text{F}}/X_{\text{Cl}}$ ratios range from 44.4 to 254.7 (Fig. 6.12). There are no obvious trends between low-Cl microphenocryst compositions from different eruptions. However, all low-Cl apatite microphenocrysts from Mt Olibano and all but one from the Accademia lava eruptions are end-member FAp (not shown on Fig. 6.12). There is no clear correlation between low-Cl apatite $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios, although the highest $X_{\text{Cl}}/X_{\text{OH}}$ values are at low $X_{\text{F}}/X_{\text{Cl}}$ (Fig. 6.12b). The highest $X_{\text{Cl}}/X_{\text{OH}}$ low-Cl apatite is also the highest $X_{\text{F}}/X_{\text{OH}}$ microphenocryst from Monte Nuovo, but there is otherwise no correlation between $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{OH}}$ (Fig. 6.12a).

The Accademia lava dome was the only sample prepared both in thin sections and grain mounts. In grain mounts, apatite crystals were within the 44-250 μm size fraction (Chapter 2), whereas crystals in thin sections were analysed down to <35 μm . Considerably more low- and medium-Cl apatite microphenocrysts were observed in thin section analyses than in grain mount separates, highlighting a potential relationship between grain-size and microphenocryst volatile composition.

6.3.3.3. Apatite SO_2 compositions

The SO_2 contents of Campi Flegrei apatites show a wide compositional range with higher SO_2 concentrations measured in apatite microphenocrysts than inclusions (Fig. 6.13). Apatite microphenocrysts typically have SO_2 concentrations between <0.1 and 1.5 wt%, with one analysis at ~ 2.0 wt%. Apatite inclusions generally contain between 0.2 and 0.9 wt% SO_2 (maximum 1.2 wt%). Incorporation of SO_2 in apatite occurs through coupled substitutions with SiO_2 and Na_2O for P_2O_5 (Section 6.4.5.; Peng *et al.*, 1997). At moderate-to-high SO_2 concentrations (>0.5 wt% SO_2), there is a negative correlation between apatite SO_2 and P_2O_5 contents, and a positive correlation between SO_2 and SiO_2 but there is a lot of scatter in the inclusion dataset (Fig. 6.13). Apatite Na_2O is generally below EPMA detection limits and, although there is a slight positive correlation with SO_2 ,

its involvement in SO_2 partitioning cannot be well constrained. There is no systematic difference in the SO_2 concentrations of apatites from the different eruptions, or any correlation with other anionic volatile components (i.e. F, Cl, OH).

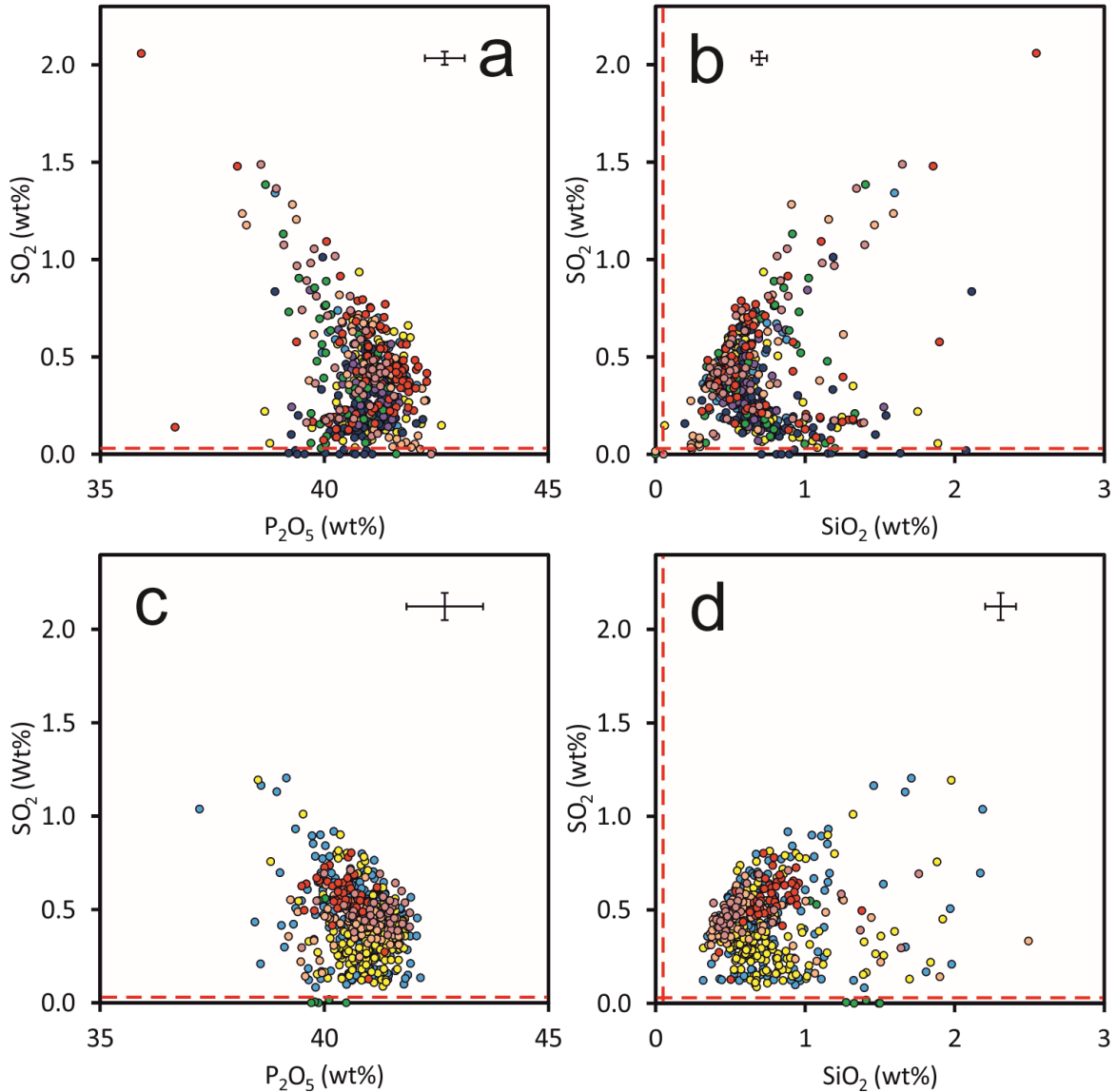


Figure 6.13 | The SO_2 compositions of Campi Flegrei apatites. **a,b**, Apatite microphenocrysts. **b,c**, Apatite inclusions. SO_2 concentrations are shown against P_2O_5 (**a,c**) and SiO_2 (**b,d**), which may be involved in the coupled substitutions that permit SO_2 incorporation in apatite (Peng *et al.*, 1997; see discussion in text). All data were measured by EPMA. Na_2O can also form part of a coupled substitution with SO_2 (Peng *et al.*, 1997) but is generally below EPMA detection limit. Errors bars represent average precision with ± 1 s.d. and dashed red lines show EPMA detection limits. Data are distinguished by eruption (see legend in Figure 6.9).

6.4. Discussion

6.4.1. Liquid line of descent and the relationship between Campi Flegrei eruptions

6.4.1.1. Comparison of empirical data with thermodynamic models

The Rhyolite-MELTS thermodynamic modelling software (Gualda *et al.*, 2012) can be used to calculate a theoretical liquid line of descent, describing the compositional evolution of a primitive Campi Flegrei liquid, during isobaric fractional crystallisation. Such modelling has been undertaken previously to determine the compositional evolution of melts in the build-up to individual Campi Flegrei eruptions, using calculated (Bohrson *et al.*, 2006; Fowler *et al.*, 2007) and measured (Cannatelli, 2012) primitive melt starting compositions. Similar models were run in Chapter 5 to investigate the timing of H₂O saturation. These studies have shown that most crystallisation likely occurred at ~150-300 MPa, close to $fO_2 = QFM+1$, and with a liquidus H₂O concentration (L_{H_2O}) of ~3 wt% (Bohrson *et al.*, 2006; Cannatelli, 2012; Fowler *et al.*, 2007). Here, these thermodynamic models are compared with the Campi Flegrei glass compositions measured in this study and in the literature. This is used to evaluate how the melts feeding different eruptions are compositionally related, and to identify their relative extents of fractionation. This provides a framework for interpreting pre-eruptive volatile contents from apatite and glass analyses.

At 150 MPa, $fO_2 = QFM+1$, $L_{H_2O} = 3$ wt%, and using a reconstructed Campi Flegrei primitive melt composition (VE1 #3 see Fowler *et al.*, 2007), Rhyolite-MELTS predicts olivine as the liquidus phase in Campi Flegrei, crystallising at $T = 1235$ °C (Fowler *et al.*, 2007). Clinopyroxene crystallises next, followed by magnetite and apatite, at 1162 °C, 1078 °C and 1018 °C, respectively (Bohrson *et al.*, 2006; Fowler *et al.*, 2007).

Biotite, plagioclase and then K-feldspar all begin to crystallise at temperatures near ~ 883 °C (Fowler *et al.*, 2007). The order and temperature of mineral precipitation do not vary significantly between different estimated Campi Flegrei primitive melt compositions ($\Delta T < 100$ °C; Cannatelli *et al.*, 2007), or with varying L_{H_2O} (Chapter 5). There is good agreement between the modelled and observed phase assemblage of Campi Flegrei samples in this study, except that olivine was not present in the natural samples (it is reported in Minopoli 1 by Cannatelli *et al.*, 2007) and leucite was observed in samples from more evolved eruptions. Minor leucite is produced in Campi Flegrei Rhyolite-MELTS fractionation models as a low temperature, late-crystallising phase at slightly higher pressures (i.e. >150 MPa; Fowler *et al.*, 2007). Fluorite is present in natural samples from all Campi Flegrei eruptions but does not appear in the models as it is not included in the Rhyolite-MELTS thermodynamic database (Gualda *et al.*, 2012). Fluorite crystallisation must be limited to low temperatures as it is absent as inclusions within other phenocrysts. Sodalite was observed in the Monte Nuovo sample, consistent with previous studies (Vona *et al.*, 2013), and has been reported in the Accademia lava dome (Melluso *et al.*, 2012). As with fluorite, this phase is absent in Rhyolite-MELTS (Gualda *et al.*, 2012) but its interstitial occurrence in lava dome samples (Melluso *et al.*, 2012) and absence as inclusions in phenocrysts imply low-temperature crystallisation.

The general negative correlation between MgO and SiO₂, Na₂O, K₂O and Al₂O₃ measured in Campi Flegrei glasses (Figs 6.5, 6.6) is in agreement with the early precipitation of olivine, clinopyroxene and magnetite in Rhyolite-MELTS models (Cannatelli, 2012; Fowler *et al.*, 2007). A modelled change in the compatibility of SiO₂ and CaO between olivine-only and olivine + clinopyroxene crystallisation (Fowler *et al.*, 2007) is not observed in clinopyroxene-hosted melt inclusions analysed in this study, but is seen in the literature dataset, which includes olivine-hosted inclusions. The observed

decrease in CaO and FeO concentrations with decreasing MgO (Figs 6.5, 6.6) is consistent with that predicted due to clinopyroxene and magnetite crystallisation, respectively (Cannatelli, 2012). Similarly, the decrease in TiO₂ and P₂O₅ (Figs 6.5, 6.6) likely reflect magnetite and apatite precipitation. High Na₂O and low K₂O concentrations in low-MgO glasses (Figs 6.5, 6.6) are reproduced by Rhyolite-MELTS fractional crystallisation models at QFM+1 after *plagioclase-in*, *biotite-in* and *K-feldspar-in*, either at a single temperature point (Bohrson *et al.*, 2006; Fowler *et al.*, 2007) or over a short (<100 °C) temperature interval (Cannatelli, 2012; Chapter 5), corresponding with an significant increase in the crystallinity of the system.

The liquid line of descent predicted by Rhyolite-MELTS modelling (Bohrson *et al.*, 2006; Cannatelli, 2012; Fowler *et al.*, 2007) is consistent with measured trends in matrix glass and melt inclusion compositions. Despite the complexity of magma storage conditions inferred from isotopic data (e.g. Arienzo *et al.*, 2009; D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2011), the conformity between thermodynamic fractional crystallisation models and natural glass compositions suggests that Campi Flegrei eruptions in the past 15 kyr can be broadly related by fractional crystallisation of a single parental magma, as previously inferred from bulk-rock major and trace element data (Civetta *et al.*, 1991). The same liquid line of descent is produced by Rhyolite-MELTS with only up to 5 to 10% skarn and syenite (but not carbonate) assimilation (Fowler *et al.*, 2007). Isotopic evidence is compatible with up to 2% assimilation of Calabrian Hercynian granitic crust (Caggianelli *et al.*, 1991; Rottura *et al.*, 1991), which represents a potential basement lithology in the Campi Flegrei region (D'Antonio *et al.*, 2007). In either case, the compositional trends indicate only minor crustal assimilation during magmatic evolution.

6.4.1.2. Inter-eruption variability in glass compositions

The eruptions analysed in this study can be clearly distinguished on the basis of matrix glass compositions (Fig. 6.6). As all analysed samples plot on a single liquid line of descent, this likely reflects varying degrees of magmatic differentiation (Villemant, 1988). In general, melt inclusion compositions overlap and most eruptions cannot be distinguished (Fig. 6.5). However, clinopyroxene-hosted melt inclusions from Minopoli 1, PP and Pisani 1 consistently preserve more mafic compositions than in other eruptions in (Figs 6.3, 6.5). Magmas from Campi Flegrei all follow a single liquid line of descent (Section 6.4.4.1., Fig. 6.5) and Rhyolite-MELTS models predict only a minor variation in clinopyroxene saturation temperatures over a range of magma storage pressures (100-500 MPa), fO_2 values (QFM-1 to QFM+3) and L_{H_2O} (2-3 wt%; Fowler *et al.*, 2007). It therefore seems unlikely that these more mafic compositions reflect differences in primitive melt composition or magma storage conditions. An alternative is that crystals are continually being extracted from the Campi Flegrei system during fractional crystallisation, forming cumulates that are not expelled on eruption. If Minopoli 1, PP and Pisani 1 had shorter crustal residence times they might experience less crystal fractionation, permitting extraction of early-formed phenocrysts that contain mafic melt inclusions. This is consistent with the less differentiated matrix glasses from these eruptions (Figs 6.3, 6.6), and with diffusion modelling, which suggests the crustal residence times of Epoch 1 magmas were shorter than in later Campi Flegrei eruptions (Smith *et al.*, in prep).

6.4.2. Deciphering pre-eruptive fluid systematics using apatite

In this section, I constrain the potential origins of the high-, medium- and low-Cl apatite trends identified in Campi Flegrei. In the Astroni 1 eruption (Chapter 5), all apatites plot

within the high-Cl population on a single compositional trajectory, except for two medium-Cl microphenocrysts (the ‘outlier’ in Chapter 5 and one additional analysis measured during preparation of this chapter; Fig. 6.10). This high-Cl trend was identified as resulting from prolonged volatile-undersaturated crystallisation (Section 5.3.1.). However, the unequivocal presence of multiple apatite populations in other eruptions indicates a more complex pre-eruptive history, reflecting variability in magma storage conditions or melt volatile composition. These can be deciphered using the *PT* models of Piccoli and Candela (1994) (see Section 5.4.3.) and the thermodynamic crystallisation models developed in Chapter 4. The models presented in Chapter 4 were run under conditions relevant to Campi Flegrei (see Section 4.3. for model input parameters).

6.4.2.1. The timing and preservation of apatite volatile records

As apatite crystallises, it attains a volatile signature reflecting the melt composition and physical conditions within the magma chamber. Volatile elements diffuse rapidly through the apatite crystal structure, so if the magma volatile composition changes during evolution, crystals may remain in equilibrium with their host melts on relatively short timescales (Brenan, 1993). However, if apatite crystals are trapped as inclusions within phenocrysts they become isolated from the melt and are unable to rehomogenise, preserving a record of the mineral-melt equilibrium at the time of entrapment (Fig. 5.1).

Biotite is a hydrous mineral, containing OH, Cl and F. A null-hypothesis is that biotite-hosted apatite inclusions do not record magmatic volatile contents on entrapment, due to partial re-equilibration with their host crystals. The similarity between the clinopyroxene- and biotite-hosted apatite inclusion compositions (Fig. 6.11) precludes this interpretation because clinopyroxene is nominally anhydrous and does not contain a volatile component that can be exchanged with apatite inclusions. Additionally, no

halogen zoning is detected in maps of biotite-hosted apatite inclusions, which might be expected if crystals had partially re-equilibrated with their hosts.

6.4.2.2. The origin of high-, medium- and low-Cl apatite populations

The high-Cl population: The high-Cl apatite population is characterised by a positive correlation between $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{OH}}$ ratios and a steep positive correlation between $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ (Figs 6.11, 6.12). For most eruptions other than Astroni 1, apatite inclusion and microphenocryst compositions overlap within analytical uncertainty, and it is difficult to determine robust temporal volatile records (as in Chapter 5) because there are relatively few analyses of apatite inclusions. Therefore, it is difficult to be certain whether $X_{\text{Halogen}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ increase or decrease during fractionation.

The modelling from Chapters 4 and 5 suggests that a trend of increasing $X_{\text{Halogen}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ could form through H_2O -saturated crystallisation at low $D_{\text{Cl}}^{\text{f/m}}$ (<6 ; Fig. 4.8), cooling or decompression (Fig. 5.2; Piccoli and Candela, 1994; Piccoli and Candela, 2002). Chlorine-saturated crystallisation is discounted as models show a strong positive correlation between $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$, even at very high $D_{\text{H}_2\text{O}}^{\text{f/m}}$ values (200; Fig. 4.10), which is not observed in the natural high-Cl apatite dataset (Figs 6.11, 6.12). Water-saturated crystallisation would cause elevated $X_{\text{Cl}}/X_{\text{OH}}$ and very high $X_{\text{F}}/X_{\text{OH}}$ ratios over a short crystallisation interval after *apatite-in* (Fig. 4.8), and such high values are not observed in the natural apatite inclusion or microphenocryst datasets (Figs 6.11, 6.12). Furthermore, even at low temperatures ($\sim 800^\circ\text{C}$), to produce the high-Cl apatite compositional range ($X_{\text{Cl}}/X_{\text{OH}} = \sim 0.5$ to >1.5 ; Figs 6.11, 6.12) by decompression would require a very large pressure change ($\Delta P \approx 1$ GPa based on the assumed liquid composition in Chapter 5; Section 5.4.3.), far exceeding current magma storage pressures at Campi Flegrei (i.e. ~ 170 - 180 MPa based on the depth of magma storage identified in

geophysical data by De Siena et al., 2010 and Zollo et al., 2008, and a melt density of $2,440 \text{ kgm}^{-3}$ calculated using Lange and Carmichael, 1990). Decreasing temperature is difficult to discount. However, models suggest that the measured high-Cl apatite $X_{\text{Cl}}/X_{\text{OH}}$ range would require significant cooling ($\Delta T > 300^\circ \text{C}$ based on the assumed liquid composition in Chapter 5) and would be accompanied by a larger increase in $X_{\text{F}}/X_{\text{OH}}$ (> 21) than is observed in the natural data (i.e. < 7 ; Figs 5.2, 6.11, 6.12; Section 5.4.3.).

The analyses from Astroni 1, where a clear temporal trend is identifiable, demonstrate that within the high-Cl population $X_{\text{Halogen}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ *decrease* with progressive crystallisation (Fig. 5.2). In this case, the thermodynamic crystallisation models can only reproduce the high-Cl trend through volatile-undersaturated crystallisation (Fig. 4.6; Section 4.8). The models in Chapter 4 show a kink in apatite compositional evolution at *fluorite-in* (Fig. 4.13). If the high-Cl apatite trend recorded *fluorite-in*, there would be an offset between apatite inclusions and high-Cl microphenocrysts, caused by low temperature fluorite saturation (Section 6.4.1.). No offset is observed, suggesting that fluorite saturation occurred on pre-eruptive timescales that were too short to be recorded by new apatite crystallisation or microphenocryst rehomogenisation.

The low-Cl population: The low-Cl apatite population is characterised by low $X_{\text{Cl}}/X_{\text{OH}}$ and very high $X_{\text{F}}/X_{\text{Cl}}$ ratios (Fig. 6.12). These crystals could have formed from a different melt to the high-Cl population, with altered mineral-melt exchange coefficients (K) or a different starting composition (i.e. C_i^0 ; Fig. 4.7). However, such low $X_{\text{Cl}}/X_{\text{OH}}$ apatite compositions would require very low C_{Cl}^0 (i.e. $< 0.1 \text{ wt\%}$; Fig. 4.7c,d) or extremely altered K values to the high-Cl population. These magma batches would have to repeatedly co-exist and mix before different eruptions and melt inclusion data do not support the presence of multiple magmas with different C_{Cl}^0 values. Furthermore, this model cannot

account for the absence of low-Cl apatite inclusions in pyroxene and biotite (Section 6.3.3.1.), as magma mixing would also involve any phenocrysts present in the magma.

The occurrence of low-Cl apatites only as microphenocrysts suggests that they were in contact with a different composition late-stage melt or fluid compared with the high-Cl population. Furthermore, if the process that resulted in formation of the low-Cl apatites occurred early in magmatic evolution, this population should occur as inclusions, which is not the case. Neither magmatic cooling or depressurisation during ascent can account for the low observed $X_{\text{Cl}}/X_{\text{OH}}$ ratios (Piccoli and Candela, 1994; Piccoli and Candela, 2002; Fig. 5.2). Chlorine-saturated crystallisation is discounted because it cannot cause trends towards very low $X_{\text{Cl}}/X_{\text{OH}}$ values (Fig. 4.10). However, compositional evolution towards low $X_{\text{Cl}}/X_{\text{OH}}$ and very high $X_{\text{F}}/X_{\text{Cl}}$ ratios is characteristic of crystallisation from H_2O -saturated melts at high $D_{\text{Cl}}^{\text{f/m}}$ values (≥ 25 ; Fig. 4.8). Such high $D_{\text{Cl}}^{\text{f/m}}$ values are typical of partitioning between melt and a supercritical hydrosaline fluid in phonolitic systems (Signorelli and Carroll, 2000). At magmatic temperatures (800 °C), the critical point occurs at ~150 MPa (Driesner and Heinrich, 2007; Lowenstern, 1994; Signorelli and Carroll, 2000), which is less than current magma storage pressures at Campi Flegrei (De Siena *et al.*, 2010; Zollo *et al.*, 2008), suggesting that a hydrosaline fluid in the magma storage region would be supercritical (as defined in Section 4.2.). The low-Cl microphenocryst population is therefore interpreted as a record of late-stage fluid saturation, as was predicted for Astroni 1 based on Rhyolite-MELTS models (Section 5.3.3.). The absence of the low-Cl apatite population in deposits from Astroni 1 may reflect short timescales between volatile-saturation and eruption, preventing the new melt environment from being recorded by crystallisation of overgrowths or re-equilibration of microphenocryst rims.

The medium-Cl population: The medium-Cl apatite population is characterised by a general positive correlation between $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{OH}}$, and between $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$, both with a shallower gradient than the high-Cl trend (Fig. 6.12). As with the low-Cl population, there are no textural constraints to determine the direction of medium-Cl compositional change during magmatic evolution. The trend could have formed through volatile-undersaturated crystallisation, with different C_1^0 (Fig. 4.7) or K values to the high-Cl trend. However, this again requires mixing of different magma batches, which is difficult to reconcile with the absence of medium-Cl inclusions.

The occurrence of medium-Cl apatites only as microphenocrysts again suggests that they formed through a late-stage process that did not affect the early-formed inclusions in the high-Cl population. Decreasing magma pressure or temperature would increase apatite $X_{\text{Halogen}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios (Fig. 5.2) and could account for the medium-Cl trend. However, depressurisation alone cannot account for the medium-Cl $X_{\text{Cl}}/X_{\text{OH}}$ range (which requires $\Delta P > 1$ GPa, based on the assumed liquid composition in Chapter 5) or the increase in $X_{\text{F}}/X_{\text{OH}}$ (Fig. 5.2; Piccoli and Candela, 1994; Piccoli and Candela, 2002). Fractionation modelling in Chapter 4 shows that the medium-Cl trend is consistent with volatile-saturated crystallisation. The medium-Cl trajectory could form through Cl-saturated crystallisation at high $D_{\text{H}_2\text{O}}^{\text{f/m}}$ (i.e. $\gtrsim 100$; Fig. 4.10) and/or high C_{Cl}^{s} (Fig. 4.11). Alternatively, the trend could reflect H_2O -saturated crystallisation at low $D_{\text{Cl}}^{\text{f/m}}$ (i.e. $\lesssim 10$; Fig. 4.8) and/or low $C_{\text{H}_2\text{O}}^{\text{s}}$ (Fig. 4.9), under sub-critical conditions at lower pressures than the high-Cl population (Driesner and Heinrich, 2007; Signorelli and Carroll, 2000).

If the medium-Cl apatites formed through increasing $X_{\text{Halogen}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ (i.e. decreasing PT or volatile-saturated crystallisation), relating them to the high-Cl population is difficult. The lowest $X_{\text{Halogen}}/X_{\text{OH}}$ apatites in the medium-Cl population have

lower $X_{\text{Cl}}/X_{\text{OH}}$ and higher $X_{\text{F}}/X_{\text{Cl}}$ ratios than the lowest $X_{\text{Halogen}}/X_{\text{OH}}$ high-Cl apatites (inset Fig. 6.12b). Moving from the high-Cl to the medium-Cl population (which would require decreasing $X_{\text{Cl}}/X_{\text{OH}}$ and increasing $X_{\text{F}}/X_{\text{Cl}}$) is therefore inconsistent with the volatile-undersaturated or fluorite-saturated crystallisation models in Chapter 4 (Figs 4.6, 4.13), or with decreasing pressure/temperature (Piccoli and Candela, 1994; Piccoli and Candela, 2002; Fig. 5.2). Decreasing $X_{\text{Cl}}/X_{\text{OH}}$ and increasing $X_{\text{F}}/X_{\text{Cl}}$ could be achieved though volatile-undersaturated crystallisation at $\bar{D}_{\text{Cl}}^{\text{c/m}} > 1$. This was not modelled in Chapter 4, as it contradicts the melt inclusion trend (Fig. 6.7a) but could occur during widespread late-stage sodalite crystallisation. However, although sodalite is present in some evolved Campi Flegrei eruptions (Melluso *et al.*, 1995; Vona *et al.*, 2013), it is absent in mafic eruptions, and both the Minopoli 1 and Pisani 1 include low $X_{\text{Cl}}/X_{\text{OH}}$ medium-Cl apatites. The only models in Chapter 4 that decrease $X_{\text{Cl}}/X_{\text{OH}}$ and increase $X_{\text{F}}/X_{\text{Cl}}$ are low $D_{\text{H}_2\text{O}}^{\text{f/m}}$ (i.e. ≤ 100) Cl-saturated crystallisation (Fig. 4.10) at low C_{Cl}^{s} (Fig. 4.11) or high $D_{\text{Cl}}^{\text{f/m}}$ (i.e. ≥ 10) H₂O-saturated crystallisation (Fig. 4.8) at high $C_{\text{H}_2\text{O}}^{\text{s}}$ (Fig. 4.9). Thus, identifying a single model that relates the high- and medium-Cl apatites and explains the medium-Cl trend is not possible. The medium-Cl signature likely formed in a fluid-saturated system, but may have experienced changing magmatic conditions (i.e. pressure and/or temperature) or $D_1^{\text{f/m}}$ as it formed.

6.4.2.3. Syn-eruptive processes

The following section attempts to account for some outliers in the dataset, which cannot be explained by varying extents of fractional crystallisation or changes in magma storage conditions, as detailed above. As magmas ascend and cool at the surface they undergo syn-eruptive crystallisation (Blundy and Cashman, 2001; Blundy and Cashman, 2005; Humphreys *et al.*, 2008). Apatites may continue to precipitate, forming newly crystallised

overgrowth rims of a different composition to their cores, and/or rehomogenise if they remain in equilibrium with a changing melt and/or fluid composition. In these cases, apatite cores preserving pre-eruptive compositions will be overgrown by new rims in equilibrium with a changing volatile signature. Subsequent rehomogenisation (e.g. during prolonged cooling) may cause the cores to be partially or completely overprinted. Syn-eruptive crystallisation has been identified in some explosive Campi Flegrei eruptions (e.g. Monte Nuovo) based on crystal size distributions (Piochi *et al.*, 2005), but this process is likely most prevalent in lava dome samples, which have a trachytic texture in thin section, indicating that they were not quenched on eruption and had a protracted cooling history at the surface.

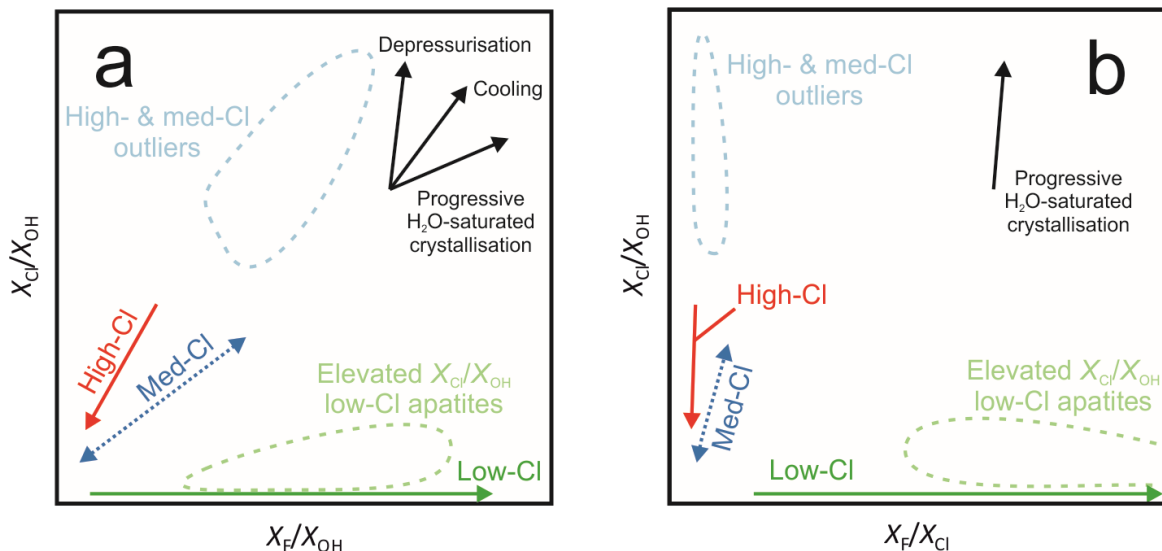


Figure 6.14 | Schematic figure showing the apatite populations identified in Campi Flegrei. Apatite volatile compositions are shown in X_{Cl}/X_{OH} versus X_F/X_{OH} space (a) and X_{Cl}/X_{OH} versus X_F/X_{Cl} space (b). Red = high-Cl trend, blue = medium-Cl trend, green = low-Cl trend. Single headed arrows show trajectories where the direction of compositional evolution is known, either from texturally constrained analyses or because only a single thermodynamic model (Chapters 4 and 5) can produce the range of observed apatite compositions. The double headed arrow shows where the direction of compositional evolution is unknown. The black arrows show the approximate trajectories of apatite compositional evolution during syn-eruptive cooling, depressurisation and low pressure H₂O-saturated crystallisation. The effects cooling and depressurisation on apatite X_F/X_{Cl} cannot be calculated using the model of Piccoli and Candela (1994). Dashed lines show where apatite compositions may have been affected by syn-eruptive processes (see discussion in text).

Thermodynamic expressions for the equilibrium constants (Piccoli and Candela, 1994) indicate that depressurisation and cooling would change apatite-melt K values, such that crystal $X_{\text{Halogen}}/X_{\text{OH}}$ ratios would increase, even if the melt composition remained constant (Piccoli and Candela, 1994; Piccoli and Candela, 2002; Fig. 5.2). Depressurisation reduces H_2O solubility in alkali melts (Fig. 4.4; Carroll and Blank, 1997; Di Matteo *et al.*, 2004; Schmidt and Behrens, 2008) and decreases $D_{\text{Cl}}^{\text{f/m}}$ values (Signorelli and Carroll, 2000). Therefore, low pressure H_2O -saturated crystallisation would also drive apatite compositions towards higher $X_{\text{Halogen}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios (Figs 4.8, 4.9), eventually forming end-member FAp (Boyce and Hervig, 2008; McCubbin *et al.*, 2011; Chapter 4). These processes are shown schematically in Figure 6.14.

Syn-eruptive apatite crystallisation or partial equilibration can explain a number of features in the Campi Flegrei dataset (Fig. 6.14): (1) although high-Cl apatites generally have a limited compositional range and plot on a near-linear array at low $X_{\text{Cl}}/X_{\text{OH}}$ ratios (typically <1.5), a single high-Cl microphenocryst from Minopoli 1 has a significantly higher $X_{\text{Cl}}/X_{\text{OH}}$ ratio (~ 2.5) and plots away from the main high-Cl population, towards the FAp end-member, in both binary (Fig. 6.12) and ternary (Fig. 6.9) space. This is consistent with crystallisation or partial re-equilibration on ascent, at lower pressures/temperatures or under low pressure H_2O -saturated conditions. (2) Partial syn-eruptive re-equilibration can explain the variability in low-Cl apatite $X_{\text{Cl}}/X_{\text{OH}}$ ratios. Supercritical hydrosaline fluid-saturated crystallisation is the only mechanism by which apatite compositions can evolve to low $X_{\text{Cl}}/X_{\text{OH}}$ and very high $X_{\text{F}}/X_{\text{Cl}}$ ratios (Section 4.8; Figs 4.8, 5.2) and is therefore necessarily implicated in forming the low-Cl apatite population. However, partial syn-eruptive re-equilibration at lower pressures/temperatures (with different apatite-melt K values), or during low pressure H_2O -saturated crystallisation, would variably increase $X_{\text{Halogen}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios even between

crystals from a single eruption (i.e. Monte Nuovo; Fig. 6.12), so low-Cl crystals that initially had $X_{\text{Cl}}/X_{\text{OH}} \approx 0$ would attain an elevated $X_{\text{Cl}}/X_{\text{OH}}$ signature (Fig. 6.14). (3) Degassing and low pressure/temperature crystallisation or re-equilibration is the likely cause of abundant end-member FAp microphenocrysts in lava dome eruptions, which may have spent decades cooling and crystallising at atmospheric pressure. (4) Syn-eruptive re-equilibration or crystallisation can account for high $X_{\text{Cl}}/X_{\text{OH}}$ (>1.5) medium-Cl microphenocryst ‘outliers’ from PP and the lava dome (i.e. Mt Olibano and Accademia) eruptions (Figs 6.12, 6.14). These are transitional between high- and medium-Cl populations (Fig. 6.9) and may have formed through partial re-equilibration of either population. Many of the medium-Cl apatites plot near to these ‘outliers’ at near end-member FAp compositions in ternary space (Fig. 6.9), suggesting that the medium-Cl trend formed from, or has been significantly affected by, shallow-crustal processes.

6.4.2.4. Crystallisation versus rehomogenisation

Having identified potential processes that formed the different apatite populations in Campi Flegrei, it would be useful to constrain *when* crystals attained their volatile signature. The high-, medium- and low-Cl apatite populations must either formed during primary crystallisation or by re-equilibration of existing crystals when changes occurred in the apatite-melt-fluid system, but these are difficult to distinguish. If crystals continually nucleated and preserve primary compositions, there may be a correlation between apatite core compositions and grain-size, as smaller microphenocrysts record conditions closer to the time of eruption. If the different populations formed through diffusive rehomogenisation, there may be a gradation between compositions that formed early in magmatic evolution in the cores of large crystals to compositions that formed later in magmatic evolution close to the rim. In the latter case, the smallest crystals could have rehomogenised their cores, entirely overwriting any primary record. This is difficult

to assess using the existing dataset, as most analyses were collected in the middle of crystals prepared in grain mounts; crystals were variably ground during sample preparation and the position of analyses in three dimensions (i.e. if crystal faces were on

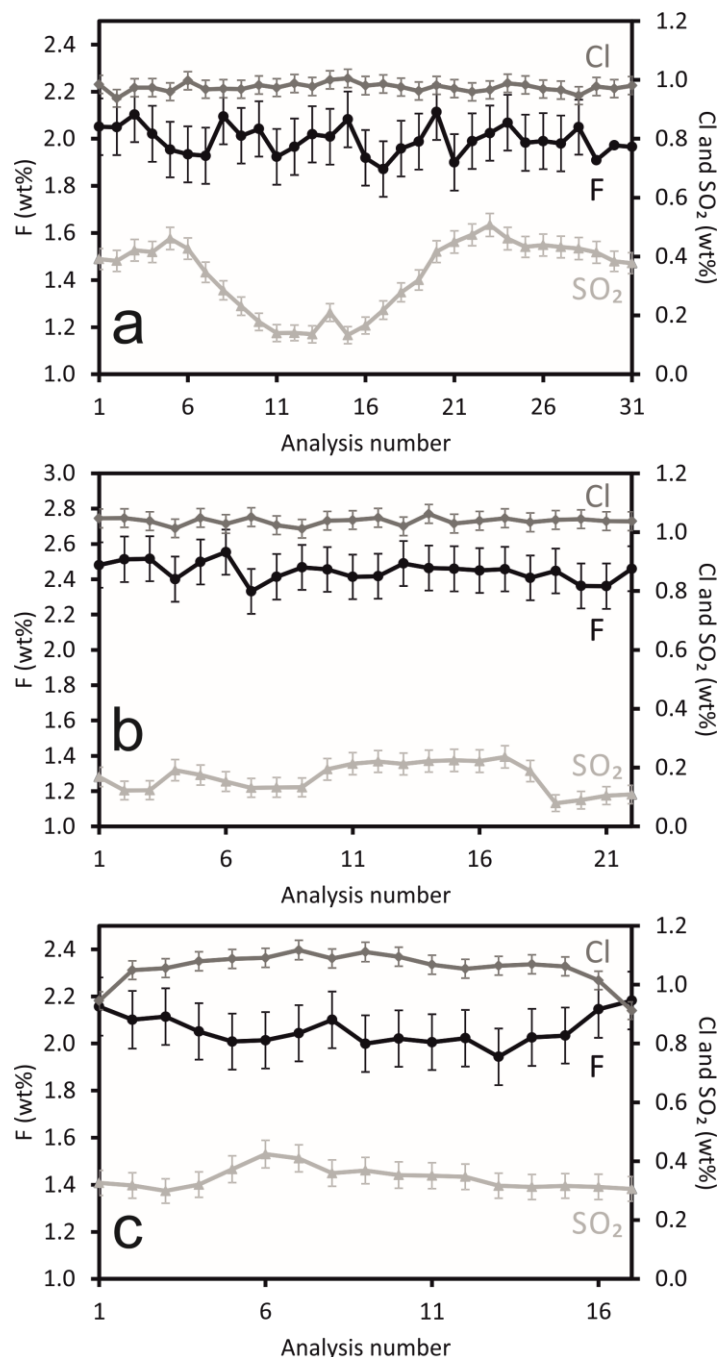


Figure 6.15 | Preliminary volatile zoning profiles across Campi Flegrei apatite microphenocrysts, measured by EPMA. Crystals are from the Monte Nuovo (a), Astroni 1 (b) and Pomici Principali (c) eruptions. Profiles were run rim-to-rim and F (black circles), Cl (dark grey diamonds) and SO₂ (light grey triangles) compositions are shown. Errors bars represent average precision with ± 1 s.d. Although there is some compositional variability across crystals, all analyses plot within the high-Cl population.

the plane of the mount, or crystals were ground to their centre) is unknown; and all grain mount microphenocrysts were in the 44-250 μm size fraction.

SIMS analyses close to rims of high-Cl Astroni 1 apatite microphenocrysts show no evidence of partial re-equilibration towards volatile-saturated (low- or medium-Cl) compositions (Chapter 5). However, this may be expected, given that no low-Cl crystals and few medium-Cl microphenocrysts were identified in this eruption (Fig. 6.11), suggesting short timescales between volatile-saturation and eruption (Section 6.4.2.2.). Preliminary EPMA transects across microphenocrysts (Fig. 6.15) show no transition between apatite populations (all profiles plot in the high-Cl population) and generally have constant F and Cl concentrations. However, there is a slight Cl depletion and F enrichment close to apatite rims in some profiles (Fig. 6.15c). Accademia was the only eruption in which microphenocrysts were analysed in both thin section and grain mounts. There is no systematic compositional variation with grain size in large crystals in grain mounts but smaller crystals ($<44\text{ }\mu\text{m}$) were measured in the thin sections and far more low-Cl compositions were identified. These data suggest that the apatite populations may have been affected by re-equilibration of pre-existing microphenocrysts but further investigation is required to confirm this interpretation.

6.4.3. The hydrous glass volatile record

Melt inclusion Cl concentrations correlate negatively with MgO, indicating Cl incompatibility during crystallisation prior to all Campi Flegrei eruptions in the past 15 kyr (Fig. 6.7a), and the preservation of primary magmatic concentrations. If melt inclusion halogens were altered post-entrapment they would be reset to the same F and Cl concentration regardless of their MgO content. Even partial re-equilibration would induce a non-linear correlation with MgO, as the degree of rehomogenisation would be a

function of the diffusive distance (i.e. the distance between inclusions and the crystal rim). There is no evidence of Cl buffering in the melt during magmatic evolution, negating brine-saturated crystallisation. Melt inclusion F concentrations show a lot of scatter, particularly at high MgO. This may be due to: minor post-entrapment crystallisation (although this was visually assessed before analysis); analytical difficulties associated with low-concentration F analysis; or post-entrapment re-equilibration of melt inclusion F contents. The latter is discounted as, although halogen diffusivities have not been measured in pyroxene, they are very slow in olivine (Bucholz *et al.*, 2013) and H diffusion is considerably faster in olivine than clinopyroxene (Ingrin and Blanchard, 2006). Fluorine correlates positively with MgO in more evolved Campi Flegrei melt inclusions (Fig. 6.7b), indicating incompatible behaviour and preservation of a primary magmatic volatile signature.

Melt inclusion H₂O concentrations do not correlate with MgO in any analysed samples, despite high-Cl apatite inclusions recording volatile-undersaturated crystallisation (Section 6.4.2.2.). In Chapter 5, this was attributed to rapid H diffusion ($\sim 10^{-2.1} \text{ ms}^{-2}$ to $\sim 10^{-3.4} \text{ ms}^{-2}$ at 700-850 °C) through clinopyroxene causing melt inclusion H₂O rehomogenisation within hours under magmatic conditions (Woods *et al.*, 2000). In contrast, apatite inclusion re-equilibration requires coupled volatile (OH-halogen or halogen-halogen) exchange and is rate-limited by host crystal halogen diffusion. Melt inclusions in this chapter show a larger range of H₂O contents than those measured in Astroni 1 (Figs 5.3, 6.7d). The highest H₂O concentration measured ($\sim 5.5 \text{ wt\%}$) was in an evolved, clinopyroxene-hosted melt inclusion from Monte Nuovo. However, assuming that melt inclusions have very low CO₂ contents, as is consistently reported in the Campi Flegrei literature (e.g. Arienzo *et al.*, 2010; Marianelli *et al.*, 2006; Appendix 3), this is significantly below H₂O saturation in evolved alkali melts at the assumed depth of magma

storage (i.e. 7-7.5 km, equating to pressures of ~170-180 MPa; De Siena *et al.*, 2010; Zollo *et al.*, 2008; Section 6.4.2.2), which is between ~6.33 wt% (at 150 MPa, 870 °C; Carroll and Blank, 1997) and ~7.5 wt% (at 200 MPa, 900-950 °C; Fig. 4.4; Webster *et al.*, 2014). If melt inclusions were trapped during volatile-undersaturated crystallisation, I would expect H₂O to correlate positively with MgO, as H₂O behaves incompatibly during magmatic evolution (Fig. 5.4). As this is not observed, melt inclusions must record H₂O concentrations at lower pressures, where phonolite H₂O solubilities are reduced (e.g. Fig. 4.4; Carroll and Blank, 1997). It is unlikely that low pressure crystallisation during ascent was sufficient to have formed all of the melt inclusion-bearing phenocrysts analysed in this study. Thus, melt inclusions must have re-equilibrated at shallow crustal levels during ascent, recording variably degassed compositions, as inferred for Astroni 1 (Section 5.3.1.).

Melt inclusion H₂O concentrations measured in this study cluster at 2-3 wt% (Fig. 6.7d), which is the H₂O solubility of CO₂-free phonolites at 50-65 MPa (Fig. 4.4) and equates to a storage depth of ~2-3 km (based on a melt density of 2,440 kgm⁻³, calculated using the method of Lange and Carmichael, 1990). This is the depth of a regional crustal discontinuity at Campi Flegrei, caused by a change in the basement lithology (Zollo *et al.*, 2008). Melts stalled at this depth during Campi Flegrei seismic crises in the 1980s (Woo and Kilburn, 2010) and during renewed activity in 2012/13 (D'Auria *et al.*, 2015). The melt inclusion data from past deposits therefore suggest that magmas repeatedly stalled at the same shallow depth, re-setting their H₂O contents before eruption. Greater variability is observed in melt inclusion H₂O concentrations from evolved eruptions (Fig. 6.7d), potentially reflecting faster ascent and shorter timescales of shallow crustal storage and re-equilibration.

Matrix glasses consistently record low H₂O concentrations that correlate negatively with MgO (Fig. 6.8d). The range of matrix H₂O concentrations within a single eruption (i.e. 0.1-1.1 wt% in PP) precludes the interpretation that this reflects variations in H₂O solubility at atmospheric pressure. More likely, the trend reflects variably efficient syn-eruptive degassing, with mafic eruptions entirely degassed and more rapidly quenched felsic samples retaining H₂O. In this case, the range of matrix glass H₂O concentrations within a single eruption may reflect proximity to bubble walls or cracks and thus the dynamics of ascent (i.e. bubble size distribution).

Fluorine concentrations are approximately constant in matrix glasses from most eruptions (except Monte Nuovo) but show a slight positive correlation with MgO (Fig. 6.8b). This contrasts with melt inclusions, which typically show a negative correlation between F and MgO (Figs 5.2, 6.7b; Section 6.4.3.), suggesting a change in F compatibility late in magmatic evolution (after biotite-hosted melt inclusion entrapment). As $D_F^{v/m} < 1$ in magmatic systems (Aiuppa et al., 2009a; Baker and Alletti, 2012), F is retained in the melt during vapour exsolution and the decrease in matrix glass F concentration must either reflect partitioning into apatite or fluorite. Apatite saturates early in crystallisation and Rhyolite-MELTS models show no evidence for increased modal apatite crystallisation at low temperatures (Fig. 5.4). Furthermore, high-Cl apatite F concentrations typically only differ by <1 wt% and there is no systematic variability in the F contents of low- or medium-Cl apatites between different eruptions, which could account for the correlation between matrix glass F and MgO. The variability in Campi Flegrei matrix glass F concentrations is therefore likely related to late-stage fluorite saturation. The concentration at which fluorite buffers F in melts increases with temperature and A/NK in CaO-rich, peraluminous and metaluminous systems (Dolejš and Baker, 2006; Scaillet and Macdonald, 2004), such as the eruptions analysed in this study

(except Monte Nuovo; Fig. 6.4). Campi Flegrei matrix glass A/NK ratios generally decrease with magmatic evolution (Fig. 6.4b). Thus, the correlation between matrix glass MgO and F concentrations likely reflects a small change in fluorite stability, due to decreasing A/NK and/or temperature during magmatic evolution. Additionally, fluorite stability is suppressed by low melt μCaO (where μ is chemical potential; Dolejš and Baker, 2004; Dolejš and Baker, 2006; Scaillet and Macdonald, 2004) and is therefore expected to be limited in magmas that crystallised significant quantities of plagioclase feldspar, as this extracts Ca from the melt (Bohrson *et al.*, 2006; Cannatelli, 2012; Fowler *et al.*, 2007). This may explain the marked enrichment of F in Monte Nuovo matrix glass, which has the lowest Ca concentration and underwent significant feldspar crystallisation during magma ascent (Piochi *et al.*, 2005).

Under magmatic conditions, phonolite $D_{\text{Cl}}^{\text{v/m}} > 1$ (Signorelli and Carroll, 2002) but matrix glasses have similar Cl contents to clinopyroxene-hosted melt inclusions, indicating that the Cl did not degas after vapour saturation (Figs 6.8, 6.9). In Chapter 5, this was attributed to slower diffusion of Cl than H_2O in silicate melts (Baker *et al.*, 2005) inducing a kinetic vapour-melt Cl disequilibrium during ascent, and the preservation of Cl-enriched matrix glass compositions. Inter-eruptive variability in matrix glass Cl concentrations therefore likely reflects different degrees of enrichment by fractional crystallisation. Low Cl (<0.6 wt% Cl) analyses in evolved (i.e. ≤ 0.5 wt% MgO) matrix glasses from Astroni 1 and Monte Nuovo (Fig. 6.8a) may be close to a crack or vesicle wall and record syn-eruptive degassing, whereby Cl has been extracted into the vapour phase (e.g. Signorelli and Carroll, 2000). Alternatively, they could record sodalite saturation in the most evolved melts, whereby Cl became compatible in the crystallising mineral assemblage. Sodalite-saturated crystallisation could cause depleted apatite $X_{\text{Cl}}/X_{\text{OH}}$ and elevated $X_{\text{F}}/X_{\text{Cl}}$ ratios. However, it cannot be responsible for the low-Cl

apatite population, as this is present in deposits from mafic eruptions (e.g. Minopoli 1 and Pisani 1), which do not have depleted matrix glass Cl concentrations. There is no apatite population exclusive to the most evolved eruptions, suggesting that if sodalite is responsible for depleted matrix glass Cl concentrations *sodalite-in* is not recorded by apatite compositions. As with fluorite (Section 6.4.2.2.), this may be because pre-eruptive sodalite saturation occurred on shorter timescales than are recorded by apatite crystallisation or re-equilibration.

6.4.4. A three-stage model of pre-eruptive fluid evolution at Campi Flegrei

The glass and apatite analyses in this chapter suggest a three-stage model of pre-eruptive fluid evolution at Campi Flegrei, which holds for all the analysed eruptions from the past 15 kyr, except Fondi di Baia (see Section 6.4.4.1.). The model is summarised in the schematic Figures 6.14 and 6.16.

Stage 1: Campi Flegrei melts initially undergo volatile-undersaturated crystallisation (t_1 in Fig. 6.16; Chapter 5), forming the high-Cl apatite population (Figs 4.6, 6.11, 6.12). These are trapped within clinopyroxene and biotite phenocrysts and become isolated from the melt. Halogens behave incompatibly at this time and become concentrated in the melt. Melt inclusions trapped during this stage, would initially record volatile-undersaturated crystallisation (i.e. H_2O and MgO negatively correlate). This crystallisation is assumed to occur at 7-7.5 km based on the current magma storage depth at Campi Flegrei (De Siena *et al.*, 2010; Zollo *et al.*, 2008). Shallower storage (i.e. <150 MPa) would cause volatile saturation before *biotite-in* (Fig. 5.4) and clinopyroxene- and biotite-hosted apatite inclusions would record different compositional trends (Section 4.8.), which is not observed in the natural dataset.

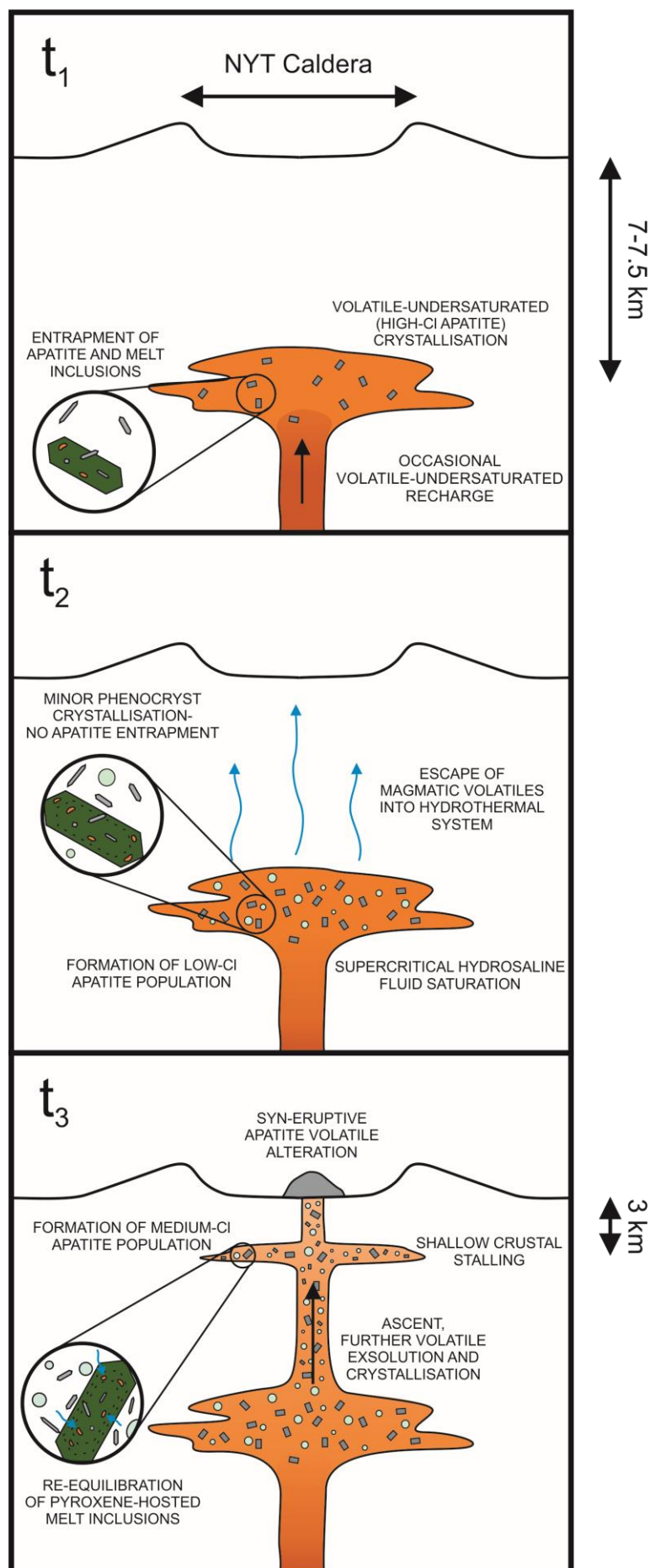


Figure 6.16 | (previous page) Schematic figure showing the three-stage model of pre-eruptive fluid evolution in Campi Flegrei from the past 15 kyr. At t_1 , the melt undergoes volatile-undersaturated crystallisation, forming the high-Cl apatite population. These are trapped as inclusions within pyroxene and biotite. At t_2 , the melt saturates in H_2O , forming a supercritical hydrosaline fluid. Apatites crystallise and/or partially re-equilibrate to form the low-Cl population. Magmas ascend and erupt at t_3 . Melt inclusions rehomogenise and the medium-Cl apatite population forms during ascent and short-term stalling at shallow crustal levels. All apatite populations show some evidence of syn-eruptive re-equilibration. Approximate depths are shown on the right (not to scale).

Stage 2: Protracted crystallisation concentrates H_2O in the melt, which eventually saturates, forming a free fluid (t_2 in Fig. 6.16). At 7-7.5 km (170-180 MPa), this would be supercritical (as defined in Section 4.2.; Driesner and Heinrich, 2007). Rhyolite-MELTS models (Fig. 5.4) and the absence of low- or medium-Cl (i.e. volatile-saturated) apatite populations in biotite-hosted inclusions (trapped at low-temperature; Chapter 5) suggest that substantial crystallisation occurs before H_2O saturation. Melt inclusion compositions show that Cl behaves incompatibly during magmatic evolution (Figs 6.7, 6.8; Section 6.4.3.) and Cl will therefore be concentrated in melt at the point of H_2O -saturation. Supercritical hydrosaline fluid-melt ‘apparent’ Cl partition coefficients ($\hat{D}_{Cl}^{f/m}$) are higher in more Cl-enriched systems (up to >100; Signorelli and Carroll, 2000). Thus, after supercritical hydrosaline fluid exsolution, further crystallisation rapidly extracts Cl from the melt into the fluid phase, and apatites crystallise and/or re-equilibrate to form the low-Cl population (Fig. 4.8; 6.12). Magma storage after supercritical hydrosaline fluid exsolution must be brief (days-months), to prevent microphenocryst re-equilibration with their host melts (Section 5.3.2.). The lack of low-Cl apatite inclusions also suggests only limited growth of new phenocrysts. At low temperatures, the H_2O content of Campi Flegrei melts will increase significantly over a short temperature interval (Fig. 5.4), leading to volatile-saturation and pressurisation, causing the chamber walls to fail (Fig. 5.6) and permitting magma ascent after H_2O -saturation.

Stage 3: As evolved alkali magmas ascend to low pressure, the solubilities of H₂O (Carroll and Blank, 1997; Schmidt and Behrens, 2008) and Cl (Signorelli and Carroll, 2000; Signorelli and Carroll, 2002) are reduced, the NaCl-H₂O fluid becomes sub-critical (Driesner and Heinrich, 2007) and $D_{\text{Cl}}^{\text{f/m}}$ decreases overall (Signorelli and Carroll, 2000; Signorelli and Carroll, 2002). These effects cause apatite compositions to evolve towards elevated $X_{\text{Halogen}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios (Figs 4.8, 4.9). Furthermore, alteration of apatite-melt K values increases crystal $X_{\text{Cl}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{OH}}$ ratios (Fig. 5.2; Piccoli and Candela, 1994; Piccoli and Candela, 2002). During ascent, some crystals in the high- and low-Cl populations partially re-equilibrate, producing elevated $X_{\text{Cl}}/X_{\text{OH}}$ outliers (Fig. 6.14), and the medium-Cl population forms, either through re-equilibration or primary crystallisation (Fig. 6.12). Melt inclusion H₂O concentrations are reset on ascent, clustering at ~2-3 wt%, indicating short-term stalling or slowing at ~2-3 km depth. Melt inclusion rehomogenisation can occur within hours at magmatic temperatures (Woods *et al.*, 2000) but the timescales of shallow storage must be short to prevent complete apatite microphenocryst rehomogenisation (days-months; Section 5.3.2.) or entrapment of medium- and low-Cl apatite inclusions that would indicate volatile-saturated conditions. Short timescales of pre-eruptive shallow crustal storage are consistent with the timescales of seismicity and uplift reported prior to the Monte Nuovo eruption (Guidoboni and Ciuccarelli, 2011).

6.4.4.1. Fondi di Baia

Fondi di Baia contains medium- and low-Cl apatite microphenocryst populations (Fig. 6.12), which suggests that it shares the same late-stage pre-eruptive fluid history as other Campi Flegrei eruptions (above). However, Fondi di Baia also contains clinopyroxene- and biotite-hosted apatite inclusions with low $X_{\text{Cl}}/X_{\text{OH}}$ and high $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ ratios

relative to inclusions in other eruptions, which plot within the medium-Cl apatite population (Fig. 6.11). Fondi di Baia clinopyroxene-hosted apatite inclusions extend to lower $X_{\text{Cl}}/X_{\text{OH}}$ and higher $X_{\text{F}}/X_{\text{Cl}}$ ratios than the biotite-hosted apatite inclusions. Both clinopyroxene- and biotite-hosted inclusions have lower $X_{\text{Cl}}/X_{\text{OH}}$ and higher $X_{\text{F}}/X_{\text{Cl}}$ ratios than high-Cl microphenocryst (Figs 6.11, 6.12). This is different to the temporal trend identified in apatite inclusions from Astroni 1 (Figs 5.1, 5.2).

In Section 6.4.2.3., increasing $X_{\text{F}}/X_{\text{Cl}}$ in the medium-Cl apatite population was interpreted as demonstrating volatile-saturated crystallisation. However, the temporal trend of decreasing $X_{\text{F}}/X_{\text{Cl}}$ with crystallisation in Fondi di Baia apatites (identified through comparison of apatite inclusions and microphenocrysts, as in Chapter 5) is inconsistent with crystallisation in the presence of a free fluid phase (which always causes increasing apatite $X_{\text{F}}/X_{\text{Cl}}$ ratios; Section 4.8.). The temporal trend in Fondi di Baia apatites is consistent with isothermal decompression but would require high ΔP (hundreds of MPa), with no change in melt composition (Fig. 5.2; Piccoli and Candela, 1994; Piccoli and Candela, 2002). Alternatively, Fondi di Baia apatites may record volatile-undersaturated crystallisation with different $\bar{D}_i^{c/m}$ values to other Campi Flegrei eruptions (lower $\bar{D}_F^{c/m}$ or $\bar{D}_{\text{Cl}}^{c/m}$, or higher $\bar{D}_{\text{H}_2\text{O}}^{c/m}$; Fig. 4.6), for example through a change in the modal assemblage. Fondi di Baia was the first eruption of Epoch 2 and occurred on the western side of the caldera after a long hiatus in activity. The deposits are highly evolved (Figs 6.5, 6.6) and comprise crystal-poor pumices (crystallinity $\ll 1\%$; Mastrolorenzo and Pappalardo, 2006), suggesting long timescales of crystallisation and mush accumulation. Fondi di Baia is one of a small number of isotopically distinct Epoch 2 eruptions (Di Renzo *et al.*, 2011) and produced glasses with unique trace element compositions (Smith *et al.*, 2011). One interpretation is that prolonged crustal assimilation during magma storage subtly altered the melt composition, changing the liquid lines of descent for volatile and trace

elements, thus causing a different trajectory of volatile-undersaturated apatite evolution compared with the other analysed eruptions, and distinctive matrix glass trace element compositions. The degree of assimilation must have been insufficient to change the magmatic major element composition, as Fondi di Baia sits on the same evolutionary trend as the other analysed eruptions (Figs 6.5, 6.6; Section 6.4.1.). Campi Flegrei major element liquid lines of descent can remain unaltered with <5-10% syenite/skarn assimilation (Fowler *et al.*, 2007) or ~2% assimilation of the granitic basement beneath in the Campanian region (D'Antonio *et al.*, 2007). The data presented here are limited and further research is required to establish how the distinctive Fondi di Baia compositions were generated.

6.4.5. The sulphur content of Campi Flegrei melts

Sulphur is incorporated into the apatite through substitutions for PO_4^{3-} (Pan and Fleet, 2002; Peng *et al.*, 1997), and absolute concentrations can therefore be interpreted independently of the F-Cl-OH exchange. The negative correlation between SO_2 and P_2O_5 and the weak positive correlation with SiO_2 (Fig. 6.13) in Campi Flegrei apatite, supports incorporation primarily through the $\text{S}^{6+} + \text{Si}^{4+} \rightleftharpoons 2\text{P}^{5+}$ substitution mechanism (Pan and Fleet, 2002; Peng *et al.*, 1997). A weak correlation with Na_2O (largely below EPMA detection limit) suggests that some of the SO_2 versus SiO_2 scatter may be due to limited $\text{S}^{6+} + \text{Na}^+ \rightleftharpoons \text{P}^{5+} + \text{Ca}^{2+}$ substitution (Pan and Fleet, 2002; Peng *et al.*, 1997). In either case, although apatite SO_2 diffusivities have not been determined in apatite, coupled substitution likely inhibits diffusion and re-homogenisation (as is the case for REEs, which are also incorporated into apatite as a coupled substitution; Cherniak, 2000), causing crystals to retain SO_2 records on longer timescales than other volatiles.

There is a positive correlation between SO_2 and MgO in melt inclusion analyses (Fig. 6.7c), indicating SO_2 compatibility during magmatic evolution. This is supported by

the observed presence of sulphide minerals in Campi Flegrei samples. Apatite microphenocryst SO_2 concentrations are higher than in apatite inclusions. Additionally, a single preliminary transects across a large apatite microphenocryst has a defined SO_2 -poor core, with an SO_2 -enriched overgrowth mantle (Fig. 6.15a). These provide information about magmatic processes in the build-up to eruption (e.g. degassing, mixing, fractionation) and could be used to quantify pre-eruptive gas emissions (e.g. Scott *et al.*, 2015). However, in addition to melt composition, apatite SO_2 incorporation depends on $f\text{O}_2$ and temperature, which can vary crystal SO_2 concentrations by up to two orders of magnitude (Peng *et al.*, 1997). I currently have insufficient data to deconvolve these controls on apatite SO_2 compositions. However, the evidence outlined above suggests a complex history of pre-eruptive magmatic sulphur evolution, which should be explored in future work (Section 7.2.3.).

6.4.6. Inter-eruption variability in pre-eruptive magma volatile contents

The high-Cl apatite population records volatile-undersaturated crystallisation during the entrapment of apatite inclusions in clinopyroxene and biotite, and while high-Cl microphenocrysts were in equilibrium with the melt (Chapter 5; Section 6.4.4.). Although there is significant overlap, high-Cl apatites from individual eruptions have distinct volatile compositions. In this section, I attempt to identify the cause of variability in high-Cl apatite microphenocryst compositions between different eruptions.

Thermodynamic modelling results (Chapters 4 and 5; Candela, 1986; Piccoli and Candela, 1994) indicate that the most likely factors producing the distinctive high-Cl apatite compositions in different eruptions are variations in magma storage conditions (i.e. PT) or volatile composition during crystallisation. Pressure variations are unrealistic because a very large pressure range would be required to cause the compositional

diversity of high-Cl apatites ($\Delta P \approx 1$ GPa based on the assumed liquid composition in Chapter 5; Section 5.4.3.) and this is significantly greater than current Campi Flegrei magma storage pressures (~ 170 - 180 MPa; De Siena *et al.*, 2010; Zollo *et al.*, 2008). Furthermore, shallow storage ($\lesssim 150$ MPa, based on comparison of Rhyolite-MELTS models and experimental H_2O solubility data; Fig. 5.4) would cause volatile-saturation before *biotite-in* and I would expect to see medium- or low-Cl apatite populations (i.e. compositions consistent with volatile saturation) as biotite-hosted inclusions: these are not present.

Variations in temperature are difficult to discount because high-Cl apatite microphenocrysts typically have higher $X_{\text{Halogen}}/X_{\text{OH}}$ ratios in more evolved eruptions, which underwent greater cooling and are further down the fractionation path defined by Rhyolite-MELTS (Section 6.4.1.). Elevated $X_{\text{Halogen}}/X_{\text{OH}}$ is the predicted effect of decreasing temperature changing apatite-melt K values (Fig. 5.2; Piccoli and Candela, 1994). A significant temperature control would therefore be expected to produce a correlation between the degree of magmatic evolution (i.e. decreasing matrix glass MgO; Fig. 6.6) and high-Cl apatite $X_{\text{Halogen}}/X_{\text{OH}}$ ratios (Fig. 6.12). A weak correlation is seen (Figs 6.6, 6.12) but despite being more evolved (and thus cooler), high-Cl apatite $X_{\text{Halogen}}/X_{\text{OH}}$ ratios from PP are similar to those from Pisani 1 and Minopoli 1; Astroni 1 is significantly more evolved than PP but apatite $X_{\text{Halogen}}/X_{\text{OH}}$ ratios overlap; $X_{\text{Halogen}}/X_{\text{OH}}$ ratios from more mafic latitic-trachytic lava domes (based on whole rock data; Melluso *et al.*, 2012; Pappalardo and Mastrolorenzo, 2012) are significantly higher than those from the highly evolved Monte Nuovo eruption (Fig. 6.3). As discussed in Section 6.4.2., modelling suggests that, if the high-Cl population represents a cooling trend, the $X_{\text{Cl}}/X_{\text{OH}}$ diversity would require a large temperature change ($\Delta T > 300$ °C based on the assumed liquid composition in Chapter 5) and should be accompanied by a greater variation in

X_F/X_{OH} than is observed in the natural data (Fig. 5.2; Section 5.4.3.). Furthermore, in Astroni 1, textural constraints demonstrate that apatites within the high-Cl population have $X_{Halogen}/X_{OH}$ ratios that decrease during magmatic evolution. This is inconsistent with changing temperature and suggests that melt composition has a greater effect on the high-Cl apatite compositions. High-Cl apatite $X_{Halogen}/X_{OH}$ ratios group more clearly by their eruption date (see below) than by degree of fractionation (and thus temperature). For these reasons, I suggest that inter-eruptive variability in high-Cl apatite $X_{Halogen}/X_{OH}$ ratios likely reflects differences in the pre-eruptive magmatic volatile budgets of Campi Flegrei eruptions, rather than a cooling trend.

There is no clear compositional distinction between the medium- or low-Cl apatite populations from the different eruptions. This may be because crystals record variable timescales of re-equilibration or crystallisation under volatile-saturated conditions.

6.4.6.1. Temporal variability in pre-eruptive H_2O concentrations

Excluding the high X_{Cl}/X_{OH} (values >2) crystal, which was likely affected by syn-eruptive rehomogenisation (Section 6.4.2.3.), the high-Cl apatite microphenocryst $X_{Halogen}/X_{OH}$ ratios are generally similar in the Epochs 1 and 2 deposits but distinctly higher in Epoch 3 (Fig. 6.17). Post-Epoch 3 high-Cl microphenocrysts from Monte Nuovo cover the entire compositional range measured in other eruptions. Epoch 3 apatite inclusions also have higher $X_{Halogen}/X_{OH}$ ratios than those from Epoch 1 (Fig. 6.11). In Monte Nuovo, apatite inclusions have a more limited compositional range than microphenocrysts, with similar $X_{Halogen}/X_{OH}$ and X_F/X_{Cl} ratios to the Epoch 3 Astroni 1 eruption. Epoch 2 apatite inclusions (from Fondi di Baia) have high X_F/X_{OH} ratios and low X_{Cl}/X_{OH} (Section 6.4.4.1.).

In Astroni 1, apatites have $X_{Halogen}/X_{OH}$ ratios that decrease during magmatic evolution, from clinopyroxene-hosted apatite inclusions to biotite-hosted apatite

inclusions to microphenocrysts (Fig. 5.2). At the same time, there is an increase in glass halogen concentrations (Fig. 5.3). Although the high-Cl apatite population identified in this chapter follows the same compositional trend as the Astroni 1 apatites, glass halogen

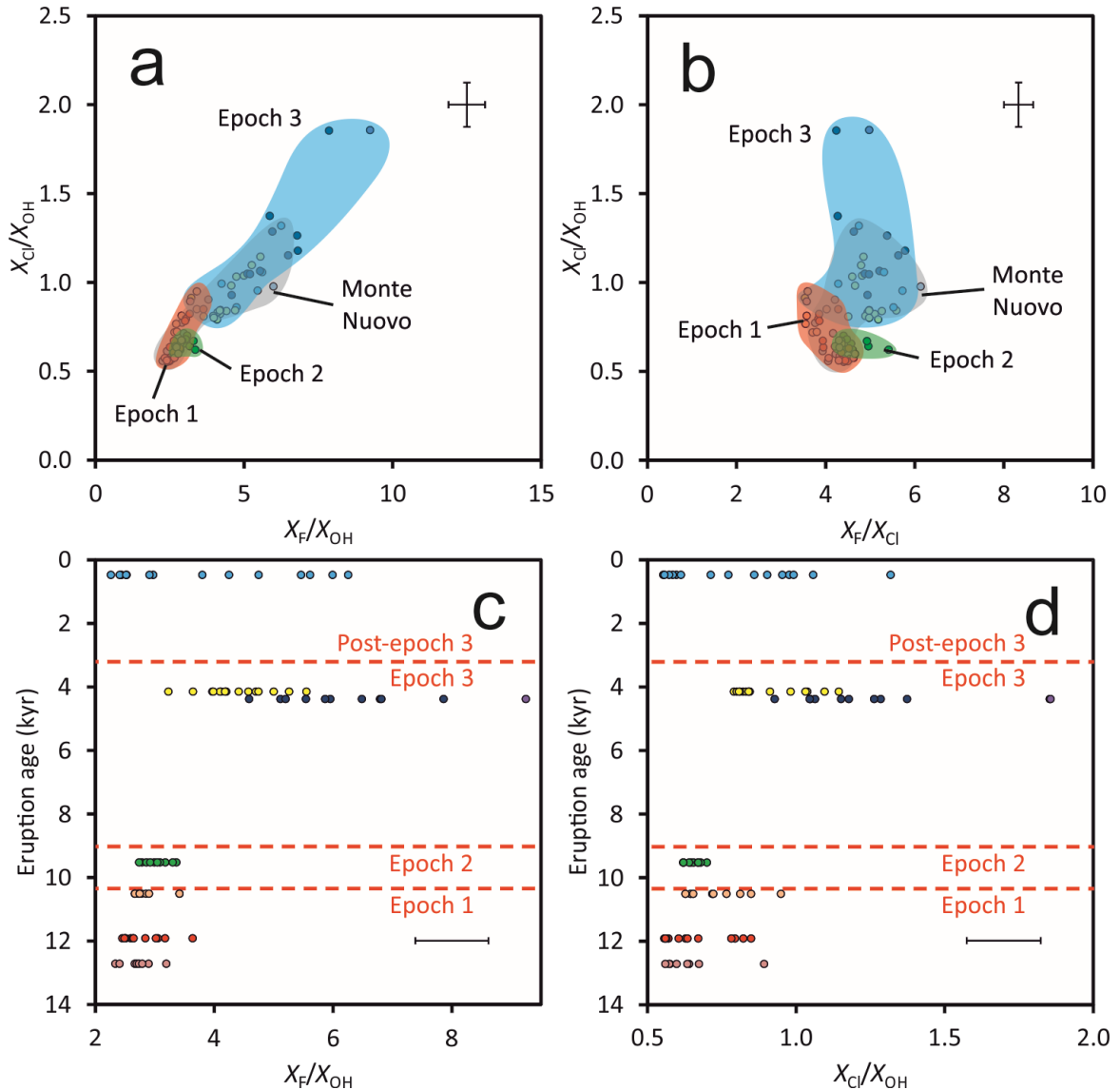


Figure 6.17 | The correlation between high-Cl apatite microphenocryst volatile composition and eruption age. **a**, Apatite compositions in X_{Cl}/X_{OH} versus X_F/X_{OH} space. **b**, Apatite compositions in X_{Cl}/X_{OH} versus X_F/X_{Cl} space. Coloured fields show the range of apatite compositions from Epoch 1 (red), Epoch 2 (green), Epoch 3 (blue) and the post-Epoch 3 Monte Nuovo eruption (grey). **c,d**, Eruption ages from Smith *et al.* (2011) versus apatite X_F/X_{OH} and X_{Cl}/X_{OH} , respectively. All apatite compositions were measured by SIMS. Red dashed lines show repose periods between the different epochs of activity. The Minopoli 1 high-Cl ‘outlier’ is excluded as it likely re-equilibrated syn-eruption (see discussion in text). Errors bars represent precision with a 95% confidence interval. Data are distinguished by eruption (see legend in Figure 6.9).

concentrations are typically higher in eruptions which contain the highest $X_{\text{Halogen}}/X_{\text{OH}}$ high-Cl apatites (Figs 6.7, 6.11, 6.12); in Epoch 1, high-Cl apatites have lower $X_{\text{Cl}}/X_{\text{OH}}$ ratios than in Epoch 3 but melt inclusions also have lower Cl concentrations (Figs 6.7, 6.11, 6.17). The reduced halogen contents of Epoch 1 glasses is consistent with their more primitive major element compositions (Figs 6.5, 6.6) but H_2O concentrations should be correspondingly lower because H_2O is less compatible than F and Cl during magmatic evolution at Campi Flegrei. Thus, I would expect Epoch 1 apatites to have higher $X_{\text{Halogen}}/X_{\text{OH}}$ ratios than Epoch 3 apatites. This disparity in high-Cl apatite compositions is unlikely due to variations in $\bar{D}_i^{c/m}$, as glass compositions follow the same liquid line of descent (Figs 6.5, 6.6) and apatite evolution follows the same compositional trajectory within analytical uncertainty (Figs 6.11, 6.12). One way to interpret this is that the disparity between Epoch 1 and Epoch 3 high-Cl apatites (Fig. 6.17) reflects a systematic difference in the melt compositions at *apatite-in* (C_i^0), altering apatite compositions without significantly changing mineral phase stabilities or the trajectory of apatite compositional evolution. Specifically, the offset to lower $X_{\text{Halogen}}/X_{\text{OH}}$ ratios suggests higher starting H_2O concentrations ($C_{\text{H}_2\text{O}}^0$), in Epoch 1 than Epoch 3 (Fig. 4.7). A slight offset to lower $X_{\text{F}}/X_{\text{Cl}}$ ratios in Epoch 1 high-Cl apatites (Fig. 6.17b) may also reflect a change in C_{F}^0 and/or C_{Cl}^0 within analytical uncertainty.

High-Cl apatite microphenocrysts $X_{\text{Halogen}}/X_{\text{OH}}$ ratios from Fondi di Baia (Epoch 2) are similar to those from Epoch 1 eruptions (Fig. 6.17). However, matrix glass halogen concentrations are comparable to those from Epoch 3 (Fig. 6.8). This suggests that pre-eruptive Epoch 2 H_2O concentrations were higher than those in Epoch 3 but lower than in Epoch 1, assuming a similar K_D . This may reflect variability in Epoch 2 C_i^0 values. However, Fondi di Baia apatites follow a different compositional trajectory to other eruptions during magmatic evolution, and glasses have a unique trace element signature

(Smith *et al.*, 2011). As discussed in Section 6.4.4.1., this may reflect prolonged crustal assimilation altering the magmatic volatile budget by changing $\bar{D}_i^{c/m}$ values during on long timescales crustal storage. Further research is required to verify this hypothesis and to identify whether Fondi di Baia is representative of Epoch 2 eruptions.

Monte Nuovo apatite and melt inclusions are compositionally similar to those from the Epoch 3 Astroni 1 eruption (Fig. 6.11), suggesting similar C_i^0 values. However, high-Cl apatite microphenocrysts from Monte Nuovo cover almost the entire compositional range identified in other eruptions (Fig. 6.17). As this range is not observed in apatite inclusions, it must reflect a late-stage process. Monte Nuovo matrix glasses have high F concentrations relative to other eruptions (Fig. 6.8b) but the F-enriching process (possibly syn-eruptive feldspar crystallisation; Section 6.4.3.) must have occurred on shorter pre-eruptive timescales than apatite microphenocryst crystallisation or re-equilibration with the melt, as significantly elevated X_F/X_{OH} and X_F/X_{Cl} ratios are not observed. This therefore cannot explain the range of high-Cl microphenocryst compositions. Monte Nuovo is the only analysed eruption that shows evidence for magma mingling in glass major and trace element compositions (Smith *et al.*, 2011) and one possible explanation is that the apatite compositional range also reflects late-stage mixing between different magma batches. However, if the high-Cl apatite compositional diversity is the result of pre-eruptive magma mixing, I would expect to see a similar variability in inclusion compositions (as clinopyroxene and biotite phenocrysts would also be mixed) and a range in matrix glass halogen concentrations, which is not observed. Consequently, the mechanism by which Monte Nuovo preserves a restricted range of apatite inclusion compositions but a diversity of microphenocryst compositions is currently unclear.

Rhyolite-MELTS modelling demonstrates that magmatic H_2O concentrations at *apatite-in* ($C_{H_2O}^0$) do not change significantly due to variations in pressure (50-300 MPa)

or fO_2 ($QFM+1 < fO_2 < NNO+1.5$; Fig. 5.4). Rather, the H_2O concentration of Campi Flegrei melts at *apatite-in* is more dependent on L_{H_2O} (Fig. 5.4). This suggests that the variability in apatite compositions in deposits from different epochs of activity does not reflect changing magma storage conditions, which could occur as a result of spatial differences in vent locations (i.e. along the NYT caldera rim in Epoch 1 and centralised within the caldera in Epochs 2 and 3; D'Antonio *et al.*, 1999b; Smith *et al.*, 2011), but temporal variability in the H_2O concentration of primitive melts feeding the Campi Flegrei system. This is compatible with isotopic evidence, which suggests that Epochs 1 and 2 were fed by the 'Minopoli 2 end-member' and 'NYT end-member' (i.e. high crustal contamination, plus a high slab derived fluid and/or low subducted sediment mantle wedge input) primitive melts, whereas Epoch 3 and post-Epoch 3 Monte Nuovo eruptions were fed by the 'NYT end-member' and 'Astroni 6 end-member' (i.e. low crustal interaction, plus a reduced slab derived fluid and/or low subducted sediment mantle wedge input) components (Section 6.1.1.; D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2011). The difference in primitive H_2O concentrations between Campi Flegrei eruptions can only be assessed qualitatively from apatite analysis because my interpretation of the melt inclusions is that their H_2O concentrations have been reset during shallow storage (Section 6.4.3.). However, L_{H_2O} can vary within the range 2 to 3 wt% without significantly altering the liquid line of descent of Campi Flegrei melts (Cannatelli, 2012; Fowler *et al.*, 2007).

In summary, of the eruptions analysed, apatite compositions suggest that PP, Pisani 1 and Minopoli 1 had the highest pre-eruptive H_2O contents, the Epoch 2 Fondi di Baia eruption had lower pre-eruptive H_2O than the Epoch 1 events, and that the Epoch 3 Astroni 1 eruption had the lowest pre-eruptive H_2O concentrations. These are interpreted as representing a progressive decrease in the H_2O content of primitive melts (i.e. the

parental magma) feeding the Campi Flegrei system with time. Apatite inclusion compositions suggest that H₂O content of the post-Epoch 3 Monte Nuovo primitive melt was similar to that of Astroni 1.

6.4.6.2. *Links between pre-eruptive H₂O concentration and volcanic eruption style*

Assuming that variability in high-Cl microphenocryst volatile contents largely reflects variability pre-eruptive H₂O concentrations, apatite compositions can be used to explore the link between magmatic volatile composition and eruptive style at Campi Flegrei. The viscosity of silicate melt exerts a fundamental control on the size and style of volcanic eruptions (Cashman and Sparks, 2013; Giordano *et al.*, 2008) and is largely a function of major element chemistry (Lange, 1994). However, there is no correlation between glass composition and eruption style at Campi Flegrei: Fondi di Baia was a highly evolved, but small, pyroclastic eruption, whereas PP was a large Plinian eruption that produced less fractionated melts (Fig. 6.6); the Accademia lava dome eruption was trachytic (Melluso *et al.*, 2012), whereas the tephri-phonolitic Minopoli 1 event was explosive (Fig. 6.3). Volatile exsolution drives volcanic eruptions (Cashman, 2004), and variability in pre-eruptive volatile concentrations has previously been implicated in controlling the style of volcanic eruptions (Raia *et al.*, 2000). This relationship is poorly-constrained (Barclay *et al.*, 1996; Roggensack *et al.*, 1997), partly due to limitations of melt inclusion analysis (Lowenstern, 1995), but may be investigated using the late-stage volatile record preserved by apatite microphenocrysts.

There is not a well-defined link between eruption size and the inferred pre-eruptive volatile contents of Campi Flegrei eruptions analysed in this chapter (Fig. 6.18). However, matrix glasses from PP are less evolved than those from Astroni 1 and therefore have less viscous anhydrous compositions (Giordano *et al.*, 2008). The former eruption produced ~14 times more material (DRE; Smith *et al.*, 2011) and has significantly lower

$X_{\text{Halogen}}/X_{\text{OH}}$ ratios in the high-Cl apatite microphenocrysts (Fig. 6.18), despite comparable matrix glass halogen concentrations (Fig. 6.8), implying higher pre-eruptive H_2O concentrations in the larger eruption. Similarly, although matrix glasses from Fondi di Baia were more evolved than PP, it was significantly smaller (Smith *et al.*, 2011) and apatite analyses suggest lower melt H_2O concentrations (Section 6.4.6.1.). $X_{\text{Halogen}}/X_{\text{OH}}$ ratios are lower in Minopoli 1 and Pisani 1 high-Cl microphenocrysts than in Fondi di Baia and Astroni 1, suggesting that the melts were more H_2O rich. This may be responsible for their producing larger eruptions (Smith *et al.*, 2011), despite their low-viscosity mafic anhydrous compositions (Giordano *et al.*, 2008). Finally, despite their trachytic and latitic compositions, undegassed high-Cl microphenocrysts from the Accademia and Mt Olibano eruptions extend to the lowest $X_{\text{Halogen}}/X_{\text{OH}}$ ratios of any eruption analysed. Although glass halogen analyses could not be obtained for these eruptions, this implies very low melt H_2O concentrations.

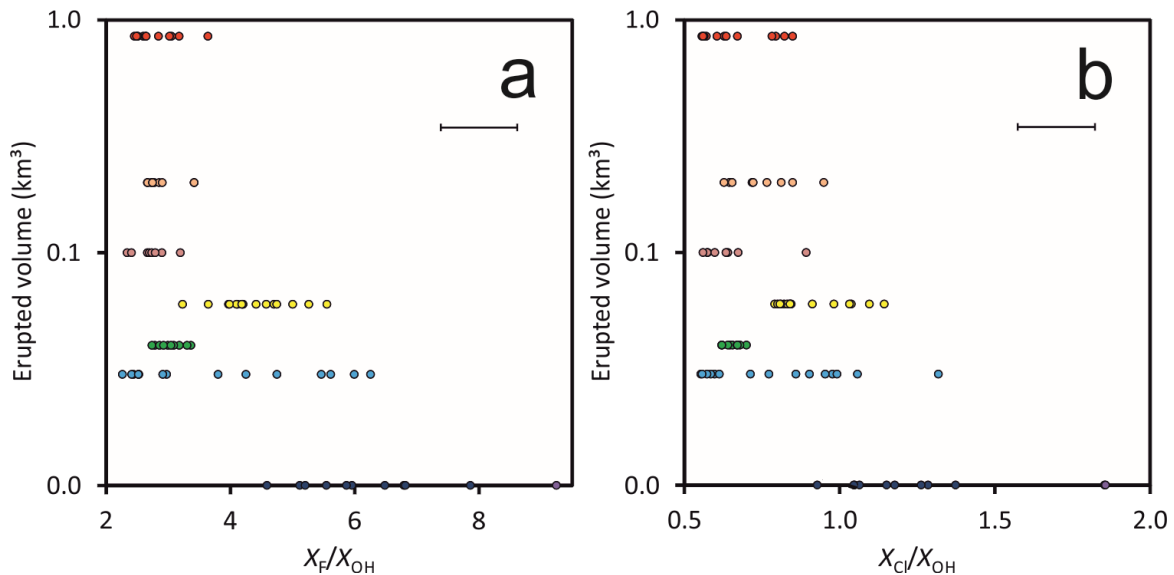


Figure 6.18 | High-Cl apatite microphenocryst volatile compositions versus erupted volume. a,b, Erupted volume estimates from Smith *et al.* (2011) versus $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{Cl}}/X_{\text{OH}}$, respectively. All apatite compositions were measured by SIMS. The Minopoli 1 high-Cl ‘outlier’ is excluded as it likely re-equilibrated syn-eruption (see discussion in text). Error bars represent precision with a 95% confidence interval. Data are distinguished by eruption (see legend in Figure 6.9).

The style of volcanic activity is a complex function of magma ascent velocity and supply rate, melt rheology, conduit geometry, and the efficiency of syn-eruptive gas loss (Barclay *et al.*, 1996; Cashman, 2004; Cashman and Sparks, 2013; Dunbar and Hervig, 1992; Edmonds *et al.*, 2014; Melnik and Sparks, 1999). Although the major controls on eruption style and magnitude are the magma supply rate and syn-eruptive factors (e.g. ascent velocity, melt rheology) that control the ability for gas to escape (Cashman, 2004), the data in this chapter suggest that variability in pre-eruptive H₂O concentrations may also influence the size and style of eruptions at Campi Flegrei, as in the tectonically and compositionally similar Vesuvius system (Raia *et al.*, 2000). Explosive mafic eruptions in Epoch 1 have high inferred H₂O contents and effusive lava domes or smaller explosive eruptions in Epoch 3 have lower inferred pre-eruptive H₂O budgets (Fig. 6.18). Thus, larger or more explosive eruptions could reflect increased volatile oversaturation and/or greater fluid phase expansion during the ascent of volatile-enriched melts (Edmonds *et al.*, 2014; Métrich and Wallace, 2008). Furthermore, higher inferred L_{H₂O} concentrations in more mafic Epoch 1 eruptions would suggest that volatile saturation occurred earlier in magmatic evolution during Epoch 1. Although late-stage volatile saturation (Chapter 5) is not a ubiquitous triggering mechanism, the attainment of volatile saturation earlier in magmatic evolution is consistent with this mechanism initiating eruptions with more primitive matrix glass compositions in Epoch 1.

6.5. Conclusions

Apatite inclusions indicate that magmas were volatile-undersaturated until late in the crystallisation history of eight Campi Flegrei eruptions from the past 15 kyr, spanning the entire range of volcanic eruption styles. Distinct compositional trends in apatite microphenocrysts suggest a three-stage model of magmatic fluid evolution on short pre-eruptive timescales for Campi Flegrei eruptions, which can be interpreted through

comparison with the thermodynamic fractionation models developed in Chapter 4. In the first stage, magmas evolve through volatile-undersaturated crystallisation at depth, giving rise to high-Cl apatite inclusions and microphenocrysts. In the second stage, the magmas were saturated with a supercritical hydrosaline fluid at high pressure, resulting in apatites with very low X_F/X_{OH} and high X_F/X_{Cl} . Finally, apatite microphenocrysts preserve evidence of low pressure, vapour-saturated conditions on ascent into the shallow crust, causing crystal compositions to trend towards end-member FAp. In all eruptions, melt inclusion H_2O concentrations have been reset and record only low pressure, H_2O -saturated conditions. The clustering of melt inclusion H_2O concentrations at 2-3 wt% suggests rehomogenisation at ~2-3 km, corresponding with the depth of magma emplacement during recent seismic crises at Campi Flegrei (D'Auria *et al.*, 2015; Woo and Kilburn, 2010).

Comparison between high-Cl apatite microphenocryst and inclusion compositions reveals systematic differences in pre-eruptive magma volatile concentrations between different Campi Flegrei eruptions. This is interpreted as the result of a decrease in the H_2O concentration of primitive melts feeding the Campi Flegrei system through time. Changes in the inferred primitive melt volatile composition broadly correlate with the different epochs of activity at Campi Flegrei, in agreement with isotopic evidence for different melts entering the system (D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2011). Variations in pre-eruptive H_2O concentrations are not obviously linked with eruption style, likely reflecting the complexity of other syn-eruptive processes that give rise to different types volcanic activity (Cashman, 2004; Cashman and Sparks, 2013). However, they may explain part of the variability in the volume of material produced in different eruptions, the occurrence of explosive mafic eruptions, and the restricted timing of effusive volcanic activity in the Campi Flegrei system.

Chapter 7

Summary and conclusions

In this thesis, I have explored the use of apatite as a novel petrologic method for assessing magmatic volatile compositions, and used this to gain new insights into pre-eruptive processes at Campi Flegrei. Apatite analysis has major advantages over the established melt inclusion approach, principally due to the timescales of mineral-melt equilibration. Fluorine-Cl-OH diffusion is rapid in apatite, causing crystals to remain in equilibrium with their host melts on geologically short timescales (Brenan, 1993). However, these timescales are longer than those of ascent (Cashman and Sparks, 2013), permitting microphenocrysts to preserve a record of pre-eruptive conditions when matrix glasses degas at low crustal pressures. Melt inclusion H₂O contents may rehomogenise syn-eruption, due to the rapid diffusion of H through host phenocrysts (Ingrin and Blanchard, 2006; Woods *et al.*, 2000). In contrast, OH is incorporated into apatite as part of a coupled substitution with F and Cl, and very slow halogen diffusion through the host mineral limits the rate of diffusive rehomogenisation: apatite inclusions preserve a record of entrapment conditions.

The disadvantage of the apatite approach is its inability to provide *quantitative* information about magmatic volatile concentrations. Using the approach developed in this thesis, *qualitative* determination of magmatic fluid systematics can be achieved through comparison of apatite populations and identification of broad compositional trends.

However, the key limitation of using minerals where volatiles are incorporated as integral constituents is that the mineral compositions can only be related to their host melts as volatile ratios (i.e. X_{Cl}/X_{OH} , X_F/X_{OH} and X_F/X_{Cl}), inhibiting quantitative interpretation.

In the introduction, I subdivided this thesis into three main themes: analysis, interpretation and application. Below, I summarise how each of these research objectives has been addressed, reviewing the conclusions of Chapters 3, 4, 5 and 6. I close by briefly outlining possible avenues for future research.

7.1. Summary of chapter conclusions

7.1.1. Analysis

Chapter 3 investigates the cause of widely-reported time-dependent variability in halogen X-ray count rates during apatite electron microprobe analysis (EPMA; e.g. Goldoff *et al.*, 2012; Stormer *et al.*, 1993). This was found to be an intrinsic crystallographic response to electron-beam exposure. Sample irradiation induces steep thermal gradients that increase halogen diffusivity close to the surface (Nouiri *et al.*, 2006; Shan *et al.*, 2013). Simultaneously, charge build-up repels volatile anions away from the centre of the EPMA interaction volume. These combined effects result in migration of halogen ions towards the surface, likely through interstitial crystal sites in the *c*-axis channel. As halogen ions accumulate at the surface, emerging X-rays experience less matrix attenuation, causing an increase in halogen count rates. After prolonged electron-beam exposure, apatite crystals begin to undergo thermally-induced breakdown and halogens are lost from the surface, reducing X-ray counts. Higher beam currents amplify the thermal and electric fields, increasing the propensity for halogen migration. The effect is highly anisotropic, due to the orientation of the anion channel site parallel to *c*-axis, and detectable migration is only possible in the *a*-axis direction at high beam currents. Furthermore, migration is

considerably more prevalent in F-rich apatites, because large anions (Cl^- and likely OH^-) are incorporated off mirror planes in the crystal structure, altering the geometry of the interstitial sites and inhibiting migration. By identifying the mechanism of electron-beam induced halogen X-ray count rate variability in apatite, this study permits the identification of optimal EPMA operating conditions. Furthermore, the inferred mechanism suggests that halogens may relax back to their original positions with sufficient time or with sample heating, following irradiation.

7.1.2. Interpretation

In Chapter 4, thermodynamic models were developed to determine some theoretical trajectories of apatite compositional evolution during fractional crystallisation, building on preliminary work by Candela (1986). The models either describe volatile undersaturated crystallisation, or fractionation in the presence of one or more magmatic fluid phase. All of the models presented in this chapter are relevant to the Campi Flegrei system. Input parameters were varied over a realistic range, to investigate the compositional space that can be accessed in each crystallisation scenario. Although some compositional trajectories are reproduced by more than one model, overlap often involves extreme, end-member input parameters. In most cases, the compositional evolution of apatite in $X_{\text{Cl}}/X_{\text{OH}}$ versus $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{Cl}}/X_{\text{OH}}$ versus $X_{\text{F}}/X_{\text{Cl}}$ space can be used to distinguish magmatic fluid systematics. For example, volatile-undersaturated crystallisation typically causes a decrease in apatite $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ as a function of magmatic evolution. In contrast, $X_{\text{F}}/X_{\text{OH}}$ and $X_{\text{F}}/X_{\text{Cl}}$ increase if the melt is saturated in H_2O or Cl. Under H_2O -saturated conditions at low pressure, vapour-melt Cl partition coefficients are low (Signorelli and Carroll, 2002) and consequently apatite $X_{\text{Cl}}/X_{\text{OH}}$ ratios increase during magmatic evolution. In high-pressure H_2O -saturated Cl-rich systems,

supercritical hydrosaline fluid-melt Cl partition coefficients are high (Signorelli and Carroll, 2002), causing elevated apatite X_F/X_{Cl} ratios, and X_{Cl}/X_{OH} ratios to approach zero over a short crystallisation interval. In combination with simulations of apatite volatile evolution as a function of pressure and temperature (Piccoli and Candela, 1994; Piccoli and Candela, 2002), these models can be compared with the compositional diversity of natural apatite populations to qualitatively constrain magmatic fluid systematics at the time of apatite-melt equilibrium.

7.1.3. Application to Campi Flegrei

Chapters 5 and 6 investigate pre-eruptive processes at Campi Flegrei on different temporal scales, through comparison of apatite and hydrous glass compositions. The aim of these chapters is to explore the information that can be attained through the novel use of apatite as a magmatic volatile ‘probe’ in terrestrial sub-volcanic systems. In Chapter 5, the compositions of melt inclusions, apatite inclusions and matrix phases are used to determine how pre-eruptive magmatic volatile contents varied in the build-up to a single eruption: Astroni 1. Chapter 6 investigates variability in these pre-eruptive processes and the concentrations of dissolved magmatic volatile species during the long-term development of the Campi Flegrei system. In both chapters, apatite inclusions record pre-eruptive conditions, while melt inclusions can be shown to have partially re-equilibrated on ascent and matrix glasses are variably degassed.

Chapter 5 shows that in Astroni 1, the magmatic system remained persistently volatile-undersaturated throughout most of its crystallisation history. Even microphenocrysts in contact with the melt at the time of eruption preserve volatile-undersaturated compositions close to their rims. Rhyolite-MELTS models (Gualda *et al.*, 2012) suggest that volatile saturation occurred shortly after entrapment of biotite-hosted

inclusions. Once saturation is achieved, the volume of the exsolved volatile phase would increase markedly over a short temperature interval, which means that magma storage region would become pressurised and the fracture criterion could be exceeded with very little additional crystallisation. Late-stage volatile saturation is therefore suggested as a likely trigger for the Astroni 1 eruption. As H_2O becomes concentrated in the melt phase during volatile-undersaturated crystallisation, mafic magma chamber recharge may introduce lower- H_2O melts into the system, effectively ‘diluting’ the volatile content. This implies that the interval between eruptions at Campi Flegrei depends directly on recharge rate and the timescale of upper crystal storage. Furthermore, diffusion constraints show that volatile saturation and final ‘priming’ of the system into a genuinely pre-eruptive state may only occur a few days to months before eruption. This has significant implications for monitoring of Campi Flegrei and other hazardous systems, suggesting that ground-deformation and seismic evidence for long-term magma chamber assembly may not represent legitimate precursory activity. Rather, pre-eruptive activity may be characterised by the attainment of volatile saturation. As saturation may only occur shortly before eruption, this study provides a potential mechanism to explain the occurrence of some eruptions with little or no geodetic ‘warning’.

Apatite inclusions and microphenocrysts from other eruptions also retain a volatile-undersaturated signature, again suggesting that saturation occurred late in magmatic evolution. However, two additional microphenocryst populations are identified, based on their distinct Cl compositions. Through comparison with the thermodynamic models developed in Chapter 4, these are used to construct a three-stage model of pre- or syn-eruptive magmatic fluid evolution for Campi Flegrei eruptions. The first stage is characterised by volatile-undersaturated crystallisation at depth, forming ‘high-Cl’ apatites. This continues over a significant crystallisation interval, until after entrapment of

biotite-hosted apatite inclusions. The depth of crystallisation is assumed to be ~ 7 -7.5 km, corresponding with the current magma storage region at Campi Flegrei (De Siena *et al.*, 2010; Zollo *et al.*, 2008). Protracted crystallisation causes H₂O to become concentrated in the melt. It eventually saturates (through second boiling), causing exsolution of a supercritical hydrosaline fluid. Chlorine partitions strongly into the aqueous phase, forming a ‘low-Cl’ apatite population with depleted $X_{\text{Cl}}/X_{\text{OH}}$ ratios. In the final stage of the model, a third ‘medium-Cl’ apatite population forms due to lower fluid-melt Cl partition coefficients during ascent at low pressures. Melt inclusions from Campi Flegrei are variably degassed, but H₂O concentrations cluster at ~ 2 -3 wt%. This equates to a rehomogenisation depth of ~ 2 -3 km, corresponding with a regional change in basement lithology (Zollo *et al.*, 2008) and magma emplacement depths during recent seismic crises (D’Auria *et al.*, 2015; Woo and Kilburn, 2010).

Apatite microphenocrysts also reveal a systematic difference in the pre-eruptive volatile contents of different Campi Flegrei eruptions. The data suggest variability in the H₂O concentrations of primitive melts feeding the system, which is linked with the different epochs of activity. This is in agreement with isotopic evidence, which suggests a temporal change in the composition of primitive melt feeding the system (Di Renzo *et al.*, 2011). Controls on the style of volcanic activity are complex (e.g. Barclay *et al.*, 1996; Cashman, 2004; Cashman and Sparks, 2013; Dunbar and Hervig, 1992; Edmonds *et al.*, 2014; Melnik and Sparks, 1999). However, explosive mafic eruptions appear to have high pre-eruptive H₂O concentrations, whereas evolved effusive eruptions only occur in the epoch characterised by low apparent pre-eruptive H₂O concentrations. Higher inferred pre-eruptive H₂O concentrations correlate with eruptive volume in samples with similar anhydrous compositions. This may indicate that pre-eruptive volatile concentrations influence the style of volcanic eruptions at Campi Flegrei.

7.2. Future work

In Chapters 5 and 6, interpretation of apatite compositions has provided new constraints on magmatic volatile evolution at Campi Flegrei, both in the build-up to explosive eruptions and over the long-term evolution of the system. Important foci for future work should be further development of the theoretical thermodynamic framework for interpreting igneous apatite compositions, and broader application of apatite as a magmatic volatile ‘probe’, both at Campi Flegrei and in other volcanic systems. This will allow refinement of the hypotheses developed in this thesis and determination of their wider validity. A few particularly important topics for future research are outlined below.

7.2.1. Investigate the effect of electron-beam exposure on pure ternary apatites

The effect of electron-beam exposure on apatite was determined in natural, near end-member fluorapatite and chlorapatite only (Chapter 3). The study was therefore unable to constrain the electron-beam effect on OH migration. It was hypothesised that incorporation of large anions (Cl^- and OH^-) essentially ‘closes’ the interstitial sites exploited by migrating halogens. However, the propensity for electron-beam induced migration in ternary F-Cl-OH apatite remains unknown. One possibility is that electron-beam induced halogen migration only occurs in near end-member fluorapatite. In this case, ternary compositions may not be subject to the same analytical limitations and higher beam currents could be employed to reduce detection limits and analytical uncertainties. Goldoff *et al.* (2012) report a non-linear relationship between X-ray count rate variability and halogen compositions in Cl-rich apatites. In Chapter 3 this was suggested to result from variable trace element incorporation in natural samples, affecting the nature of interstitial sites in the *c*-axis channel. Future work should therefore focus on

systematically investigating halogen migration in pure, synthetic ternary apatites (e.g. Hovis and Harlov, 2010; Hovis et al., 2014a) to mitigate this effect.

7.2.2. Develop and validate the theoretical framework for apatite interpretation

Experimental validation: The models developed in Chapter 4 provide theoretical trajectories of apatite compositional development during magmatic evolution. Future studies should validate these experimentally by cooling and fractional crystallisation of volatile-saturated and undersaturated melts, in which apatite is on the liquidus. Preliminary experiments of this type have been undertaken on lunar samples by Ustunisik *et al.* (2015) and Ustunisik *et al.* (2011). In their experiments, there is a decrease in the apatite Cl component during open-system degassing, with compositions trending towards end-member fluorapatite (Ustunisik *et al.*, 2011). In volatile-undersaturated experiments, they observe a trend towards OH-rich compositions (Ustunisik *et al.*, 2015). This is in good agreement with the thermodynamic predictions in Chapter 4 but further experimental constraints are required. In particular, Mathez and Webster (2005) suggest that apatites may trend towards Cl-rich compositions during near-solidus equilibrium crystallisation in layered intrusions, where co-existing melts and fluids were trapped in intercumulus layers and became highly saline. In volcanic systems, there is unlikely to be sufficient crystallisation to trap such Cl-rich liquids within localised closed-systems. However, further experimental and theoretical development may permit any effect of melt composition on apatite-melt volatile exchange to be integrated into the thermodynamic models.

Quantification of model outputs: A powerful application of the thermodynamic fractionation models would be to quantitatively relate apatite compositions to dissolved

magmatic volatile concentrations. This represents the next step in the development of the methods used in this thesis and should be a focus for future research. Quantification of natural magmatic volatile concentrations from apatite analysis is challenging, due to the incorporation of volatiles into crystals as part of an exchange equilibria. However, this may be possible through combined empirical analysis, thermodynamic modelling and experimental work. Quantification would specifically require a precise understanding of apatite-melt exchange coefficients and the concentrations of two of F, Cl or H₂O in the melt phase at the time of apatite-melt equilibration. The concentrations of two magmatic volatile components could be estimated using fractionation models if mineral-melt and/or fluid-melt partition coefficients, starting compositions and the degree of crystallisation are known. This would be easiest in systems where significant experimental work has already been undertaken, particularly in alkaline systems that contain abundant modal apatite (e.g. Laacher See; Berndt *et al.*, 2001; Harms *et al.*, 2004). Although difficult, development of a quantifiable apatite hygrometer would be extremely useful, given the increasing concern regarding reliability of the melt inclusion volatile record (Lowenstern, 2003; Moore *et al.*, 2015).

Constraining volatile diffusivities in apatite: The timescales of crystal-melt volatile diffusion and re-equilibration are a major advantage of the apatite approach. Measured F-Cl-OH diffusivities in apatite are rapid, permitting crystals to re-equilibrate with their host melts on geologically short timescales (Brenan, 1993); the lack of evidence for syn-eruptive rehomogenisation indicates short residence times in the new melt/fluid composition. Furthermore, unlike melt inclusions, apatite inclusions appear not to re-equilibrate through their host phenocrysts on pre-eruptive timescales at Campi Flegrei. However, volatile diffusion rates in apatite remain poorly constrained, with the only quantitative diffusivity estimates provided by Brenan (1993) at 1 atm and 1 GPa. For this

reason, the timescales of pre-eruptive volatile saturation in Astroni 1 (at ~170 MPa, Chapter 5) can only be estimated in the range $10 - 10^3$ days. Experimental work to determine mineral-melt re-equilibration times under magmatic conditions (i.e. hundreds of MPa) would permit this timescale to be constrained further. Additionally, investigation of halogen diffusion rates through common host phenocrysts would permit determination of the timescales within which apatite inclusions can preserve a record of entrapment conditions. This would be particularly important if apatites were to be used for assessing fluid conditions in slow cooling plutonic settings.

7.2.3. Further determine magmatic processes at Campi Flegrei

Magmatic processes in Fondi di Baia: Apatite compositions indicate that pre-eruptive magmatic processes in the Fondi di Baia eruption are clearly different to the other eruptions analysed in Chapter 6. This is supported by major and trace element compositions of erupted glasses (Smith *et al.*, 2011). However, the cause of this anomaly remains largely unknown. Further research should aim to understand processes in the build-up to the Fondi di Baia event. Specifically, exploring major element, trace element and isotopic zoning in phenocrysts (e.g. Arienzo *et al.*, 2016) could aid in re-constructing magmatic processes and verify the hypothesised role of crustal contamination in magmatic evolution. Fondi di Baia is particularly significant because it represents the first eruption in Epoch 2, following a long repose period (Smith *et al.*, 2011), and may therefore be analogous to the next eruption of the Campi Flegrei system.

Further constraint on temporal variability: Data presented in Chapter 6 suggest that there was a temporal change in the H₂O contents of primitive melts feeding the Campi Flegrei system, which correlates with the different epochs of volcanic activity. Further analysis of apatite microphenocrysts expelled during other eruptions from the past 15 kyr will test

this hypothesis. In particular, apatites should be measured in other eruptions from Epoch 2 (e.g. St Martino), so that the pre-eruptive H₂O concentrations in this period may be better compared with Epochs 1 and 3. A second priority might be the Agnano-Monte Spina eruption, which is the only large explosive event in Epoch 3. The hypothesis developed in Chapter 6 suggests that this eruption should have low pre-eruptive H₂O concentrations, despite being of a similar size and bulk composition (i.e. phonolitic-trachytic) to Pomici Principali (Smith *et al.*, 2011). Analysis of apatite microphenocrysts and melt inclusions from this eruption may permit further investigation of the relationship between pre-eruptive H₂O concentrations and the size and style of volcanic activity at Campi Flegrei.

Investigate pre-eruptive SO₂ evolution: In combination, a difference between the SO₂ contents of apatite inclusions and microphenocrysts, preliminary apatite zoning profiles, and melt inclusion data presented in Chapter 6 suggest a complex history of pre-eruptive magmatic SO₂ evolution. Apatite SO₂ concentrations are a function of magma composition, temperature and *f*O₂ (Peng *et al.*, 1997). These variables are currently insufficiently constrained to permit interpretation of apatite SO₂ contents in Campi Flegrei. However, the data presented in this thesis demonstrate that this would be a valuable avenue for future work, which could provide new constraints on magmatic processes (e.g. degassing, mixing, fractionation) and, importantly, may allow the first quantification of pre-eruptive SO₂ emissions at Campi Flegrei (e.g. Scott *et al.*, 2015).

7.2.4. Apply apatite as a volatile ‘probe’ in other volcanic systems

In this thesis, apatite analysis has been shown to provide useful constraints on pre-eruptive magmatic volatile contents and fluid systematics. The next stage of research will see this method applied in other volcanic systems.

Use in independently-constrained systems: In addition to experimental constraints, the use of apatite as a pre-eruptive volatile ‘probe’ may be corroborated through application in natural magmatic systems with independently-constrained volatile systematics. Pre-eruptive fluid systematics may be identified through phase equilibria constraints (Barclay *et al.*, 1998; Devine *et al.*, 1998), other hydrous minerals (e.g. amphibole; Humphreys *et al.*, 2009; Rowe *et al.*, 2008) or fluid inclusions (Roedder, 1992). Analysis of apatite inclusions and microphenocrysts in these systems (e.g. Soufrière Hills) offers an opportunity to further validate the thermodynamic models and interpretations in this thesis.

Wider identification of volatile-undersaturation: Many studies of Campi Flegrei have assumed that olivine- and pyroxene-hosted melt inclusions preserve a record of volatile-saturated conditions at the time of entrapment (e.g. Arienzo *et al.*, 2016; Arienzo *et al.*, 2010; Isaia *et al.*, 2009; Mangiacapra *et al.*, 2008). This represents a common assumption in the volcanological literature. However, apatite inclusions and thermodynamic Rhyolite-MELTS modelling in Campi Flegrei show the preservation of volatile-undersaturated conditions until late in the crystallisation history of the evolving magmas (i.e. after biotite-saturation), suggesting that melt inclusion compositions have been altered post-entrapment. The potential for post-entrapment melt inclusion degassing is not surprising, given the fast diffusion of H in pyroxene (Woods *et al.*, 2000) and olivine (i.e. the most common melt inclusion host phenocrysts; Ingrin and Blanchard, 2006), but this has only been recognised recently. Apatite could provide a viable check on the fidelity of melt inclusion records. Even qualitatively, the apatite approach presented in this thesis has the ability to test the assumption of volatile saturation in volcanic systems. Future work should apply this in other volcanic systems to identify whether they are saturated in volatiles or, instead, whether prolonged volatile undersaturation (as identified in Chapter

5) is more common than has been previously recognised. It would be particularly useful to compare the results of this study with a similar investigation of an evolved tholeiitic system, such as Santorini, where magmatic H₂O solubilities are lower (Baker and Alletti, 2012).

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Appendix 1

Secondary ion mass spectrometry depth profiles

The data in this appendix were published as supplementary material in:

Stock M.J., Humphreys M.C.S., Smith V.C., Johnson R.D., Pyle D.M., and EIMF, 2015.

New constraints on electron-beam induced halogen migration in apatite.

American Mineralogist, 100, 281-293, doi: 10.2138/am-2015-4949.

The baseline-normalised SIMS depth profiles presented in this appendix are used in Chapter 3 to determine the anionic redistribution in apatite crystals that results from electron-beam exposure. ‘Low power’ and ‘routine’ electron-beam operating conditions are detailed in Table 3.2.

FAp parallel to c-axis, 'low power' conditions 540 second irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	2.59	0.06	3.66	1.41
3	0.033	2.69	0.05	2.46	0.91
4	0.044	2.06	0.04	1.63	0.58
5	0.055	1.72	0.03	1.38	0.50
6	0.066	1.51	0.03	1.35	0.50
7	0.077	1.37	0.02	1.29	0.46
8	0.088	1.30	0.02	1.29	0.45
9	0.099	1.23	0.02	1.16	0.42
10	0.110	1.17	0.02	1.03	0.37
11	0.121	1.14	0.02	1.24	0.43
12	0.132	1.11	0.02	1.05	0.38
13	0.143	1.10	0.02	1.20	0.43
14	0.154	1.08	0.02	1.08	0.38
15	0.165	1.06	0.02	1.18	0.43
16	0.176	1.03	0.02	0.92	0.31
17	0.187	1.03	0.02	1.04	0.36
18	0.198	1.04	0.02	1.20	0.44
19	0.209	1.03	0.02	1.08	0.39
20	0.220	0.99	0.02	0.99	0.34
22	0.242	0.97	0.02	1.00	0.36
23	0.253	0.98	0.02	0.98	0.35
24	0.264	1.01	0.02	1.14	0.39
25	0.275	0.98	0.02	0.92	0.31
26	0.286	0.98	0.02	1.04	0.38
27	0.297	0.96	0.02	1.00	0.35
28	0.308	0.98	0.02	1.02	0.37
29	0.319	0.96	0.02	1.12	0.40
30	0.330	0.96	0.02	1.07	0.38
31	0.341	0.98	0.02	1.01	0.36
32	0.352	0.97	0.02	1.00	0.35
33	0.363	0.97	0.02	0.95	0.33
34	0.374	0.96	0.02	0.89	0.30
35	0.385	0.96	0.02	1.05	0.36
36	0.396	0.95	0.02	1.07	0.37
37	0.407	0.95	0.02	1.05	0.37
38	0.418	0.96	0.02	0.99	0.34
39	0.429	0.95	0.02	0.94	0.32
40	0.440	0.95	0.02	0.99	0.35
41	0.451	0.96	0.02	1.07	0.37
42	0.462	0.96	0.02	0.91	0.31
43	0.473	0.97	0.02	1.00	0.35
44	0.484	0.97	0.02	0.93	0.32
45	0.495	0.95	0.02	1.03	0.36
46	0.506	0.94	0.02	0.93	0.32
47	0.517	0.95	0.02	0.93	0.32
48	0.528	0.94	0.02	1.04	0.36
49	0.539	0.96	0.02	0.94	0.32
50	0.550	0.94	0.02	1.01	0.35
51	0.561	0.96	0.02	1.05	0.36
52	0.572	0.96	0.02	1.01	0.34
53	0.583	0.92	0.02	0.95	0.32
54	0.594	0.91	0.02	0.93	0.32
55	0.605	0.92	0.02	0.91	0.31
56	0.616	0.92	0.02	0.97	0.33
57	0.627	0.91	0.02	0.92	0.31
58	0.638	0.91	0.02	0.92	0.31
59	0.649	0.92	0.02	0.95	0.32
60	0.660	0.92	0.02	0.97	0.33
61	0.671	0.92	0.02	0.96	0.32
62	0.682	0.92	0.02	0.95	0.32
63	0.693	0.92	0.02	1.05	0.36

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
64	0.704	0.91	0.02	0.90	0.29
65	0.715	0.91	0.02	0.92	0.30
66	0.726	0.90	0.02	0.90	0.30
67	0.737	0.90	0.02	0.95	0.32
68	0.748	0.90	0.02	0.81	0.27
69	0.759	0.92	0.02	0.92	0.31
70	0.770	0.91	0.02	0.96	0.32

Table A1.1 | Secondary ion mass spectrometry time scan of FAp irradiated for 540 seconds, with the c-axis oriented parallel to the electron beam under 'low power' beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp parallel to c-axis, 'low power' conditions 120 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	1.72	0.04	1.09	0.49
3	0.033	1.42	0.03	1.26	0.51
4	0.044	1.25	0.02	1.12	0.42
5	0.055	1.20	0.02	1.09	0.40
6	0.066	1.13	0.02	1.24	0.45
7	0.077	1.09	0.02	1.12	0.41
8	0.088	1.07	0.02	1.06	0.38
9	0.099	1.01	0.02	1.02	0.37
10	0.110	0.99	0.02	1.05	0.36
11	0.121	1.03	0.02	1.13	0.39
12	0.132	1.03	0.02	1.09	0.38
13	0.143	1.01	0.02	1.23	0.43
14	0.154	1.02	0.02	1.07	0.37
15	0.165	1.02	0.02	1.21	0.42
16	0.176	0.99	0.02	0.89	0.30
17	0.187	1.01	0.02	0.96	0.33
18	0.198	1.00	0.02	1.10	0.40
19	0.209	1.00	0.02	1.07	0.38
20	0.220	0.89	0.02	0.97	0.32
22	0.242	0.97	0.02	1.07	0.38
23	0.253	0.97	0.02	0.91	0.31
24	0.264	1.01	0.02	0.97	0.34
25	0.275	0.99	0.02	1.14	0.39
26	0.286	1.00	0.02	1.09	0.37
27	0.297	0.97	0.02	1.05	0.36
28	0.308	0.99	0.02	1.11	0.39
29	0.319	0.98	0.02	1.04	0.36
30	0.330	0.99	0.02	1.10	0.38
31	0.341	1.00	0.02	1.19	0.41
32	0.352	1.01	0.02	1.02	0.34
33	0.363	1.00	0.02	1.02	0.35
34	0.374	0.99	0.02	0.99	0.33
35	0.385	1.00	0.02	1.05	0.35
36	0.396	0.98	0.02	1.08	0.37
37	0.407	0.99	0.02	1.18	0.41
38	0.418	1.00	0.02	1.07	0.35
39	0.429	0.99	0.02	1.09	0.36
40	0.440	0.99	0.02	1.11	0.37
41	0.451	1.00	0.02	1.16	0.39

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
42	0.462	1.01	0.02	0.99	0.32
43	0.473	0.98	0.02	0.95	0.32
44	0.484	0.98	0.02	1.01	0.35
45	0.495	0.97	0.02	1.03	0.35
46	0.506	0.96	0.02	1.09	0.38
47	0.517	0.97	0.02	0.92	0.30
48	0.528	0.96	0.02	1.05	0.36
49	0.539	0.96	0.02	0.95	0.32
50	0.550	0.95	0.02	0.96	0.33
51	0.561	0.96	0.02	0.99	0.34
52	0.572	0.96	0.02	0.96	0.33
53	0.583	0.92	0.02	1.06	0.36
54	0.594	0.92	0.02	1.00	0.33
55	0.605	0.93	0.02	0.92	0.30
56	0.616	0.93	0.02	0.92	0.31
57	0.627	0.93	0.02	0.92	0.30
58	0.638	0.93	0.02	0.86	0.28
59	0.649	0.95	0.02	1.01	0.35
60	0.660	0.93	0.02	0.85	0.27
61	0.671	0.93	0.02	0.98	0.33
62	0.682	0.93	0.02	0.99	0.32
63	0.693	0.94	0.02	0.91	0.30
64	0.704	0.94	0.02	0.86	0.28
65	0.715	0.93	0.02	0.86	0.28
66	0.726	0.92	0.02	0.87	0.29
67	0.737	0.92	0.02	0.97	0.32
68	0.748	0.91	0.02	0.90	0.29
69	0.759	0.95	0.02	0.95	0.30
70	0.770	0.92	0.02	0.92	0.30

Table A1.2 | Secondary ion mass spectrometry time scan of FAp irradiated for 120 seconds, with the c-axis oriented parallel to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp parallel to c-axis, 'low power' conditions 60 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	1.47	0.03	1.06	0.44
3	0.033	1.23	0.02	1.27	0.48
4	0.044	1.14	0.02	1.06	0.38
5	0.055	1.08	0.02	1.17	0.40
6	0.066	1.05	0.02	1.13	0.40
7	0.077	1.03	0.02	1.16	0.40
8	0.088	1.03	0.02	1.07	0.36
9	0.099	1.03	0.02	1.09	0.38
10	0.110	1.01	0.02	1.09	0.36
11	0.121	1.01	0.02	1.07	0.36
12	0.132	1.00	0.02	0.95	0.33
13	0.143	1.01	0.02	1.00	0.36
14	0.154	0.99	0.02	1.10	0.37
15	0.165	1.02	0.02	1.20	0.42
16	0.176	0.97	0.02	0.78	0.26
17	0.187	0.98	0.02	0.95	0.32
18	0.198	0.99	0.02	1.32	0.45

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
19	0.209	1.01	0.02	1.11	0.37
20	0.220	0.95	0.02	0.95	0.31
22	0.242	0.95	0.02	1.05	0.35
23	0.253	0.96	0.02	1.00	0.33
24	0.264	1.01	0.02	1.01	0.32
25	0.275	0.98	0.02	1.03	0.34
26	0.286	0.97	0.02	1.10	0.36
27	0.297	0.95	0.02	1.00	0.33
28	0.308	0.98	0.02	1.13	0.38
29	0.319	0.96	0.02	1.07	0.35
30	0.330	0.98	0.02	1.19	0.40
31	0.341	0.98	0.02	0.99	0.32
32	0.352	0.97	0.02	0.95	0.32
33	0.363	0.98	0.02	1.10	0.36
34	0.374	0.98	0.02	0.98	0.30
35	0.385	0.97	0.02	1.02	0.33
36	0.396	0.98	0.02	1.10	0.36
37	0.407	0.98	0.02	1.15	0.38
38	0.418	0.99	0.02	0.97	0.31
39	0.429	0.98	0.02	1.11	0.36
40	0.440	0.97	0.02	1.12	0.36
41	0.451	0.98	0.02	1.21	0.39
42	0.462	0.98	0.02	1.03	0.32
43	0.473	0.99	0.02	1.06	0.34
44	0.484	1.00	0.02	1.10	0.35
45	0.495	0.99	0.02	1.14	0.36
46	0.506	0.99	0.02	1.20	0.38
47	0.517	0.98	0.02	0.90	0.27
48	0.528	0.99	0.02	1.17	0.38
49	0.539	0.98	0.02	1.07	0.33
50	0.550	0.98	0.02	1.08	0.34
51	0.561	0.98	0.02	1.10	0.34
52	0.572	0.99	0.02	1.12	0.35
53	0.583	0.94	0.02	1.12	0.35
54	0.594	0.94	0.02	0.99	0.30
55	0.605	0.96	0.02	0.96	0.30
56	0.616	0.95	0.02	1.00	0.32
57	0.627	0.95	0.02	0.93	0.28
58	0.638	0.95	0.02	1.07	0.33
59	0.649	0.95	0.02	1.12	0.34
60	0.660	0.95	0.02	0.92	0.27
61	0.671	0.96	0.02	1.05	0.32
62	0.682	0.95	0.02	1.04	0.32
63	0.693	0.96	0.02	1.14	0.35
64	0.704	0.96	0.02	0.96	0.28
65	0.715	0.96	0.02	1.08	0.33
66	0.726	0.95	0.02	1.04	0.31
67	0.737	0.95	0.02	1.12	0.34
68	0.748	0.95	0.02	0.98	0.28
69	0.759	0.99	0.02	1.02	0.30
70	0.770	0.96	0.02	0.95	0.29

Table A1.3 | Secondary ion mass spectrometry time scan of FAp irradiated for 60 seconds, with the c-axis oriented parallel to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp parallel to c-axis, 'low power' conditions 30 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	1.37	0.03	1.22	0.54
3	0.033	1.29	0.02	1.29	0.51
4	0.044	1.18	0.02	1.14	0.42
5	0.055	1.13	0.02	1.08	0.39
6	0.066	1.10	0.02	1.23	0.44
7	0.077	1.07	0.02	1.14	0.41
8	0.088	1.05	0.02	1.19	0.41
9	0.099	1.04	0.02	1.18	0.41
10	0.110	1.03	0.02	0.98	0.35
11	0.121	1.03	0.02	1.08	0.38
12	0.132	1.02	0.02	1.07	0.37
13	0.143	1.02	0.02	1.11	0.40
14	0.154	1.02	0.02	1.06	0.37
15	0.165	1.01	0.02	1.13	0.40
16	0.176	0.99	0.02	0.93	0.30
17	0.187	0.99	0.02	1.03	0.35
18	0.198	1.00	0.02	1.15	0.41
19	0.209	1.00	0.02	1.08	0.38
20	0.220	0.97	0.02	0.93	0.31
22	0.242	0.97	0.02	1.01	0.35
23	0.253	0.97	0.02	1.01	0.34
24	0.264	1.01	0.02	1.01	0.34
25	0.275	0.99	0.02	1.00	0.34
26	0.286	0.99	0.02	1.09	0.38
27	0.297	0.97	0.02	1.13	0.38
28	0.308	0.98	0.02	1.12	0.38
29	0.319	0.98	0.02	0.98	0.34
30	0.330	0.99	0.02	1.06	0.37
31	0.341	1.01	0.02	1.12	0.39
32	0.352	0.98	0.02	0.93	0.31
33	0.363	1.01	0.02	1.04	0.36
34	0.374	1.00	0.02	0.87	0.28
35	0.385	0.99	0.02	0.94	0.33
36	0.396	1.00	0.02	1.09	0.39
37	0.407	0.99	0.02	1.19	0.42
38	0.418	1.00	0.02	1.01	0.34
39	0.429	0.98	0.02	1.06	0.36
40	0.440	1.00	0.02	0.97	0.33
41	0.451	0.99	0.02	0.99	0.35
42	0.462	0.98	0.02	1.04	0.36
43	0.473	0.99	0.02	1.01	0.34
44	0.484	1.00	0.02	1.00	0.34
45	0.495	0.98	0.02	1.04	0.36
46	0.506	1.00	0.02	1.01	0.35
47	0.517	0.99	0.02	0.97	0.32
48	0.528	0.99	0.02	1.11	0.38
49	0.539	0.99	0.02	1.06	0.35
50	0.550	0.98	0.02	1.02	0.34
51	0.561	1.00	0.02	1.05	0.35
52	0.572	1.00	0.02	1.08	0.36
53	0.583	0.95	0.02	1.07	0.36
54	0.594	0.96	0.02	1.09	0.36
55	0.605	0.97	0.02	1.05	0.34
56	0.616	0.97	0.02	1.04	0.34
57	0.627	0.96	0.02	0.90	0.29
58	0.638	0.97	0.02	1.00	0.33
59	0.649	0.98	0.02	1.13	0.37
60	0.660	0.97	0.02	0.99	0.31
61	0.671	0.97	0.02	1.08	0.35
62	0.682	0.97	0.02	1.10	0.35
63	0.693	0.98	0.02	1.14	0.37
64	0.704	0.98	0.02	0.95	0.30

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
65	0.715	0.97	0.02	1.02	0.33
66	0.726	0.96	0.02	1.00	0.32
67	0.737	0.96	0.02	1.04	0.34
68	0.748	0.96	0.02	0.91	0.29
69	0.759	0.97	0.02	1.05	0.34
70	0.770	0.96	0.02	1.00	0.31

Table A1.4 | Secondary ion mass spectrometry time scan of FAp irradiated for 30 seconds, with the *c*-axis oriented parallel to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp parallel to <i>c</i> -axis, 'low power' conditions 20 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	1.31	0.03	1.10	0.48
3	0.033	1.20	0.02	1.24	0.49
4	0.044	1.13	0.02	1.12	0.41
5	0.055	1.11	0.02	1.14	0.41
6	0.066	1.09	0.02	1.29	0.46
7	0.077	1.07	0.02	1.22	0.43
8	0.088	1.05	0.02	1.11	0.39
9	0.099	1.04	0.02	1.18	0.41
10	0.110	1.04	0.02	1.08	0.37
11	0.121	1.03	0.02	1.09	0.38
12	0.132	1.02	0.02	1.14	0.39
13	0.143	1.02	0.02	1.26	0.43
14	0.154	1.02	0.02	1.02	0.35
15	0.165	0.99	0.02	1.17	0.41
16	0.176	0.99	0.02	0.96	0.31
17	0.187	1.00	0.02	0.97	0.33
18	0.198	1.02	0.02	1.23	0.43
19	0.209	1.01	0.02	1.16	0.39
20	0.220	0.98	0.02	0.94	0.31
22	0.242	0.96	0.02	0.97	0.33
23	0.253	0.97	0.02	0.89	0.30
24	0.264	1.02	0.02	1.03	0.35
25	0.275	0.99	0.02	1.01	0.34
26	0.286	1.00	0.02	1.03	0.35
27	0.297	0.97	0.02	1.15	0.39
28	0.308	1.01	0.02	1.07	0.36
29	0.319	0.99	0.02	1.03	0.35
30	0.330	0.99	0.02	1.11	0.38
31	0.341	1.00	0.02	1.05	0.35
32	0.352	0.99	0.02	0.95	0.31
33	0.363	1.00	0.02	1.05	0.35
34	0.374	0.99	0.02	0.91	0.29
35	0.385	1.00	0.02	1.04	0.34
36	0.396	0.99	0.02	1.09	0.37
37	0.407	0.99	0.02	1.24	0.42
38	0.418	0.99	0.02	1.05	0.33
39	0.429	0.99	0.02	1.13	0.37
40	0.440	0.99	0.02	1.07	0.34
41	0.451	0.99	0.02	1.18	0.39
42	0.462	1.00	0.02	1.03	0.32

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
43	0.473	0.99	0.02	0.98	0.32
44	0.484	1.01	0.02	1.13	0.37
45	0.495	0.99	0.02	1.06	0.34
46	0.506	0.99	0.02	1.11	0.37
47	0.517	1.00	0.02	0.91	0.28
48	0.528	0.97	0.02	1.03	0.34
49	0.539	0.97	0.02	1.01	0.33
50	0.550	0.98	0.02	1.06	0.34
51	0.561	0.99	0.02	1.11	0.36
52	0.572	0.99	0.02	1.04	0.33
53	0.583	0.96	0.02	1.02	0.33
54	0.594	0.94	0.02	1.04	0.34
55	0.605	0.95	0.02	1.04	0.33
56	0.616	0.97	0.02	1.00	0.31
57	0.627	0.96	0.02	0.92	0.29
58	0.638	0.96	0.02	1.07	0.34
59	0.649	0.95	0.02	1.04	0.33
60	0.660	0.94	0.02	0.98	0.30
61	0.671	0.97	0.02	0.99	0.30
62	0.682	0.96	0.02	0.95	0.30
63	0.693	0.95	0.02	1.03	0.33
64	0.704	0.95	0.02	1.00	0.31
65	0.715	0.95	0.02	0.95	0.29
66	0.726	0.95	0.02	1.10	0.34
67	0.737	0.93	0.02	1.05	0.32
68	0.748	0.95	0.02	0.90	0.27
69	0.759	0.96	0.02	1.02	0.32
70	0.770	0.94	0.02	0.97	0.30

Table A1.5 | Secondary ion mass spectrometry time scan of FAp irradiated for 20 seconds, with the *c*-axis oriented parallel to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp parallel to <i>c</i> -axis, 'low power' conditions 10 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	1.21	0.03	1.30	0.54
3	0.033	1.15	0.02	1.33	0.52
4	0.044	1.08	0.02	1.25	0.44
5	0.055	1.07	0.02	1.21	0.42
6	0.066	1.05	0.02	1.31	0.46
7	0.077	1.03	0.02	1.15	0.41
8	0.088	1.05	0.02	1.11	0.39
9	0.099	1.02	0.02	1.26	0.43
10	0.110	1.02	0.02	1.06	0.36
11	0.121	1.02	0.02	1.11	0.38
12	0.132	1.02	0.02	1.18	0.40
13	0.143	1.04	0.02	1.20	0.41
14	0.154	1.04	0.02	1.13	0.38
15	0.165	0.97	0.02	1.30	0.44
16	0.176	1.01	0.02	0.98	0.31
17	0.187	1.02	0.02	1.08	0.36
18	0.198	1.02	0.02	1.28	0.45
19	0.209	1.02	0.02	1.22	0.41

Cycle #	Depth (µm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
20	0.220	0.99	0.02	1.02	0.33
22	0.242	0.99	0.02	1.13	0.38
23	0.253	1.00	0.02	1.01	0.33
24	0.264	1.05	0.02	1.14	0.37
25	0.275	1.03	0.02	1.18	0.38
26	0.286	1.02	0.02	1.16	0.38
27	0.297	1.01	0.02	1.11	0.36
28	0.308	1.02	0.02	1.21	0.41
29	0.319	1.02	0.02	1.18	0.39
30	0.330	1.02	0.02	1.25	0.41
31	0.341	1.04	0.02	1.16	0.38
32	0.352	1.04	0.02	1.09	0.35
33	0.363	1.04	0.02	1.16	0.38
34	0.374	1.01	0.02	0.95	0.30
35	0.385	1.00	0.02	1.05	0.34
36	0.396	1.05	0.02	1.25	0.42
37	0.407	1.04	0.02	1.24	0.40
38	0.418	1.01	0.02	1.08	0.34
39	0.429	0.98	0.02	1.15	0.37
40	0.440	0.99	0.02	1.18	0.38
41	0.451	1.04	0.02	1.26	0.41
42	0.462	1.02	0.02	1.10	0.34
43	0.473	1.03	0.02	1.13	0.36
44	0.484	1.05	0.02	1.18	0.38
45	0.495	1.02	0.02	1.21	0.38
46	0.506	1.02	0.02	1.26	0.40
47	0.517	1.03	0.02	1.06	0.32
48	0.528	1.01	0.02	1.25	0.40
49	0.539	1.01	0.02	1.08	0.34
50	0.550	1.02	0.02	1.09	0.34
51	0.561	1.02	0.02	1.08	0.34
52	0.572	1.02	0.02	1.20	0.38
53	0.583	0.97	0.02	1.05	0.33
54	0.594	0.97	0.02	1.07	0.34
55	0.605	0.98	0.02	1.16	0.37
56	0.616	0.99	0.02	1.13	0.35
57	0.627	0.97	0.02	0.95	0.29
58	0.638	0.98	0.02	1.10	0.35
59	0.649	0.99	0.02	1.21	0.38
60	0.660	0.98	0.02	0.97	0.29
61	0.671	0.98	0.02	1.17	0.36
62	0.682	0.99	0.02	1.11	0.34
63	0.693	0.99	0.02	1.21	0.37
64	0.704	1.00	0.02	1.02	0.30
65	0.715	1.00	0.02	1.14	0.35
66	0.726	1.00	0.02	1.13	0.34
67	0.737	1.00	0.02	1.20	0.37
68	0.748	0.99	0.02	1.04	0.31
69	0.759	1.00	0.02	1.23	0.37
70	0.770	0.99	0.02	1.07	0.31

Table A1.6 | Secondary ion mass spectrometry time scan of FAp irradiated for 10 seconds, with the c-axis oriented parallel to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp parallel to c-axis, 'routine' conditions 360 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	1.55	0.03	1.47	0.49
3	0.033	1.29	0.02	1.19	0.38
4	0.044	1.19	0.02	1.22	0.38
5	0.055	1.17	0.02	1.09	0.33
6	0.066	1.12	0.02	1.11	0.33
7	0.077	1.08	0.02	1.08	0.34
8	0.088	1.07	0.02	1.07	0.34
9	0.099	1.08	0.02	1.01	0.31
10	0.110	1.08	0.02	0.96	0.29
11	0.121	1.07	0.02	1.15	0.36
12	0.132	1.06	0.02	1.02	0.31
13	0.143	1.06	0.02	1.13	0.35
14	0.154	1.04	0.02	1.02	0.31
15	0.165	1.04	0.02	1.00	0.30
16	0.176	1.07	0.02	1.04	0.31
17	0.187	1.04	0.02	1.13	0.35
18	0.198	1.05	0.02	1.02	0.31
19	0.209	1.07	0.02	1.26	0.38
20	0.220	1.04	0.02	1.21	0.37
22	0.242	1.05	0.02	1.07	0.33
23	0.253	1.06	0.02	1.01	0.31
24	0.264	1.04	0.02	1.06	0.32
25	0.275	1.05	0.02	1.12	0.34
26	0.286	1.04	0.02	0.95	0.29
27	0.297	1.04	0.02	0.99	0.30
28	0.308	1.08	0.02	0.99	0.30
29	0.319	1.04	0.02	1.12	0.33
30	0.330	1.07	0.02	1.08	0.32
31	0.341	1.03	0.02	1.05	0.31
32	0.352	1.04	0.02	0.92	0.27
33	0.363	1.04	0.02	1.11	0.33
34	0.374	1.06	0.02	1.12	0.32
35	0.385	1.07	0.02	1.09	0.33
36	0.396	1.05	0.02	1.12	0.33
37	0.407	1.06	0.02	1.04	0.30
38	0.418	1.06	0.02	0.97	0.27
39	0.429	1.02	0.02	1.09	0.31
40	0.440	1.05	0.02	1.12	0.31
41	0.451	1.07	0.02	1.08	0.32
42	0.462	1.09	0.02	1.19	0.33
43	0.473	1.05	0.02	1.07	0.29
44	0.484	1.03	0.02	1.17	0.32
45	0.495	1.04	0.02	1.00	0.28
46	0.506	1.03	0.02	1.11	0.31
47	0.517	1.06	0.02	1.01	0.28
48	0.528	1.06	0.02	1.05	0.29
49	0.539	1.02	0.01	1.04	0.29
50	0.550	0.99	0.01	0.92	0.25
51	0.561	1.03	0.02	1.06	0.30
52	0.572	1.03	0.02	1.08	0.30
53	0.583	1.04	0.02	1.03	0.29
54	0.594	1.05	0.02	1.03	0.29
55	0.605	1.03	0.02	1.00	0.28
56	0.616	1.04	0.02	1.12	0.32
57	0.627	1.03	0.02	1.01	0.28
58	0.638	1.01	0.02	0.98	0.27
59	0.649	1.02	0.02	1.00	0.27
60	0.660	1.02	0.02	1.10	0.31
61	0.671	1.02	0.02	1.07	0.30
62	0.682	1.02	0.02	1.01	0.28
63	0.693	1.02	0.02	1.00	0.28
64	0.704	1.07	0.02	0.95	0.26

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
65	0.715	1.04	0.02	1.07	0.30
66	0.726	1.04	0.02	0.91	0.25
67	0.737	1.07	0.02	1.09	0.30
68	0.748	1.03	0.02	1.27	0.35
69	0.759	1.04	0.02	0.97	0.26
70	0.770	1.06	0.02	1.02	0.27

Table A1.7 | Secondary ion mass spectrometry time scan of FAp irradiated for 360 seconds, with the *c*-axis oriented parallel to the electron beam under 'routine' beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp parallel to <i>c</i> -axis, 'routine' conditions 120 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	3.18	0.07	1.79	0.71
3	0.033	2.11	0.04	1.68	0.63
4	0.044	1.63	0.03	1.35	0.48
5	0.055	1.38	0.02	1.21	0.43
6	0.066	1.24	0.02	1.25	0.44
7	0.077	1.17	0.02	1.07	0.39
8	0.088	1.12	0.02	1.00	0.36
9	0.099	1.06	0.02	1.07	0.38
10	0.110	1.03	0.02	0.96	0.34
11	0.121	1.02	0.02	1.08	0.37
12	0.132	0.98	0.02	0.91	0.33
13	0.143	0.98	0.02	1.04	0.37
14	0.154	0.97	0.02	0.93	0.33
15	0.165	0.98	0.02	1.12	0.40
16	0.176	0.94	0.02	0.83	0.28
17	0.187	0.95	0.02	0.93	0.32
18	0.198	0.96	0.02	1.12	0.40
19	0.209	0.95	0.02	1.03	0.36
20	0.220	0.92	0.02	0.79	0.27
22	0.242	0.91	0.02	1.00	0.36
23	0.253	0.92	0.02	0.81	0.27
24	0.264	0.96	0.02	0.84	0.30
25	0.275	0.94	0.02	0.92	0.33
26	0.286	0.95	0.02	0.91	0.32
27	0.297	0.92	0.02	0.96	0.34
28	0.308	0.95	0.02	1.11	0.39
29	0.319	0.92	0.02	0.95	0.32
30	0.330	0.93	0.02	1.00	0.35
31	0.341	0.94	0.02	0.93	0.33
32	0.352	0.93	0.02	0.88	0.30
33	0.363	0.94	0.02	0.97	0.33
34	0.374	0.94	0.02	0.80	0.26
35	0.385	0.95	0.02	0.96	0.33
36	0.396	0.94	0.02	0.98	0.34
37	0.407	0.94	0.02	0.99	0.35
38	0.418	0.94	0.02	0.91	0.31
39	0.429	0.93	0.02	0.97	0.33
40	0.440	0.92	0.02	0.99	0.33
41	0.451	0.92	0.02	1.04	0.36
42	0.462	0.92	0.02	0.98	0.32

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
43	0.473	0.93	0.02	0.88	0.29
44	0.484	0.94	0.02	0.84	0.29
45	0.495	0.92	0.02	0.88	0.31
46	0.506	0.94	0.02	0.90	0.31
47	0.517	0.92	0.02	0.88	0.29
48	0.528	0.96	0.02	1.09	0.37
49	0.539	0.95	0.02	1.02	0.33
50	0.550	0.95	0.02	0.91	0.29
51	0.561	0.96	0.02	1.03	0.35
52	0.572	0.96	0.02	1.04	0.34
53	0.583	0.92	0.02	1.00	0.32
54	0.594	0.92	0.02	0.96	0.31
55	0.605	0.93	0.02	0.95	0.31
56	0.616	0.94	0.02	0.99	0.32
57	0.627	0.93	0.02	0.87	0.27
58	0.638	0.94	0.02	1.00	0.32
59	0.649	0.94	0.02	1.00	0.32
60	0.660	0.94	0.02	0.87	0.28
61	0.671	0.94	0.02	1.00	0.32
62	0.682	0.94	0.02	1.08	0.34
63	0.693	0.93	0.02	0.94	0.30
64	0.704	0.92	0.02	0.87	0.28
65	0.715	0.93	0.02	1.03	0.33
66	0.726	0.91	0.02	0.97	0.30
67	0.737	0.92	0.02	0.92	0.29
68	0.748	0.92	0.02	0.79	0.25
69	0.759	0.92	0.02	0.92	0.30
70	0.770	0.91	0.02	0.87	0.28

Table A1.8 | Secondary ion mass spectrometry time scan of FAp irradiated for 120 seconds, with the *c*-axis oriented parallel to the electron beam under ‘routine’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp parallel to <i>c</i> -axis, 'routine' conditions 60 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	3.08	0.07	2.30	0.95
3	0.033	2.64	0.05	1.87	0.73
4	0.044	2.00	0.04	1.35	0.50
5	0.055	1.67	0.03	1.39	0.50
6	0.066	1.45	0.03	1.33	0.50
7	0.077	1.47	0.03	1.37	0.50
8	0.088	1.25	0.02	1.17	0.43
9	0.099	1.17	0.02	1.09	0.42
10	0.110	1.12	0.02	1.05	0.39
11	0.121	1.10	0.02	1.09	0.41
12	0.132	1.06	0.02	1.09	0.40
13	0.143	1.05	0.02	1.14	0.43
14	0.154	1.07	0.02	1.03	0.39
15	0.165	1.01	0.02	1.18	0.44
16	0.176	1.01	0.02	0.79	0.29
17	0.187	1.01	0.02	0.97	0.36
18	0.198	1.02	0.02	1.13	0.43
19	0.209	1.02	0.02	1.06	0.40

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
20	0.220	0.97	0.02	0.82	0.30
22	0.242	0.97	0.02	1.01	0.38
23	0.253	0.98	0.02	0.99	0.36
24	0.264	1.01	0.02	0.92	0.33
25	0.275	1.00	0.02	1.03	0.38
26	0.286	1.00	0.02	0.87	0.31
27	0.297	0.96	0.02	0.97	0.37
28	0.308	0.99	0.02	0.99	0.37
29	0.319	0.97	0.02	0.96	0.36
30	0.330	0.98	0.02	1.02	0.38
31	0.341	0.99	0.02	0.92	0.34
32	0.352	0.97	0.02	0.84	0.31
33	0.363	0.98	0.02	0.93	0.35
34	0.374	0.99	0.02	0.80	0.28
35	0.385	0.99	0.02	0.94	0.34
36	0.396	0.96	0.02	0.99	0.36
37	0.407	0.97	0.02	1.06	0.39
38	0.418	0.97	0.02	0.98	0.35
39	0.429	0.96	0.02	1.00	0.35
40	0.440	0.97	0.02	0.96	0.34
41	0.451	0.97	0.02	0.98	0.36
42	0.462	0.96	0.02	0.85	0.30
43	0.473	0.97	0.02	0.96	0.35
44	0.484	0.97	0.02	0.81	0.29
45	0.495	0.97	0.02	0.95	0.35
46	0.506	0.96	0.02	1.00	0.36
47	0.517	0.96	0.02	0.89	0.31
48	0.528	0.95	0.02	0.93	0.33
49	0.539	0.95	0.02	0.93	0.34
50	0.550	0.95	0.02	0.93	0.33
51	0.561	0.95	0.02	0.97	0.35
52	0.572	0.96	0.02	0.99	0.35
53	0.583	0.92	0.02	0.91	0.32
54	0.594	0.92	0.02	0.93	0.33
55	0.605	0.94	0.02	1.01	0.35
56	0.616	0.94	0.02	0.87	0.30
57	0.627	0.92	0.02	0.88	0.31
58	0.638	0.94	0.02	0.88	0.30
59	0.649	0.93	0.02	0.99	0.35
60	0.660	0.94	0.02	0.84	0.28
61	0.671	0.94	0.02	1.00	0.35
62	0.682	0.93	0.02	0.94	0.32
63	0.693	0.94	0.02	1.02	0.35
64	0.704	0.94	0.02	0.88	0.29
65	0.715	0.94	0.02	0.94	0.32
66	0.726	0.92	0.02	0.86	0.29
67	0.737	0.92	0.02	0.91	0.32
68	0.748	0.92	0.02	0.87	0.29
69	0.759	0.93	0.02	0.89	0.30
70	0.770	0.92	0.02	0.89	0.30

Table A1.9 | Secondary ion mass spectrometry time scan of FAp irradiated for 60 seconds, with the c-axis oriented parallel to the electron beam under ‘routine’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp parallel to c-axis, 'routine' conditions 30 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	2.29	0.05	1.36	0.53
3	0.033	1.51	0.03	1.50	0.56
4	0.044	1.29	0.02	1.21	0.43
5	0.055	1.20	0.02	1.14	0.40
6	0.066	1.13	0.02	1.18	0.42
7	0.077	1.09	0.02	1.18	0.41
8	0.088	1.06	0.02	1.17	0.39
9	0.099	1.05	0.02	0.98	0.35
10	0.110	1.03	0.02	1.02	0.35
11	0.121	1.02	0.02	1.08	0.37
12	0.132	1.02	0.02	1.10	0.37
13	0.143	1.02	0.02	1.15	0.39
14	0.154	1.01	0.02	0.97	0.33
15	0.165	1.00	0.02	1.14	0.39
16	0.176	1.09	0.02	0.95	0.31
17	0.187	0.97	0.02	0.98	0.33
18	0.198	1.01	0.02	1.27	0.44
19	0.209	1.00	0.02	1.04	0.36
20	0.220	0.97	0.02	0.87	0.29
22	0.242	0.96	0.02	0.99	0.33
23	0.253	0.95	0.02	1.03	0.34
24	0.264	1.01	0.02	1.00	0.32
25	0.275	0.98	0.02	0.99	0.33
26	0.286	0.99	0.02	0.98	0.33
27	0.297	0.97	0.02	1.01	0.34
28	0.308	1.00	0.02	1.11	0.38
29	0.319	0.97	0.02	0.99	0.33
30	0.330	0.99	0.02	1.02	0.35
31	0.341	0.99	0.02	1.09	0.37
32	0.352	0.99	0.02	1.01	0.33
33	0.363	0.99	0.02	1.01	0.33
34	0.374	0.99	0.02	0.92	0.29
35	0.385	0.98	0.02	0.97	0.31
36	0.396	0.98	0.02	1.18	0.39
37	0.407	0.98	0.02	1.13	0.37
38	0.418	0.99	0.02	1.05	0.34
39	0.429	0.97	0.02	0.99	0.32
40	0.440	0.98	0.02	1.01	0.33
41	0.451	0.98	0.02	1.12	0.37
42	0.462	0.99	0.02	1.07	0.33
43	0.473	0.99	0.02	1.12	0.35
44	0.484	1.01	0.02	1.10	0.35
45	0.495	0.99	0.02	1.15	0.37
46	0.506	1.00	0.02	1.18	0.37
47	0.517	1.00	0.02	0.99	0.30
48	0.528	0.99	0.02	1.16	0.37
49	0.539	0.99	0.02	1.00	0.31
50	0.550	0.99	0.02	1.10	0.35
51	0.561	1.00	0.02	1.07	0.34
52	0.572	1.01	0.02	1.16	0.37
53	0.583	0.95	0.02	1.04	0.32
54	0.594	0.95	0.02	1.09	0.34
55	0.605	0.96	0.02	0.99	0.31
56	0.616	0.97	0.02	1.08	0.34
57	0.627	0.96	0.02	0.92	0.28
58	0.638	0.97	0.02	1.03	0.32
59	0.649	0.96	0.02	1.02	0.32
60	0.660	0.96	0.02	0.99	0.30
61	0.671	0.97	0.02	1.03	0.31
62	0.682	0.97	0.02	1.11	0.34
63	0.693	0.97	0.02	1.09	0.34
64	0.704	0.96	0.02	0.99	0.30

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
65	0.715	0.95	0.02	0.96	0.29
66	0.726	0.96	0.02	1.09	0.34
67	0.737	0.95	0.02	1.04	0.32
68	0.748	0.96	0.02	0.89	0.27
69	0.759	0.97	0.02	1.04	0.32
70	0.770	0.96	0.02	1.01	0.31

Table A1.10 | Secondary ion mass spectrometry time scan of FAp irradiated for 30 seconds, with the c-axis oriented parallel to the electron beam under 'routine' beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp parallel to c-axis, 'routine' conditions 20 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	2.36	0.05	1.21	0.52
3	0.033	1.79	0.03	1.35	0.53
4	0.044	1.47	0.03	1.14	0.42
5	0.055	1.30	0.02	1.07	0.39
6	0.066	1.19	0.02	1.27	0.45
7	0.077	1.16	0.02	1.27	0.44
8	0.088	1.09	0.02	1.05	0.37
9	0.099	1.08	0.02	1.15	0.41
10	0.110	1.07	0.02	1.01	0.36
11	0.121	1.05	0.02	1.12	0.39
12	0.132	1.04	0.02	1.10	0.38
13	0.143	1.04	0.02	1.19	0.42
14	0.154	1.03	0.02	1.04	0.36
15	0.165	1.01	0.02	1.18	0.42
16	0.176	1.00	0.02	0.82	0.28
17	0.187	1.01	0.02	0.96	0.33
18	0.198	1.02	0.02	1.19	0.43
19	0.209	1.02	0.02	1.10	0.38
20	0.220	0.97	0.02	0.92	0.31
22	0.242	0.97	0.02	1.12	0.40
23	0.253	0.98	0.02	0.96	0.32
24	0.264	1.02	0.02	1.05	0.35
25	0.275	0.99	0.02	0.93	0.31
26	0.286	0.99	0.02	1.04	0.36
27	0.297	0.96	0.02	1.11	0.38
28	0.308	1.00	0.02	1.07	0.36
29	0.319	0.98	0.02	1.08	0.37
30	0.330	0.97	0.02	1.10	0.38
31	0.341	1.00	0.02	0.98	0.34
32	0.352	0.99	0.02	0.96	0.33
33	0.363	1.01	0.02	1.01	0.34
34	0.374	0.99	0.02	0.88	0.29
35	0.385	0.98	0.02	0.94	0.32
36	0.396	0.98	0.02	1.16	0.40
37	0.407	0.98	0.02	1.12	0.38
38	0.418	0.99	0.02	1.02	0.34
39	0.429	0.99	0.02	1.04	0.34
40	0.440	0.97	0.02	1.08	0.36
41	0.451	0.99	0.02	0.95	0.32
42	0.462	0.98	0.02	0.96	0.32

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
43	0.473	0.98	0.02	1.05	0.35
44	0.484	0.99	0.02	1.08	0.35
45	0.495	0.98	0.02	0.98	0.32
46	0.506	0.99	0.02	1.08	0.36
47	0.517	0.97	0.02	0.94	0.30
48	0.528	0.97	0.02	1.04	0.34
49	0.539	0.97	0.02	0.99	0.33
50	0.550	0.97	0.02	1.06	0.35
51	0.561	0.99	0.02	1.01	0.33
52	0.572	0.98	0.02	0.99	0.33
53	0.583	0.93	0.02	0.94	0.31
54	0.594	0.94	0.02	1.01	0.33
55	0.605	0.94	0.02	0.95	0.31
56	0.616	0.95	0.02	0.95	0.31
57	0.627	0.93	0.02	0.89	0.28
58	0.638	0.95	0.02	0.96	0.31
59	0.649	0.94	0.02	1.09	0.35
60	0.660	0.94	0.02	0.84	0.26
61	0.671	0.94	0.02	0.95	0.31
62	0.682	0.92	0.02	0.98	0.32
63	0.693	1.00	0.02	1.14	0.37
64	0.704	0.97	0.02	0.87	0.26
65	0.715	0.93	0.02	0.95	0.30
66	0.726	0.93	0.02	1.01	0.32
67	0.737	0.93	0.02	0.97	0.31
68	0.748	0.94	0.02	0.84	0.26
69	0.759	0.93	0.02	0.96	0.31
70	0.770	0.92	0.02	0.95	0.30

Table A1.11 | Secondary ion mass spectrometry time scan of FAp irradiated for 20 seconds, with the *c*-axis oriented parallel to the electron beam under ‘routine’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp parallel to <i>c</i> -axis, 'routine' conditions 10 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	1.74	0.04	1.62	0.72
3	0.033	1.76	0.04	1.57	0.64
4	0.044	1.48	0.03	1.23	0.48
5	0.055	1.39	0.03	1.31	0.49
6	0.066	1.28	0.02	1.21	0.47
7	0.077	1.21	0.02	1.14	0.44
8	0.088	1.19	0.02	1.22	0.45
9	0.099	1.13	0.02	1.15	0.43
10	0.110	1.11	0.02	1.10	0.40
11	0.121	1.10	0.02	0.95	0.37
12	0.132	1.09	0.02	1.11	0.41
13	0.143	1.08	0.02	1.18	0.44
14	0.154	1.08	0.02	0.98	0.37
15	0.165	1.06	0.02	1.15	0.43
16	0.176	1.05	0.02	0.82	0.30
17	0.187	1.04	0.02	0.99	0.36
18	0.198	1.03	0.02	1.22	0.46
19	0.209	1.04	0.02	1.16	0.42

Cycle #	Depth (µm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
20	0.220	1.00	0.02	0.87	0.32
22	0.242	0.99	0.02	0.95	0.36
23	0.253	1.00	0.02	1.01	0.37
24	0.264	1.06	0.02	0.93	0.33
25	0.275	1.01	0.02	0.92	0.34
26	0.286	1.02	0.02	1.03	0.38
27	0.297	0.99	0.02	1.03	0.38
28	0.308	1.02	0.02	1.06	0.39
29	0.319	1.01	0.02	1.08	0.40
30	0.330	1.03	0.02	1.02	0.37
31	0.341	1.03	0.02	0.96	0.36
32	0.352	1.02	0.02	0.94	0.34
33	0.363	1.03	0.02	1.06	0.39
34	0.374	1.03	0.02	0.92	0.32
35	0.385	1.01	0.02	0.93	0.33
36	0.396	1.02	0.02	1.16	0.43
37	0.407	1.01	0.02	1.09	0.39
38	0.418	1.03	0.02	0.91	0.32
39	0.429	1.02	0.02	0.98	0.36
40	0.440	1.02	0.02	1.08	0.39
41	0.451	1.01	0.02	1.09	0.39
42	0.462	1.01	0.02	0.96	0.33
43	0.473	1.01	0.02	0.97	0.34
44	0.484	1.02	0.02	1.00	0.35
45	0.495	1.01	0.02	0.98	0.35
46	0.506	1.03	0.02	0.99	0.36
47	0.517	1.02	0.02	0.90	0.31
48	0.528	1.00	0.02	1.04	0.37
49	0.539	1.01	0.02	0.96	0.34
50	0.550	1.00	0.02	0.93	0.33
51	0.561	1.00	0.02	0.93	0.34
52	0.572	1.00	0.02	0.98	0.35
53	0.583	0.97	0.02	0.97	0.34
54	0.594	0.96	0.02	0.88	0.31
55	0.605	0.98	0.02	1.10	0.39
56	0.616	0.98	0.02	0.97	0.32
57	0.627	0.97	0.02	0.84	0.29
58	0.638	0.97	0.02	0.84	0.29
59	0.649	0.97	0.02	0.95	0.34
60	0.660	0.97	0.02	0.89	0.30
61	0.671	0.99	0.02	0.98	0.34
62	0.682	0.97	0.02	0.99	0.34
63	0.693	0.96	0.02	1.07	0.37
64	0.704	0.97	0.02	0.92	0.30
65	0.715	0.97	0.02	0.97	0.32
66	0.726	0.96	0.02	0.90	0.30
67	0.737	0.96	0.02	0.86	0.30
68	0.748	0.97	0.02	0.86	0.30
69	0.759	0.95	0.02	0.93	0.31
70	0.770	0.96	0.02	0.90	0.30

Table A1.12 | Secondary ion mass spectrometry time scan of FAp irradiated for 10 seconds, with the c-axis oriented parallel to the electron beam under ‘routine’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAP perpendicular to c-axis, 'low power' conditions 360 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	1.08	0.09	1.10	0.08
3	0.033	1.06	0.09	1.01	0.07
4	0.044	1.05	0.10	1.07	0.09
5	0.055	1.02	0.10	1.02	0.08
6	0.065	1.02	0.10	0.92	0.07
7	0.076	1.01	0.10	1.00	0.08
8	0.087	1.00	0.10	1.01	0.09
9	0.098	0.98	0.09	1.00	0.09
10	0.109	1.01	0.10	0.93	0.08
11	0.120	1.00	0.10	1.06	0.10
12	0.131	1.00	0.10	0.95	0.08
13	0.142	1.00	0.10	1.03	0.09
14	0.153	1.03	0.11	0.85	0.06
15	0.164	1.03	0.11	0.93	0.08
16	0.174	0.99	0.10	1.03	0.10
17	0.185	1.00	0.11	1.04	0.10
18	0.196	0.98	0.10	1.01	0.10
19	0.207	0.93	0.09	0.88	0.07
20	0.218	0.98	0.10	1.03	0.10
21	0.229	0.98	0.10	1.00	0.09
22	0.240	1.00	0.11	0.90	0.07
23	0.251	1.02	0.11	1.01	0.09
24	0.262	1.00	0.10	0.92	0.08
25	0.273	1.00	0.11	0.94	0.08
26	0.283	0.99	0.10	0.96	0.09
27	0.294	0.98	0.10	0.98	0.09
28	0.305	0.97	0.10	1.00	0.09
29	0.316	0.98	0.10	0.97	0.09
30	0.327	0.98	0.10	0.87	0.07
31	0.338	0.99	0.11	1.02	0.10
32	0.349	0.97	0.10	0.92	0.08
33	0.360	0.98	0.10	0.98	0.09
34	0.371	0.98	0.10	0.98	0.09
35	0.382	0.96	0.10	1.13	0.12
36	0.392	0.99	0.10	1.07	0.11
37	0.403	0.98	0.10	0.84	0.06
38	0.414	0.98	0.10	0.99	0.09
39	0.425	0.97	0.10	0.91	0.08
40	0.436	0.99	0.11	0.91	0.08
41	0.447	0.99	0.11	1.02	0.10
42	0.458	0.98	0.10	0.96	0.09
43	0.469	0.97	0.10	1.00	0.09
44	0.480	0.95	0.10	1.02	0.10
45	0.491	0.99	0.10	0.96	0.09
46	0.501	0.97	0.10	0.89	0.07
47	0.512	0.96	0.09	1.03	0.10
48	0.523	0.96	0.10	1.02	0.09
49	0.534	0.97	0.10	0.87	0.07
50	0.545	0.97	0.10	0.83	0.06
51	0.556	0.98	0.10	0.98	0.09
52	0.567	0.95	0.10	0.92	0.08
53	0.578	0.96	0.10	0.94	0.08
54	0.589	0.96	0.10	0.88	0.07
55	0.600	1.03	0.11	1.04	0.10
56	0.610	1.02	0.11	1.09	0.11
57	0.621	1.02	0.11	1.15	0.12
58	0.632	1.13	0.13	1.04	0.10
59	0.643	0.96	0.10	0.91	0.08
60	0.654	0.95	0.10	0.86	0.07
61	0.665	0.94	0.09	0.94	0.08
62	0.676	0.95	0.10	0.93	0.08
63	0.687	0.93	0.09	0.98	0.09

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
64	0.698	0.92	0.09	0.84	0.07
65	0.709	0.93	0.09	0.84	0.07
66	0.719	0.94	0.10	0.84	0.07
67	0.730	0.93	0.09	0.79	0.06
68	0.741	0.92	0.09	0.83	0.06
69	0.752	0.91	0.09	0.85	0.07
70	0.763	0.92	0.09	0.95	0.08

Table A1.13 | Secondary ion mass spectrometry time scan of FAp irradiated for 360 seconds, with the *c*-axis oriented perpendicular to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp perpendicular to <i>c</i> -axis, 'low power' conditions 120 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	0.96	0.07	0.98	0.06
3	0.033	0.96	0.08	1.02	0.08
4	0.044	0.96	0.08	0.96	0.07
5	0.055	0.95	0.08	0.92	0.07
6	0.065	0.94	0.08	0.90	0.07
7	0.076	0.96	0.09	0.92	0.07
8	0.087	0.94	0.09	0.95	0.08
9	0.098	0.93	0.09	0.91	0.07
10	0.109	0.93	0.09	0.96	0.08
11	0.120	0.93	0.08	0.95	0.08
12	0.131	0.93	0.09	0.92	0.07
13	0.142	0.92	0.08	0.96	0.08
14	0.153	0.93	0.09	0.84	0.06
15	0.164	0.90	0.08	0.87	0.07
16	0.174	0.93	0.09	0.91	0.08
17	0.185	0.96	0.10	0.96	0.09
18	0.196	0.92	0.09	1.01	0.10
19	0.207	0.94	0.09	0.93	0.08
20	0.218	0.93	0.09	0.93	0.08
21	0.229	0.93	0.09	0.92	0.08
22	0.240	0.93	0.09	0.91	0.08
23	0.251	0.93	0.09	1.00	0.09
24	0.262	0.95	0.09	0.98	0.09
25	0.273	0.94	0.09	1.00	0.09
26	0.283	0.92	0.09	0.92	0.08
27	0.294	0.93	0.09	0.92	0.08
28	0.305	0.92	0.09	0.94	0.08
29	0.316	0.92	0.09	0.89	0.07
30	0.327	0.92	0.09	0.92	0.08
31	0.338	0.94	0.09	0.98	0.09
32	0.349	0.92	0.09	0.94	0.08
33	0.360	0.93	0.09	0.99	0.09
34	0.371	0.94	0.10	0.84	0.07
35	0.382	0.91	0.09	0.96	0.09
36	0.392	0.93	0.09	1.06	0.11
37	0.403	0.94	0.09	0.89	0.07
38	0.414	0.92	0.09	1.02	0.10
39	0.425	0.93	0.09	0.94	0.08
40	0.436	0.91	0.09	0.90	0.08

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
41	0.447	0.92	0.09	1.02	0.10
42	0.458	0.91	0.09	0.91	0.08
43	0.469	0.91	0.09	0.91	0.08
44	0.480	0.89	0.08	0.85	0.07
45	0.491	0.92	0.09	0.90	0.07
46	0.501	0.91	0.09	0.97	0.09
47	0.512	0.91	0.08	1.04	0.10
48	0.523	0.93	0.09	1.07	0.10
49	0.534	0.94	0.09	0.95	0.08
50	0.545	0.93	0.09	0.88	0.07
51	0.556	0.92	0.09	0.94	0.08
52	0.567	0.92	0.09	0.90	0.07
53	0.578	0.92	0.09	1.05	0.10
54	0.589	0.94	0.09	1.02	0.10
55	0.600	0.91	0.09	0.95	0.08
56	0.610	0.93	0.09	0.97	0.09
57	0.621	0.91	0.09	1.05	0.10
58	0.632	0.95	0.10	0.95	0.08
59	0.643	0.93	0.09	0.95	0.08
60	0.654	0.90	0.09	0.94	0.08
61	0.665	0.91	0.09	0.97	0.09
62	0.676	0.92	0.09	0.96	0.09
63	0.687	0.91	0.09	0.87	0.07
64	0.698	0.92	0.09	1.05	0.10
65	0.709	0.91	0.09	0.96	0.09
66	0.719	0.93	0.09	0.90	0.08
67	0.730	0.91	0.09	0.87	0.07
68	0.741	0.93	0.09	0.97	0.09
69	0.752	0.91	0.09	1.01	0.09
70	0.763	0.92	0.09	1.03	0.10

Table A1.14 | Secondary ion mass spectrometry time scan of FAp irradiated for 120 seconds, with the *c*-axis oriented perpendicular to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp perpendicular to <i>c</i> -axis, 'low power' conditions 60 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	1.04	0.08	1.15	0.09
3	0.033	1.03	0.09	0.99	0.07
4	0.044	1.03	0.09	1.14	0.10
5	0.055	1.02	0.09	0.97	0.08
6	0.065	1.00	0.09	0.97	0.08
7	0.076	1.14	0.12	1.23	0.13
8	0.087	1.02	0.10	1.05	0.10
9	0.098	1.01	0.10	1.04	0.09
10	0.109	1.02	0.10	0.94	0.08
11	0.120	1.00	0.10	0.95	0.08
12	0.131	1.00	0.10	1.04	0.10
13	0.142	1.00	0.10	0.99	0.09
14	0.153	1.01	0.10	0.82	0.06
15	0.164	0.99	0.10	0.94	0.08
16	0.174	1.00	0.10	0.97	0.09
17	0.185	1.02	0.11	0.97	0.09

Cycle #	Depth (µm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
18	0.196	1.01	0.11	1.00	0.09
19	0.207	1.01	0.10	0.99	0.09
20	0.218	1.01	0.11	0.97	0.09
21	0.229	1.01	0.10	0.96	0.08
22	0.240	1.03	0.11	0.94	0.08
23	0.251	1.03	0.11	1.07	0.11
24	0.262	1.02	0.11	0.96	0.08
25	0.273	1.03	0.11	1.02	0.10
26	0.283	1.02	0.11	1.00	0.09
27	0.294	1.03	0.11	1.03	0.10
28	0.305	1.01	0.11	1.08	0.11
29	0.316	1.03	0.11	0.98	0.09
30	0.327	1.01	0.11	0.90	0.07
31	0.338	1.02	0.11	1.06	0.11
32	0.349	1.01	0.11	1.00	0.09
33	0.360	1.02	0.11	1.15	0.13
34	0.371	1.02	0.11	0.95	0.09
35	0.382	1.01	0.11	1.03	0.10
36	0.392	1.02	0.11	1.06	0.11
37	0.403	1.01	0.11	0.93	0.08
38	0.414	1.02	0.11	1.05	0.10
39	0.425	1.00	0.11	0.99	0.09
40	0.436	1.01	0.11	0.95	0.08
41	0.447	1.01	0.11	1.11	0.12
42	0.458	1.01	0.11	0.89	0.07
43	0.469	1.02	0.11	1.04	0.10
44	0.480	0.98	0.10	0.97	0.09
45	0.491	1.02	0.11	0.99	0.09
46	0.501	1.02	0.11	1.04	0.10
47	0.512	0.99	0.10	1.05	0.10
48	0.523	1.02	0.11	1.08	0.11
49	0.534	1.02	0.11	0.90	0.07
50	0.545	1.00	0.10	0.87	0.07
51	0.556	1.03	0.11	1.03	0.10
52	0.567	0.99	0.10	0.88	0.07
53	0.578	0.98	0.10	1.00	0.09
54	0.589	1.00	0.11	1.05	0.10
55	0.600	1.01	0.11	0.95	0.08
56	0.610	0.99	0.10	1.02	0.09
57	0.621	0.99	0.10	0.93	0.08
58	0.632	1.01	0.11	0.95	0.08
59	0.643	1.01	0.11	0.90	0.08
60	0.654	1.01	0.11	0.93	0.08
61	0.665	1.00	0.11	1.08	0.11
62	0.676	0.98	0.10	0.95	0.08
63	0.687	0.97	0.10	0.94	0.08
64	0.698	0.97	0.10	0.97	0.09
65	0.709	0.98	0.10	0.97	0.09
66	0.719	0.99	0.11	0.92	0.08
67	0.730	0.96	0.10	0.83	0.06
68	0.741	0.99	0.11	0.96	0.09
69	0.752	0.97	0.10	0.94	0.08
70	0.763	0.97	0.10	0.94	0.08

Table A1.15 | Secondary ion mass spectrometry time scan of FAp irradiated for 60 seconds, with the c-axis oriented perpendicular to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAP perpendicular to c-axis, 'low power' conditions 30 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	1.03	0.08	1.11	0.08
3	0.033	1.01	0.08	1.03	0.08
4	0.044	1.08	0.10	1.03	0.09
5	0.055	1.03	0.10	0.93	0.07
6	0.065	0.98	0.09	0.97	0.08
7	0.076	1.01	0.10	0.94	0.07
8	0.087	0.99	0.10	1.04	0.09
9	0.098	1.13	0.13	1.18	0.12
10	0.109	1.00	0.10	1.04	0.09
11	0.120	1.00	0.10	0.93	0.08
12	0.131	1.01	0.10	0.95	0.08
13	0.142	1.17	0.14	1.12	0.11
14	0.153	0.99	0.10	0.88	0.07
15	0.164	0.99	0.10	0.94	0.08
16	0.174	1.00	0.10	0.99	0.09
17	0.185	0.99	0.10	0.92	0.08
18	0.196	1.00	0.11	1.01	0.10
19	0.207	0.99	0.10	0.98	0.09
20	0.218	1.01	0.11	0.97	0.09
21	0.229	1.01	0.11	0.91	0.07
22	0.240	1.03	0.11	1.02	0.10
23	0.251	1.02	0.11	1.14	0.12
24	0.262	1.03	0.11	0.96	0.08
25	0.273	1.02	0.11	0.98	0.09
26	0.283	1.01	0.11	1.05	0.10
27	0.294	1.02	0.11	1.04	0.10
28	0.305	1.01	0.11	1.03	0.10
29	0.316	1.01	0.11	0.97	0.09
30	0.327	0.99	0.11	0.92	0.08
31	0.338	1.02	0.11	1.05	0.10
32	0.349	1.00	0.11	0.94	0.08
33	0.360	1.01	0.11	1.03	0.10
34	0.371	1.00	0.11	0.96	0.09
35	0.382	0.98	0.10	1.00	0.09
36	0.392	1.00	0.11	1.08	0.11
37	0.403	0.99	0.10	0.92	0.08
38	0.414	1.00	0.11	1.01	0.10
39	0.425	0.99	0.11	1.00	0.09
40	0.436	1.00	0.11	0.95	0.08
41	0.447	0.99	0.11	0.97	0.09
42	0.458	1.00	0.11	1.01	0.10
43	0.469	0.99	0.11	0.99	0.09
44	0.480	0.97	0.10	0.93	0.08
45	0.491	1.00	0.11	0.99	0.09
46	0.501	1.00	0.10	0.98	0.09
47	0.512	0.99	0.10	1.05	0.10
48	0.523	1.00	0.10	0.99	0.09
49	0.534	1.01	0.11	0.90	0.07
50	0.545	0.99	0.10	0.80	0.06
51	0.556	0.99	0.10	0.97	0.09
52	0.567	0.98	0.10	0.90	0.08
53	0.578	0.97	0.10	0.90	0.08
54	0.589	1.01	0.11	0.98	0.09
55	0.600	0.98	0.10	0.95	0.08
56	0.610	0.98	0.10	0.99	0.09
57	0.621	0.97	0.10	0.93	0.08
58	0.632	0.99	0.10	0.94	0.08
59	0.643	0.96	0.10	0.92	0.08
60	0.654	0.97	0.10	0.85	0.07
61	0.665	0.97	0.10	0.98	0.09
62	0.676	0.97	0.10	0.89	0.07
63	0.687	0.97	0.10	0.90	0.08

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
64	0.698	0.95	0.10	0.87	0.07
65	0.709	0.97	0.10	0.87	0.07
66	0.719	0.97	0.10	0.87	0.07
67	0.730	0.95	0.10	0.82	0.06
68	0.741	0.95	0.10	0.92	0.08
69	0.752	0.95	0.10	0.95	0.08
70	0.763	0.95	0.09	0.86	0.07

Table A1.16 | Secondary ion mass spectrometry time scan of FAp irradiated for 30 seconds, with the *c*-axis oriented perpendicular to the electron beam under 'low power' beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp perpendicular to <i>c</i> -axis, 'low power' conditions 20 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	1.00	0.02	1.16	0.34
3	0.033	1.00	0.01	0.97	0.27
4	0.044	1.00	0.01	0.96	0.26
5	0.055	1.01	0.01	0.93	0.24
6	0.065	0.98	0.01	0.89	0.23
7	0.076	0.99	0.01	0.98	0.25
8	0.087	0.98	0.01	1.03	0.25
9	0.098	0.98	0.01	1.05	0.26
10	0.109	0.99	0.01	0.91	0.23
11	0.120	0.97	0.01	1.00	0.24
12	0.131	0.97	0.01	0.95	0.23
13	0.142	0.98	0.01	0.98	0.24
14	0.153	0.98	0.01	0.85	0.21
15	0.164	0.98	0.01	0.94	0.23
16	0.174	0.98	0.01	0.98	0.24
17	0.185	0.99	0.01	0.92	0.23
18	0.196	0.98	0.01	0.93	0.24
19	0.207	0.98	0.01	0.94	0.23
20	0.218	0.98	0.01	0.92	0.23
21	0.229	0.98	0.01	0.90	0.22
22	0.240	0.99	0.01	0.91	0.23
23	0.251	0.99	0.01	0.99	0.25
24	0.262	0.99	0.01	1.01	0.24
25	0.273	0.99	0.01	0.93	0.23
26	0.283	0.99	0.01	0.96	0.24
27	0.294	0.99	0.01	1.02	0.24
28	0.305	0.98	0.01	1.01	0.25
29	0.316	0.98	0.01	0.93	0.23
30	0.327	0.98	0.01	0.84	0.21
31	0.338	0.98	0.01	1.02	0.24
32	0.349	0.96	0.01	0.94	0.22
33	0.360	0.96	0.01	1.00	0.24
34	0.371	0.98	0.01	0.93	0.22
35	0.382	0.95	0.01	1.04	0.24
36	0.392	0.98	0.01	0.96	0.24
37	0.403	0.98	0.01	0.85	0.21
38	0.414	0.97	0.01	0.98	0.23
39	0.425	0.96	0.01	0.92	0.22

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
40	0.436	0.97	0.01	0.93	0.22
41	0.447	0.96	0.01	0.91	0.22
42	0.458	0.98	0.01	0.76	0.20
43	0.469	0.96	0.01	0.89	0.22
44	0.480	0.94	0.01	0.93	0.22
45	0.491	0.97	0.01	0.89	0.22
46	0.501	0.96	0.01	0.92	0.22
47	0.512	0.97	0.01	1.04	0.24
48	0.523	0.98	0.01	0.95	0.22
49	0.534	0.98	0.01	0.90	0.21
50	0.545	0.97	0.01	0.90	0.20
51	0.556	0.97	0.01	0.93	0.22
52	0.567	0.95	0.01	0.93	0.21
53	0.578	0.96	0.01	0.95	0.22
54	0.589	0.98	0.01	1.02	0.23
55	0.600	0.97	0.01	0.95	0.22
56	0.610	0.97	0.01	0.95	0.22
57	0.621	0.97	0.01	0.96	0.22
58	0.632	0.97	0.01	0.93	0.22
59	0.643	0.95	0.01	0.89	0.20
60	0.654	0.96	0.01	0.83	0.19
61	0.665	0.95	0.01	0.90	0.21
62	0.676	0.96	0.01	0.83	0.20
63	0.687	0.95	0.01	0.84	0.20
64	0.698	0.91	0.01	0.93	0.21
65	0.709	0.94	0.01	0.80	0.19
66	0.719	0.95	0.01	0.84	0.19
67	0.730	0.93	0.01	0.82	0.19
68	0.741	0.94	0.01	0.88	0.20
69	0.752	0.91	0.01	0.85	0.20
70	0.763	0.93	0.01	0.87	0.20

Table A1.17 | Secondary ion mass spectrometry time scan of FAp irradiated for 20 seconds, with the *c*-axis oriented perpendicular to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

FAp perpendicular to <i>c</i> -axis, 'low power' conditions 10 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.022	0.94	0.07	1.61	0.17
3	0.033	1.02	0.09	1.23	0.11
4	0.044	1.00	0.09	1.37	0.15
5	0.055	1.00	0.09	1.21	0.12
6	0.065	0.95	0.08	1.11	0.10
7	0.076	0.91	0.08	1.02	0.09
8	0.087	0.97	0.09	1.11	0.11
9	0.098	0.98	0.09	1.18	0.12
10	0.109	0.98	0.10	1.02	0.09
11	0.120	0.97	0.09	1.03	0.09
12	0.131	0.98	0.10	1.02	0.09
13	0.142	0.98	0.10	1.16	0.12
14	0.153	0.98	0.10	0.89	0.07
15	0.164	0.97	0.09	1.04	0.10
16	0.174	0.98	0.10	1.06	0.10

Cycle #	Depth (µm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
17	0.185	1.00	0.11	0.98	0.09
18	0.196	0.98	0.10	1.05	0.10
19	0.207	0.98	0.10	0.91	0.08
20	0.218	0.98	0.10	0.91	0.08
21	0.229	0.98	0.10	0.95	0.08
22	0.240	0.99	0.10	0.86	0.07
23	0.251	0.99	0.10	0.99	0.09
24	0.262	1.00	0.10	0.93	0.08
25	0.273	1.00	0.11	0.97	0.09
26	0.283	0.98	0.10	0.98	0.09
27	0.294	0.98	0.10	0.95	0.08
28	0.305	0.97	0.10	1.06	0.11
29	0.316	0.98	0.10	0.96	0.09
30	0.327	0.98	0.10	0.92	0.08
31	0.338	0.98	0.10	1.01	0.10
32	0.349	0.97	0.10	0.97	0.09
33	0.360	0.98	0.10	1.00	0.10
34	0.371	0.98	0.10	0.94	0.08
35	0.382	0.97	0.10	0.92	0.08
36	0.392	0.98	0.10	1.00	0.09
37	0.403	0.97	0.10	0.89	0.07
38	0.414	0.98	0.10	0.97	0.09
39	0.425	0.96	0.10	0.94	0.08
40	0.436	0.97	0.10	0.92	0.08
41	0.447	0.99	0.11	0.96	0.09
42	0.458	0.98	0.10	0.88	0.07
43	0.469	0.98	0.10	0.93	0.08
44	0.480	0.96	0.10	0.94	0.08
45	0.491	0.98	0.10	0.93	0.08
46	0.501	0.96	0.10	0.96	0.08
47	0.512	0.97	0.10	1.07	0.10
48	0.523	0.98	0.10	1.04	0.10
49	0.534	0.98	0.10	0.94	0.08
50	0.545	0.97	0.10	0.78	0.05
51	0.556	0.98	0.10	1.01	0.09
52	0.567	0.97	0.10	0.85	0.07
53	0.578	0.97	0.10	0.93	0.08
54	0.589	0.97	0.10	1.00	0.09
55	0.600	0.96	0.10	0.88	0.07
56	0.610	0.95	0.10	0.89	0.07
57	0.621	0.94	0.09	0.84	0.06
58	0.632	0.96	0.10	0.95	0.08
59	0.643	0.96	0.10	0.81	0.06
60	0.654	0.95	0.10	0.82	0.06
61	0.665	0.97	0.10	0.93	0.08
62	0.676	0.94	0.10	0.86	0.07
63	0.687	0.94	0.10	0.89	0.07
64	0.698	0.93	0.09	0.85	0.07
65	0.709	0.94	0.10	0.90	0.08
66	0.719	0.95	0.10	0.82	0.06
67	0.730	0.95	0.10	0.77	0.05
68	0.741	0.96	0.10	0.87	0.07
69	0.752	0.94	0.09	0.91	0.08
70	0.763	0.93	0.09	0.93	0.08

Table A1.18 | Secondary ion mass spectrometry time scan of FAp irradiated for 10 seconds, with the *c*-axis oriented perpendicular to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

ClAp parallel to c-axis, 'low power' conditions 360 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.025	0.70	0.02	0.86	0.05
3	0.038	0.62	0.05	0.95	0.05
4	0.050	0.67	0.05	0.98	0.05
5	0.063	0.70	0.05	0.97	0.05
6	0.075	0.73	0.05	0.96	0.05
7	0.088	0.79	0.06	0.96	0.05
8	0.100	0.78	0.06	0.99	0.05
9	0.113	0.76	0.06	0.92	0.05
10	0.125	0.82	0.06	0.90	0.05
11	0.138	0.83	0.06	0.89	0.05
12	0.150	0.81	0.06	0.91	0.05
13	0.163	0.83	0.06	0.89	0.05
14	0.175	0.84	0.06	0.86	0.05
15	0.188	0.82	0.06	0.85	0.05
16	0.200	0.80	0.06	0.84	0.05
17	0.213	0.83	0.06	0.87	0.05
18	0.225	0.81	0.06	0.86	0.05
19	0.238	0.82	0.06	0.83	0.05
20	0.250	0.80	0.06	0.84	0.05
21	0.263	0.82	0.06	0.83	0.04
22	0.275	0.79	0.06	0.82	0.04
23	0.288	0.81	0.06	0.83	0.05
24	0.300	0.80	0.06	0.84	0.04
25	0.313	0.78	0.06	0.85	0.05
26	0.325	0.77	0.06	0.85	0.05
27	0.338	0.79	0.06	0.84	0.05
28	0.350	0.78	0.06	0.85	0.05
29	0.363	0.79	0.06	0.90	0.05
30	0.375	0.80	0.06	0.92	0.05
31	0.388	0.78	0.06	0.88	0.05
32	0.400	0.77	0.06	0.93	0.05
33	0.413	0.79	0.06	0.92	0.05
34	0.425	0.77	0.06	0.91	0.05
35	0.438	0.78	0.06	0.95	0.05
36	0.450	0.79	0.06	0.95	0.05
37	0.463	0.78	0.06	0.97	0.05
38	0.475	0.82	0.06	0.96	0.05
39	0.488	0.80	0.06	0.98	0.05
40	0.500	0.84	0.06	0.98	0.05
41	0.513	0.82	0.06	0.98	0.05
42	0.525	0.81	0.06	0.99	0.05
43	0.538	0.82	0.06	1.01	0.05
44	0.550	0.80	0.06	1.00	0.05
45	0.563	0.84	0.06	1.02	0.05
46	0.575	0.81	0.06	0.98	0.05
47	0.588	0.83	0.06	1.00	0.05
48	0.600	0.83	0.06	1.00	0.05
49	0.613	0.84	0.06	1.03	0.05
50	0.625	0.81	0.06	1.04	0.05
51	0.638	0.85	0.06	1.01	0.05
52	0.650	0.81	0.06	1.03	0.05
53	0.663	0.82	0.06	1.07	0.05
54	0.675	0.81	0.06	1.05	0.05
55	0.688	0.84	0.06	1.07	0.05
56	0.700	0.86	0.06	1.08	0.05
57	0.713	0.82	0.06	1.09	0.05
58	0.725	0.83	0.06	1.09	0.05
59	0.738	0.83	0.06	1.08	0.05
60	0.750	0.87	0.06	1.09	0.05
61	0.763	0.82	0.06	1.07	0.05
62	0.775	0.88	0.06	1.14	0.05
63	0.788	0.85	0.06	1.15	0.05

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
64	0.800	0.88	0.06	1.20	0.05
65	0.813	0.89	0.06	1.20	0.05
66	0.825	0.87	0.06	1.20	0.05
67	0.838	0.87	0.06	1.20	0.05
68	0.850	0.87	0.06	1.19	0.05
69	0.863	0.88	0.06	1.20	0.05
70	0.875	0.87	0.07	1.23	0.08

Table A1.19 | Secondary ion mass spectrometry time scan of ClAp irradiated for 360 seconds, with the c-axis oriented parallel to the electron beam under 'low power' beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

ClAp parallel to c-axis, 'low power' conditions 120 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.025	0.71	0.02	0.89	0.06
3	0.038	0.62	0.05	0.97	0.06
4	0.050	0.70	0.05	1.00	0.06
5	0.063	0.75	0.06	1.04	0.06
6	0.075	0.78	0.06	1.03	0.06
7	0.088	0.86	0.06	1.01	0.05
8	0.100	0.86	0.06	1.08	0.06
9	0.113	0.84	0.06	1.01	0.05
10	0.125	0.93	0.07	1.00	0.05
11	0.138	0.95	0.07	0.99	0.05
12	0.150	0.94	0.07	1.03	0.05
13	0.163	0.98	0.07	1.01	0.05
14	0.175	0.97	0.07	0.96	0.05
15	0.188	0.97	0.07	0.98	0.05
16	0.200	1.00	0.07	0.97	0.05
17	0.213	1.01	0.07	0.97	0.05
18	0.225	1.00	0.07	0.96	0.05
19	0.238	1.07	0.08	0.96	0.05
20	0.250	1.03	0.07	0.98	0.05
21	0.263	1.05	0.08	0.95	0.05
22	0.275	1.02	0.07	0.97	0.05
23	0.288	1.05	0.07	0.97	0.05
24	0.300	1.05	0.07	0.94	0.05
25	0.313	1.07	0.08	0.95	0.05
26	0.325	1.02	0.07	0.96	0.05
27	0.338	1.07	0.08	0.95	0.05
28	0.350	1.07	0.08	0.99	0.05
29	0.363	1.09	0.08	0.98	0.05
30	0.375	1.08	0.08	1.01	0.05
31	0.388	1.07	0.08	1.02	0.05
32	0.400	1.08	0.08	1.05	0.05
33	0.413	1.11	0.08	1.03	0.05
34	0.425	1.08	0.08	1.03	0.05
35	0.438	1.05	0.07	1.07	0.05
36	0.450	1.08	0.08	1.03	0.05
37	0.463	1.06	0.08	1.11	0.06
38	0.475	1.09	0.08	1.06	0.05
39	0.488	1.08	0.08	1.06	0.05
40	0.500	1.10	0.08	1.05	0.05

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
41	0.513	1.08	0.08	1.07	0.05
42	0.525	1.10	0.08	1.07	0.05
43	0.538	1.11	0.08	1.09	0.05
44	0.550	1.11	0.08	1.06	0.05
45	0.563	1.10	0.08	1.06	0.05
46	0.575	1.11	0.08	0.99	0.05
47	0.588	1.10	0.08	1.05	0.05
48	0.600	1.11	0.08	1.04	0.05
49	0.613	1.11	0.08	1.06	0.05
50	0.625	1.11	0.08	1.05	0.05
51	0.638	1.14	0.08	1.05	0.05
52	0.650	1.11	0.08	1.09	0.05
53	0.663	1.10	0.08	1.09	0.05
54	0.675	1.11	0.08	1.06	0.05
55	0.688	1.12	0.08	1.10	0.05
56	0.700	1.11	0.08	1.12	0.05
57	0.713	1.09	0.07	1.13	0.05
58	0.725	1.08	0.07	1.10	0.05
59	0.738	1.07	0.07	1.13	0.05
60	0.750	1.12	0.08	1.14	0.05
61	0.763	1.06	0.07	1.09	0.05
62	0.775	1.14	0.08	1.13	0.05
63	0.788	1.14	0.08	1.15	0.05
64	0.800	1.12	0.08	1.17	0.06
65	0.813	1.15	0.08	1.15	0.05
66	0.825	1.11	0.08	1.18	0.06
67	0.838	1.11	0.08	1.17	0.06
68	0.850	1.12	0.08	1.15	0.05
69	0.863	1.15	0.08	1.15	0.06
70	0.875	1.15	0.08	1.11	0.07

Table A1.20 | Secondary ion mass spectrometry time scan of ClAp irradiated for 120 seconds, with the *c*-axis oriented parallel to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

ClAp parallel to <i>c</i> -axis, 'low power' conditions 60 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.025	0.88	0.04	0.94	0.09
3	0.038	0.88	0.08	0.96	0.08
4	0.050	0.94	0.07	0.97	0.07
5	0.063	0.96	0.07	1.01	0.07
6	0.075	0.94	0.07	1.00	0.07
7	0.088	0.97	0.08	0.97	0.07
8	0.100	0.96	0.08	1.03	0.07
9	0.113	0.89	0.07	0.97	0.07
10	0.125	0.96	0.08	0.96	0.06
11	0.138	0.96	0.08	0.96	0.06
12	0.150	0.93	0.08	0.98	0.07
13	0.163	0.96	0.08	0.98	0.06
14	0.175	0.96	0.08	0.94	0.06
15	0.188	0.95	0.08	0.95	0.06
16	0.200	0.94	0.08	0.96	0.06

Cycle #	Depth (µm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
17	0.213	0.96	0.08	0.97	0.06
18	0.225	0.94	0.08	0.96	0.06
19	0.238	0.97	0.08	0.94	0.06
20	0.250	0.96	0.08	0.94	0.06
21	0.263	0.94	0.08	0.93	0.06
22	0.275	0.95	0.08	0.92	0.06
23	0.288	0.98	0.08	0.97	0.06
24	0.300	0.93	0.08	0.93	0.06
25	0.313	0.94	0.08	0.97	0.06
26	0.325	0.90	0.08	0.95	0.06
27	0.338	0.92	0.08	0.94	0.06
28	0.350	0.95	0.08	0.93	0.06
29	0.363	0.91	0.08	0.93	0.06
30	0.375	0.94	0.08	1.01	0.06
31	0.388	0.92	0.08	0.96	0.06
32	0.400	0.94	0.08	0.99	0.06
33	0.413	0.92	0.08	0.97	0.06
34	0.425	0.86	0.07	0.96	0.06
35	0.438	0.88	0.07	0.97	0.06
36	0.450	0.91	0.08	0.97	0.06
37	0.463	0.89	0.07	1.00	0.06
38	0.475	0.93	0.08	0.99	0.06
39	0.488	0.90	0.08	0.97	0.06
40	0.500	0.93	0.08	0.96	0.06
41	0.513	0.90	0.08	0.95	0.06
42	0.525	0.92	0.08	0.96	0.06
43	0.538	0.89	0.08	0.98	0.06
44	0.550	0.91	0.08	0.93	0.06
45	0.563	0.92	0.08	0.94	0.06
46	0.575	0.92	0.08	0.90	0.06
47	0.588	0.93	0.08	0.91	0.06
48	0.600	0.91	0.08	0.92	0.06
49	0.613	0.91	0.08	0.94	0.06
50	0.625	0.90	0.07	0.96	0.06
51	0.638	0.95	0.08	0.94	0.06
52	0.650	0.91	0.08	0.95	0.06
53	0.663	0.91	0.08	0.95	0.06
54	0.675	0.89	0.07	0.93	0.06
55	0.688	0.91	0.08	0.95	0.06
56	0.700	0.90	0.07	0.96	0.06
57	0.713	0.87	0.07	0.97	0.06
58	0.725	0.87	0.07	0.95	0.06
59	0.738	0.88	0.07	0.96	0.06
60	0.750	0.92	0.08	0.96	0.06
61	0.763	0.89	0.07	0.95	0.06
62	0.775	0.93	0.08	0.98	0.06
63	0.788	0.90	0.07	0.98	0.06
64	0.800	0.94	0.08	1.01	0.06
65	0.813	0.93	0.08	1.04	0.06
66	0.825	0.91	0.07	1.02	0.06
67	0.838	0.92	0.07	1.03	0.06
68	0.850	0.90	0.07	0.96	0.06
69	0.863	0.90	0.07	0.99	0.06
70	0.875	0.93	0.08	1.03	0.08

Table A1.21 | Secondary ion mass spectrometry time scan of ClAp irradiated for 60 seconds, with the c-axis oriented parallel to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

CIAp parallel to c-axis, 'low power' conditions 30 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.025	1.03	0.05	0.98	0.09
3	0.038	0.95	0.08	0.99	0.08
4	0.050	0.96	0.08	0.99	0.07
5	0.063	0.94	0.07	1.00	0.07
6	0.075	0.91	0.07	0.98	0.07
7	0.088	0.90	0.07	1.00	0.07
8	0.100	0.90	0.07	1.03	0.07
9	0.113	0.84	0.07	0.94	0.06
10	0.125	0.92	0.08	0.95	0.06
11	0.138	0.91	0.07	0.95	0.06
12	0.150	0.86	0.07	0.98	0.06
13	0.163	0.92	0.08	0.99	0.06
14	0.175	0.91	0.08	0.96	0.06
15	0.188	0.92	0.08	0.96	0.06
16	0.200	1.03	0.08	0.93	0.06
17	0.213	0.88	0.07	0.97	0.06
18	0.225	0.92	0.08	0.95	0.06
19	0.238	0.92	0.08	0.94	0.06
20	0.250	0.89	0.07	0.94	0.06
21	0.263	0.93	0.08	0.93	0.06
22	0.275	0.89	0.07	0.91	0.06
23	0.288	0.91	0.08	0.94	0.06
24	0.300	0.90	0.08	0.91	0.06
25	0.313	0.89	0.07	0.93	0.06
26	0.325	0.90	0.07	0.93	0.06
27	0.338	0.91	0.07	0.95	0.06
28	0.350	0.92	0.08	0.92	0.06
29	0.363	0.91	0.07	0.93	0.06
30	0.375	0.88	0.07	0.99	0.06
31	0.388	0.90	0.08	0.96	0.06
32	0.400	0.91	0.08	0.96	0.06
33	0.413	0.89	0.07	0.96	0.06
34	0.425	0.88	0.07	0.96	0.06
35	0.438	0.86	0.07	0.98	0.06
36	0.450	0.89	0.07	0.98	0.06
37	0.463	0.88	0.07	0.99	0.06
38	0.475	0.92	0.08	0.98	0.06
39	0.488	0.91	0.07	0.95	0.06
40	0.500	0.93	0.08	0.97	0.06
41	0.513	0.89	0.07	0.96	0.06
42	0.525	0.89	0.07	0.97	0.06
43	0.538	0.88	0.07	0.97	0.06
44	0.550	0.89	0.07	0.96	0.06
45	0.563	0.89	0.07	0.95	0.06
46	0.575	0.88	0.07	0.91	0.06
47	0.588	0.90	0.07	0.94	0.06
48	0.600	0.89	0.07	0.94	0.06
49	0.613	0.88	0.07	0.94	0.06
50	0.625	0.91	0.07	0.96	0.06
51	0.638	0.89	0.07	0.92	0.06
52	0.650	0.92	0.07	0.97	0.06
53	0.663	0.88	0.07	0.97	0.06
54	0.675	0.87	0.07	0.94	0.06
55	0.688	0.89	0.07	0.95	0.06
56	0.700	0.91	0.07	0.95	0.06
57	0.713	0.86	0.07	0.95	0.06
58	0.725	0.86	0.07	0.95	0.06
59	0.738	0.89	0.07	0.94	0.06
60	0.750	0.90	0.07	0.98	0.06
61	0.763	0.85	0.07	0.96	0.06
62	0.775	0.90	0.07	0.98	0.06
63	0.788	0.91	0.07	0.97	0.06

Cycle #	Depth (µm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
64	0.800	0.92	0.08	1.03	0.06
65	0.813	0.88	0.07	0.98	0.06
66	0.825	0.89	0.07	1.01	0.06
67	0.838	0.90	0.07	0.98	0.06
68	0.850	0.88	0.07	0.98	0.06
69	0.863	0.93	0.07	0.97	0.06
70	0.875	0.89	0.08	0.98	0.07

Table A1.22 | Secondary ion mass spectrometry time scan of ClAp irradiated for 30 seconds, with the *c*-axis oriented parallel to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

ClAp parallel to <i>c</i> -axis, 'low power' conditions 20 seconds irradiation					
Cycle #	Depth (µm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.025	0.81	0.03	0.93	0.19
3	0.038	0.66	0.06	1.01	0.17
4	0.050	0.76	0.06	1.00	0.14
5	0.063	0.76	0.06	1.01	0.13
6	0.075	0.80	0.06	1.00	0.12
7	0.088	0.82	0.06	1.01	0.11
8	0.100	0.86	0.06	1.05	0.10
9	0.113	0.84	0.06	1.00	0.09
10	0.125	0.97	0.07	0.99	0.09
11	0.138	1.00	0.07	0.98	0.08
12	0.150	1.00	0.07	1.02	0.08
13	0.163	1.08	0.08	1.03	0.08
14	0.175	1.29	0.09	0.99	0.07
15	0.188	0.97	0.07	1.01	0.07
16	0.200	1.07	0.08	0.96	0.07
17	0.213	0.98	0.07	1.00	0.07
18	0.225	0.97	0.07	0.98	0.07
19	0.238	1.00	0.07	0.98	0.06
20	0.250	1.00	0.07	1.01	0.06
21	0.263	1.00	0.07	0.98	0.06
22	0.275	0.98	0.07	0.98	0.06
23	0.288	1.01	0.07	1.01	0.06
24	0.300	1.02	0.07	1.00	0.06
25	0.313	1.00	0.07	1.01	0.06
26	0.325	1.00	0.07	1.02	0.06
27	0.338	1.01	0.07	1.01	0.05
28	0.350	1.01	0.07	1.02	0.05
29	0.363	1.02	0.07	1.04	0.05
30	0.375	1.03	0.07	1.10	0.06
31	0.388	1.03	0.07	1.05	0.05
32	0.400	1.03	0.07	1.08	0.05
33	0.413	1.03	0.07	1.08	0.05
34	0.425	1.02	0.07	1.08	0.05
35	0.438	0.99	0.07	1.11	0.05
36	0.450	1.01	0.07	1.09	0.05
37	0.463	1.03	0.07	1.12	0.05
38	0.475	1.04	0.07	1.09	0.05
39	0.488	1.00	0.07	1.06	0.05
40	0.500	1.06	0.07	1.10	0.05

Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
41	0.513	1.05	0.07	1.06	0.05
42	0.525	1.04	0.07	1.09	0.05
43	0.538	1.04	0.07	1.12	0.05
44	0.550	1.05	0.07	1.11	0.05
45	0.563	1.06	0.07	1.10	0.05
46	0.575	1.04	0.07	1.06	0.04
47	0.588	1.05	0.07	1.12	0.05
48	0.600	1.06	0.07	1.08	0.04
49	0.613	1.07	0.07	1.09	0.04
50	0.625	1.03	0.07	1.09	0.04
51	0.638	1.05	0.07	1.09	0.04
52	0.650	1.05	0.07	1.13	0.04
53	0.663	1.05	0.07	1.14	0.04
54	0.675	1.05	0.07	1.13	0.04
55	0.688	1.10	0.07	1.16	0.04
56	0.700	1.07	0.07	1.15	0.04
57	0.713	1.05	0.07	1.17	0.04
58	0.725	1.02	0.07	1.11	0.04
59	0.738	1.04	0.07	1.15	0.04
60	0.750	1.09	0.07	1.16	0.04
61	0.763	1.05	0.07	1.13	0.04
62	0.775	1.10	0.07	1.15	0.04
63	0.788	1.07	0.07	1.17	0.04
64	0.800	1.10	0.07	1.20	0.04
65	0.813	1.08	0.07	1.16	0.04
66	0.825	1.06	0.07	1.20	0.04
67	0.838	1.06	0.07	1.19	0.04
68	0.850	1.04	0.07	1.18	0.04
69	0.863	1.06	0.07	1.17	0.04
70	0.875	1.09	0.07	1.19	0.06

Table A1.23 | Secondary ion mass spectrometry time scan of ClAp irradiated for 20 seconds, with the c-axis oriented parallel to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

ClAp parallel to c-axis, 'low power' conditions 10 seconds irradiation					
Cycle #	Depth (μm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
2	0.03	0.74	0.03	0.94	0.06
3	0.04	0.62	0.05	0.99	0.06
4	0.05	0.68	0.05	1.05	0.06
5	0.06	0.73	0.06	1.06	0.06
6	0.08	0.78	0.06	1.08	0.06
7	0.09	0.82	0.06	1.04	0.06
8	0.10	0.85	0.06	1.08	0.06
9	0.11	0.82	0.06	1.04	0.06
10	0.13	0.90	0.07	1.03	0.06
11	0.14	0.88	0.07	1.03	0.06
12	0.15	0.90	0.07	1.07	0.06
13	0.16	0.94	0.07	1.06	0.06
14	0.18	0.95	0.07	1.02	0.06
15	0.19	0.97	0.07	1.06	0.06
16	0.20	0.98	0.07	1.03	0.06
17	0.21	0.96	0.07	1.06	0.06

Cycle #	Depth (µm)	Baseline-normalised F/Ca (CPS)	Baseline-normalised F/Ca uncertainty (2σ)	Baseline-normalised Cl/Ca (CPS)	Baseline-normalised Cl/Ca uncertainty (2σ)
18	0.23	0.96	0.07	1.07	0.06
19	0.24	0.98	0.07	1.05	0.06
20	0.25	0.97	0.07	1.05	0.06
21	0.26	1.00	0.07	1.04	0.06
22	0.28	0.99	0.07	1.02	0.05
23	0.29	1.03	0.08	1.06	0.06
24	0.30	1.00	0.07	1.01	0.05
25	0.31	1.01	0.07	1.05	0.06
26	0.33	0.99	0.07	1.07	0.06
27	0.34	1.03	0.08	1.04	0.05
28	0.35	1.02	0.07	1.08	0.06
29	0.36	1.03	0.08	1.08	0.06
30	0.38	1.04	0.08	1.11	0.06
31	0.39	1.01	0.08	1.09	0.06
32	0.40	1.05	0.08	1.12	0.06
33	0.41	1.01	0.07	1.10	0.06
34	0.43	1.02	0.07	1.11	0.06
35	0.44	1.02	0.07	1.13	0.06
36	0.45	1.02	0.07	1.13	0.06
37	0.46	1.02	0.07	1.18	0.06
38	0.48	1.04	0.07	1.13	0.06
39	0.49	1.03	0.07	1.13	0.06
40	0.50	1.07	0.08	1.14	0.06
41	0.51	1.04	0.07	1.14	0.06
42	0.53	1.06	0.08	1.16	0.06
43	0.54	1.06	0.08	1.17	0.06
44	0.55	1.05	0.08	1.13	0.06
45	0.56	1.07	0.08	1.13	0.06
46	0.58	1.05	0.08	1.07	0.05
47	0.59	1.08	0.08	1.10	0.05
48	0.60	1.04	0.08	1.09	0.05
49	0.61	1.06	0.08	1.13	0.06
50	0.63	1.05	0.08	1.14	0.06
51	0.64	1.06	0.08	1.11	0.06
52	0.65	1.05	0.07	1.14	0.06
53	0.66	1.04	0.07	1.12	0.06
54	0.68	1.04	0.07	1.11	0.06
55	0.69	1.09	0.08	1.14	0.06
56	0.70	1.04	0.08	1.12	0.06
57	0.71	1.02	0.07	1.12	0.06
58	0.73	1.01	0.07	1.10	0.06
59	0.74	0.99	0.07	1.11	0.05
60	0.75	1.05	0.08	1.13	0.06
61	0.76	1.04	0.07	1.08	0.05
62	0.78	1.06	0.08	1.15	0.06
63	0.79	1.03	0.07	1.12	0.06
64	0.80	1.10	0.08	1.18	0.06
65	0.81	1.08	0.08	1.19	0.06
66	0.83	1.05	0.07	1.18	0.06
67	0.84	1.04	0.07	1.16	0.06
68	0.85	1.06	0.07	1.16	0.06
69	0.86	1.05	0.07	1.18	0.06
70	0.88	1.07	0.08	1.19	0.08

Table A1.24 | Secondary ion mass spectrometry time scan of ClAp irradiated for 10 seconds, with the *c*-axis oriented parallel to the electron beam under ‘low power’ beam conditions. Fully propagated two standard deviation counting uncertainties are given for each analysis.

Appendix 2

Campi Flegrei biotite compositions

This appendix presents average biotite compositions from different eruptions of Campi Flegrei, measured by EPMA. They are used in Chapters 4, 5 and 6 to aid in constraining the evolution dissolved magmatic volatile contents.

Campi Flegrei biotite compositions							
	Monte Nuovo	Astroni 1	Accademia	Fondi di Baia	Pisani 1	Pomici Principali	Minopoli 1
SiO ₂	36.39	36.50	36.71	36.60	36.35	35.61	35.66
Al ₂ O ₃	14.20	14.20	14.07	14.03	14.85	14.50	14.85
TiO ₂	5.04	5.14	5.19	4.95	5.01	4.66	4.97
FeOt	12.91	13.41	13.61	13.64	12.00	13.12	10.95
MnO	0.16	0.19	0.20	0.22	0.10	0.15	0.07
MgO	15.23	15.18	15.20	15.12	16.04	15.09	16.60
K ₂ O	9.33	9.37	9.41	9.36	9.33	9.35	9.53
Na ₂ O	0.41	0.45	0.48	0.45	0.39	0.32	0.37
CaO	0.03	0.06	0.06	0.09	0.08	0.03	0.03
F	0.96	1.03	1.07	0.64	0.72	0.78	0.84
Cl	0.12	0.14	0.14	0.09	0.11	0.14	0.09
Total	94.78	95.65	96.13	95.19	94.96	93.74	93.96
n	229	82	100	18	55	354	195
Number of ions based on 22 O							
Si ^I	5.50	5.49	5.50	5.51	5.44	5.45	5.39
Al ^I (iv)	2.50	2.51	2.50	2.49	2.56	2.55	2.61
Al ^M (vi)	0.04	0.02	0.00	0.01	0.06	0.06	0.04
Ti ^M	0.57	0.58	0.59	0.56	0.56	0.54	0.57
Fe ^M	1.63	1.69	1.71	1.72	1.50	1.68	1.39
Mn ^M	0.02	0.02	0.03	0.03	0.01	0.02	0.01
Mg ^M	3.43	3.40	3.40	3.39	3.58	3.44	3.74
K ^I	1.80	1.80	1.80	1.80	1.78	1.82	1.84
Na ^I	0.12	0.13	0.14	0.13	0.11	0.10	0.11
Ca ^I	0.01	0.01	0.01	0.01	0.01	0.01	0.00
F ^A	0.46	0.49	0.51	0.31	0.34	0.38	0.40
Cl ^A	0.03	0.03	0.04	0.02	0.03	0.04	0.02
OH ^A	3.51	3.48	3.46	3.67	3.63	3.59	3.58

Table A2.1 | Average biotite compositions from the studied Campi Flegrei eruptions. Mt Olibano biotite compositions were not analysed. Oxide compositions were measured by EPMA (Chapter 2) and are in wt%. Compositions are recalculated to show the number of atoms per formula unit, based on 22 Oxygen anions. Superscript letters refer to different sites in the biotite crystal structure; aluminium is divided between the tetrahedral and octahedral sites. OH is calculated by difference. n = number of analyses.

Appendix 3

Astroni 1 apatite and glass compositions

The data in this appendix were published as supplementary material in:

Stock M.J., Humphreys M.C.S., Smith V.C., Isaia R., and Pyle D.M., 2016.

Late-stage volatile saturation as a potential trigger for explosive volcanic eruptions.

Nature Geoscience, 9, 249-254, doi: 10.1038/ngeo2639.

This appendix presents the compositions of apatites and hydrous glasses in different ‘textural associations’ from the Astroni 1 eruption of Campi Flegrei. These data are used in Chapter 5 to determine the temporal evolution of magmatic volatile contents. Apatite occurs as inclusions within clinopyroxene and biotite phenocrysts and as a microphenocryst phase, surrounded by silicate melt. Hydrous glass analyses include clinopyroxene- and biotite-hosted melt inclusions, as well as phonolitic matrix glasses.

The sample used in this study is CF69 of Smith *et al.*, (2011).

Appendix 3.1. Astroni 1 apatite compositions

Clinopyroxene-hosted apatite inclusions								
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	OH	Total
CF69_cpx69_ap1	41.24	0.68	54.09	0.15	2.43	0.93	0.40	98.50
CF69_cpx104_ap1	40.50	0.78	53.95	0.29	2.42	0.90	0.36	97.81
CF69_cpx69_ap1a	41.24	0.68	54.09	0.15	2.32	0.98	0.38	98.47
CF69_cpx153_ap2	41.18	0.59	53.71	0.33	2.27	1.01	0.50	98.16
CF69_cpx21_ap2	41.36	0.55	54.03	0.25	2.35	0.95	0.34	98.47
CF69_cpx132_ap1	41.13	0.61	53.37	0.38	1.92	0.89	0.35	97.47
CF69_cpx139_ap2	41.33	0.57	54.14	0.18	2.52	0.88	0.39	98.57
CF69_cpx73_ap2	41.07	0.82	53.78	0.24	2.38	0.90	0.39	98.19
CF69_cpx73_ap3	41.07	0.82	53.78	0.24	2.38	0.92	0.43	98.23
CF69_cpx32_ap1	41.30	0.77	54.36	0.30	2.29	0.94	0.44	99.02
CF69_cpx95_ap2	40.95	0.67	53.81	0.24	2.41	0.91	0.37	97.95
CF69_cpx137_ap1	41.24	0.61	53.72	0.32	2.40	0.90	0.43	98.20
CF69_cpx151_ap1	40.57	0.94	53.52	0.15	2.36	0.93	0.42	97.49
CF69_cpx44_ap6	40.94	0.56	53.97	0.46	2.34	0.85	0.41	98.16
CF69_cpx10_ap2	41.31	0.68	54.05	0.09	2.39	0.92	0.32	98.39
CF69_cpx11_ap1	40.99	0.76	53.92	0.32	2.20	1.01	0.44	98.27
CF69_cpx35_ap1	41.68	0.66	54.34	0.29	2.47	0.93	0.38	99.32
CF69_cpx112_ap1	41.39	0.50	54.33	0.47	2.41	0.92	0.42	99.02
CF69_cpx65_ap2	41.33	0.72	54.62	0.17	2.51	0.91	0.43	99.24

Table A3.1 | Compositions of clinopyroxene-hosted apatite inclusions from Astroni 1. Halogens and OH were measured by SIMS, all other elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl, OH. Concentrations are in wt%.

Biotite-hosted apatite inclusions								
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	OH	Total
CF69_bi23_ap2	41.60	0.56	53.97	0.34	2.45	0.92	0.46	98.86
CF69_bi23_ap3	41.18	0.59	54.18	0.38	2.55	0.95	0.49	98.81
CF69_bi38_ap3	41.09	0.69	53.86	0.58	2.57	0.95	0.43	98.66
CF69_bi48_ap1	41.14	0.59	54.14	0.31	2.48	0.91	0.50	98.58
CF69_bi97_ap1	41.32	0.60	54.30	0.56	2.45	0.93	0.45	99.17
CF69_bi117_ap1	41.55	0.53	54.51	0.38	2.60	0.98	0.50	99.49
CF69_bi156_ap1	40.85	0.51	54.49	0.40	2.42	0.92	0.45	98.61
CF69_bi167_ap1	40.13	0.59	53.81	0.35	2.45	0.90	0.45	97.23
CF69_bi35_ap1	41.64	0.47	54.06	0.42	2.48	0.90	0.45	98.98
CF69_bi27_ap1	41.78	0.50	53.99	0.29	2.43	0.91	0.42	98.90
CF69_bi149_ap1	40.49	0.74	54.37	0.27	2.48	0.92	0.49	98.28
CF69_bi98_ap1	40.98	0.58	53.87	0.54	2.51	0.92	0.41	98.35
CF69_bi164_ap5	40.95	0.60	54.35	0.27	2.56	0.91	0.50	98.62
CF69_bi164_ap1	41.25	0.65	54.54	0.28	2.62	0.93	0.49	99.22
CF69_bi158_ap1	41.75	0.45	54.59	0.44	2.48	0.93	0.41	99.60
CF69_bi170_ap1	40.97	0.40	54.01	0.40	2.49	0.92	0.41	98.14

Table A3.2 | Compositions of biotite-hosted apatite inclusions from Astroni 1. Halogens and OH were measured by SIMS, all other elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl, OH. Concentrations are in wt%.

Apatite microphenocrysts								
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	OH	Total
CF69_mpc47	41.50	0.64	54.55	0.39	3.27	0.54	0.23	99.51
CF69_mpc32	40.85	0.80	52.57	0.10	2.67	1.07	0.52	96.97
CF69_mpc29	42.62	0.06	53.77	0.15	2.68	0.95	0.54	99.17
CF69_mpc10	41.65	0.61	53.38	0.45	2.78	0.93	0.53	98.69
CF69_mpc26	41.26	0.76	53.59	0.22	2.64	0.97	0.56	98.40
CF69_mpc6	41.40	0.56	53.84	0.63	2.58	0.97	0.55	98.97
CF69_mpc19	41.16	0.67	53.39	0.14	2.58	0.97	0.56	97.90
CF69_mpc22	42.17	0.61	53.78	0.16	2.59	0.93	0.57	99.23
CF69_mpc20	41.16	0.66	53.77	0.45	2.50	0.95	0.56	98.53
CF69_mpc21	41.78	0.62	53.98	0.28	2.52	0.94	0.57	99.15
CF69_mpc49	40.05	1.10	53.01	0.18	2.70	1.01	0.58	97.00
CF69_mpc46	41.46	0.68	53.35	0.17	2.41	1.00	0.59	98.14

Table A3.3 | Compositions of apatite microphenocrysts from Astroni 1. Halogens and OH were measured by SIMS, all other elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl, OH. Concentrations are in wt%. Low totals can be accounted for by REEs and trace elements (i.e. Sr), which were not analysed systematically but occur in concentrations up to >2.3 wt%.

Appendix 3.2. Astroni 1 glass compositions

Clinopyroxene-hosted melt inclusions															
	SiO ₂	Na ₂ O	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	F	H ₂ O	CO ₂ (ppm)	Total
CF69_cpx92_mi1	57.38	4.35	0.76	18.60	8.44	2.47	0.41	0.11	2.85	0.17	0.84	0.30	2.21	34.63	98.90
CF69_cpx116_mi1	56.44	3.65	0.78	18.40	8.84	2.37	0.51	0.02	3.27	0.15	0.73	0.22	2.33	225.28	97.73
CF69_cpx113_mi1	56.74	4.76	0.55	17.51	8.57	2.17	0.45	0.15	3.19	0.08	0.93	0.25	2.62	-	97.97
CF69_cpx127_mi3	57.17	4.07	0.54	17.63	8.36	2.31	0.49	0.14	3.60	0.16	0.88	0.20	2.57	183.81	98.14
CF69_cpx127_mi1	56.55	4.22	0.58	17.65	8.28	2.34	0.45	0.10	3.84	0.15	0.82	0.20	2.51	423.25	97.74
CF69_cpx130_mi1	56.80	4.51	0.55	17.67	8.37	2.30	0.51	0.11	3.40	0.10	0.93	0.28	2.43	-	97.95
CF69_cpx138_mi2	55.39	4.62	0.42	17.09	8.48	2.01	0.40	0.13	3.34	0.06	0.97	0.27	2.69	20.51	95.86
CF69_cpx156_mi2	58.52	4.56	0.45	17.12	8.03	2.23	0.48	0.16	3.53	0.09	0.91	0.26	2.30	-	98.63
CF69_cpx182_mi2	55.59	3.87	0.77	17.53	8.48	2.70	0.50	0.17	3.39	0.12	0.73	0.21	2.51	-	96.58
CF69_cpx182_mi1	55.35	3.76	0.71	17.52	8.53	2.64	0.48	0.12	3.90	0.20	0.74	0.19	2.39	-	96.52
CF69_cpx22_mi1	57.70	4.39	0.65	17.90	8.08	2.47	0.45	0.10	3.36	0.12	0.96	0.28	2.37	115.18	98.83
CF69_cpx23_mi2	59.17	4.25	0.42	17.84	8.36	2.19	0.49	0.19	3.65	0.10	1.00	0.28	2.22	122.16	100.17
CF69_cpx55_mi1	56.74	4.26	0.54	18.07	8.89	2.17	0.41	0.04	3.15	0.08	0.87	0.26	2.12	133.18	97.62
CF69_cpx55_mi2	56.99	4.52	0.53	17.82	8.50	2.15	0.44	0.13	3.37	0.10	0.93	0.25	2.56	-	98.28
CF69_cpx66_mi1	54.97	4.15	0.61	17.60	8.55	2.43	0.47	0.09	3.76	0.14	0.75	0.21	2.21	118.97	95.95
CF69_cpx66_mi3	56.56	4.02	0.72	18.24	8.83	2.62	0.47	0.12	4.20	0.13	0.69	0.23	2.58	-	99.41
CF69_cpx82_mi1	56.78	4.20	0.50	17.90	8.35	2.07	0.45	0.19	3.40	0.13	0.91	0.28	2.29	107.04	97.47
CF69_cpx91_mi1	58.21	4.60	0.51	17.67	8.37	2.03	0.48	0.20	3.40	0.08	1.03	0.31	2.27	108.86	99.17
CF69_cpx97_mi3	57.73	4.46	0.54	17.91	8.27	2.34	0.45	0.12	3.38	0.08	0.90	0.25	2.00	106.75	98.44

Table A3.4 | Compositions of clinopyroxene-hosted melt inclusions from Astroni

1. Water, CO₂ and F were measured by SIMS, all other elements were measured by EPMA. Concentrations are in wt% unless otherwise specified.

Biotite-hosted melt inclusions														
	SiO ₂	Na ₂ O	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	F	H ₂ O	Total
CF69_bi30_mi1	54.22	4.28	0.47	16.71	8.16	2.14	0.50	0.15	3.54	0.07	0.93	0.31	4.43	95.90
CF69_bi46_mi2	56.62	4.82	0.60	17.65	8.27	2.19	0.53	0.13	3.90	0.09	0.92	0.22	1.60	97.53
CF69_bi47_mi1	55.43	4.54	0.39	17.22	8.26	2.19	0.43	0.19	3.36	0.09	0.97	0.26	2.22	95.54
CF69_bi5_mi1	55.56	4.54	0.49	17.46	8.30	2.17	0.52	0.18	3.41	0.12	0.94	0.24	3.04	96.97
CF69_bi79_mi1	57.08	4.58	0.52	17.75	8.36	2.23	0.50	0.09	3.62	0.10	0.92	0.29	2.45	98.50
CF69_bi124_mi1	56.68	4.82	0.51	17.70	8.25	2.26	0.40	0.23	3.45	0.10	0.88	0.25	1.43	96.97
CF69_bi169_mi1	55.47	4.39	0.51	17.49	8.26	2.28	0.39	0.07	3.27	0.15	0.87	0.24	1.27	94.68

Table A3.5 | Compositions of biotite-hosted melt inclusions from Astroni 1. Water, and F were measured by SIMS, all other elements were measured by EPMA. Concentrations are in wt%.

Matrix glasses														
	SiO ₂	Na ₂ O	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	F	H ₂ O	Total
CF69_mg2_1	59.14	3.90	0.54	18.37	8.61	2.29	0.48	0.16	3.27	0.04	0.91	0.25	0.71	98.67
CF69_mg9_1	56.79	2.87	0.52	18.09	8.09	2.41	0.48	0.14	3.37	0.10	0.85	0.26	0.91	94.88
CF69_mg6_1	58.83	4.50	0.58	18.11	8.56	2.36	0.37	0.07	3.41	0.05	0.92	0.25	1.26	99.27
CF69_mg5_1	59.43	4.67	0.49	18.09	8.44	2.45	0.46	0.16	3.42	0.09	0.94	0.22	0.20	99.06
CF69_mg9_2	58.68	4.52	0.59	18.01	8.67	2.49	0.45	0.20	3.33	0.13	0.92	0.29	0.95	99.23
CF69_mg3_1	57.69	4.38	0.50	17.85	8.47	2.28	0.42	0.17	3.31	0.09	0.91	0.26	0.67	96.99
CF69_mg3_2	57.69	4.38	0.50	17.85	8.47	2.28	0.42	0.17	3.31	0.09	0.91	-	-	96.06
CF69_mg8_1	58.84	4.26	0.48	18.19	8.65	2.10	0.40	0.18	3.06	0.09	0.86	-	-	97.10
CF69_mg8_2	56.36	4.24	0.45	17.89	8.37	2.38	0.46	0.12	3.17	0.10	0.86	-	-	94.39
CF69_mg8_3	56.77	3.36	0.47	17.80	8.28	2.34	0.42	0.14	2.98	0.08	0.89	-	-	93.55
CF69_mg9_3	58.68	4.52	0.59	18.01	8.67	2.49	0.45	0.20	3.33	0.13	0.92	-	-	98.00

Table A3.6 | Compositions of matrix glasses from Astroni 1. Water and F were measured by SIMS, all other elements were measured by EPMA. Concentrations are in wt%.

Appendix 4

Full dataset of Campi Flegrei glass compositions

This appendix presents a complete dataset of clinopyroxene- and biotite-hosted melt inclusion and matrix glass compositions from the eight studied eruptions of Campi Flegrei. These data are used in Chapter 6 to investigate the Campi Flegrei liquid line of descent and to examine the pre-eruptive volatile contents of the different eruptions.

Many of the samples used in this study are from Smith *et al.*, (2011). See Section 6.2. and Smith *et al.*, (2011) for sampling locations.

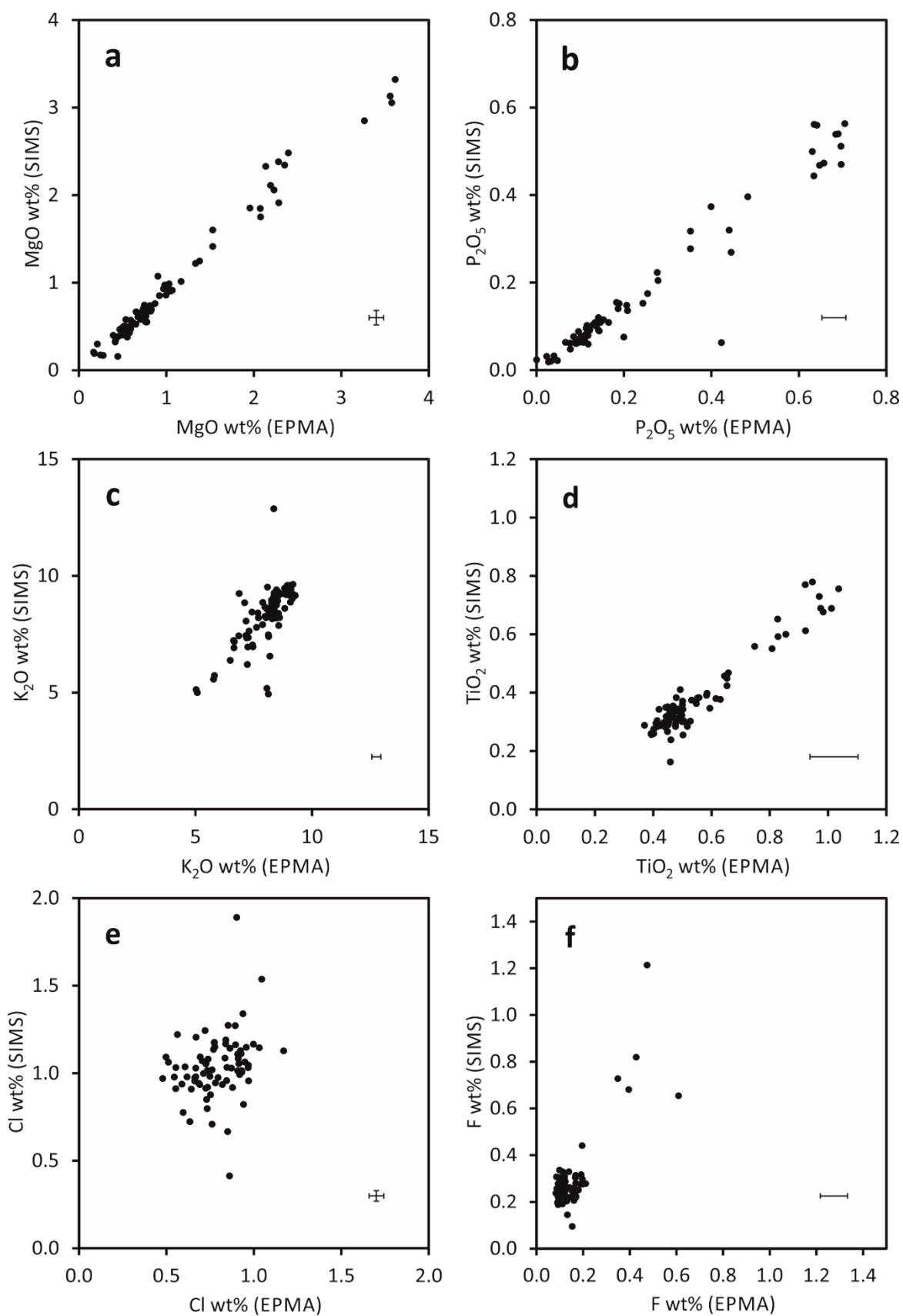


Figure A4.1 | The relationship between glass compositions measured by EPMA and SIMS. Analyses include matrix glasses and melt inclusions. Where shown, error bars represent average precision with ± 1 s.d. (EPMA) or a 95% confidence interval (SIMS); otherwise uncertainties are less than the size of the data points.

Appendix 4.1. Melt inclusion EPMA data

Monte Nuovo clinopyroxene-hosted melt inclusions													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
cf195_cpx38_m3	58.46	3.70	0.68	18.60	8.77	2.47	0.48	0.11	3.56	0.14	0.80	0.09	97.88
cf195_cpx48_m2	58.37	4.12	0.82	17.70	8.27	2.87	0.51	0.10	3.50	0.11	0.87	0.07	97.30
cf195_cpx65_m1	58.97	3.87	1.58	17.00	7.29	3.57	0.50	0.13	3.36	0.10	1.01	0.07	97.46
cf195_cpx74_m3	56.95	3.87	0.58	17.75	8.33	2.48	0.48	0.07	3.52	0.13	0.82	0.08	95.04
cf195_cpx94_m1	58.41	4.18	0.63	18.47	8.60	2.59	0.51	0.06	3.36	0.12	0.85	0.07	97.86
cf195_cpx100_m1	57.15	4.36	0.67	19.15	6.86	4.03	0.40	0.12	3.28	0.09	0.88	0.08	97.09
cf195_cpx113_m5	57.79	4.11	0.99	18.21	8.59	3.20	0.40	0.04	3.36	0.14	0.81	0.09	97.73
cf195_cpx113_m6	58.77	4.45	0.55	18.17	8.40	2.22	0.43	0.09	3.31	0.08	0.95	0.07	97.48
cf195_cpx114_m4	58.17	3.61	0.72	18.62	8.80	2.68	0.52	0.10	3.81	0.18	0.74	0.12	98.07
cf195_cpx123_m1	60.93	4.76	0.49	16.73	7.20	2.20	0.63	0.18	3.86	0.08	1.04	0.04	98.14
cf195_cpx127_m1	58.73	4.30	0.65	18.22	8.64	2.29	0.51	0.13	3.75	0.11	0.89	0.08	98.29
cf195_cpx130_m1	58.21	4.12	0.76	18.44	8.18	2.90	0.54	0.12	3.68	0.12	0.82	0.09	97.97
cf195_cpx137_m2	58.65	4.02	1.21	17.20	7.88	3.49	0.51	0.14	3.51	0.10	0.80	0.06	97.58
cf195_cpx147_m2	58.83	4.22	0.57	17.47	8.23	2.02	0.45	0.14	3.03	0.11	0.91	0.08	96.05
cf195_cpx147_m3	59.75	4.34	0.54	18.19	8.62	2.16	0.52	0.09	3.26	0.12	0.86	0.06	98.52
cf195_cpx154_m1	57.31	4.44	0.65	17.19	7.22	2.55	0.45	0.16	3.63	0.10	1.06	0.04	94.77
cf195_cpx185_m1	58.45	4.02	0.80	17.96	8.18	2.65	0.40	0.15	3.71	0.17	1.01	0.09	97.58
cf195_cpx194_m5	56.64	3.73	1.30	17.19	7.91	3.76	0.48	0.07	3.53	0.11	0.72	0.05	95.50
cf195_cpx214_m1	58.45	3.96	0.79	18.13	8.53	2.62	0.55	0.06	3.90	0.15	0.79	0.08	98.02
cf195_cpx38_mi1	56.24	4.04	0.64	17.23	8.42	2.49	0.53	0.15	3.54	0.14	0.65	0.08	94.13
cf195_cpx64_mi1	57.35	4.04	0.77	17.70	8.57	2.59	0.48	0.09	3.82	0.15	0.66	0.10	96.33
cf195_cpx86_mi2	57.81	4.11	0.75	18.27	8.49	2.55	0.48	0.11	3.46	0.13	0.73	0.09	96.97
cf195_cpx86_mi3	56.19	3.94	0.74	17.26	7.89	2.48	0.42	0.15	3.39	0.14	0.64	0.09	93.31
cf195_cpx110_mi1	58.05	5.04	0.76	16.54	6.86	2.72	0.55	0.19	3.96	0.08	0.85	0.03	95.63
cf195_cpx113_mi7	57.63	4.65	0.59	18.02	8.37	2.26	0.46	0.08	3.38	0.12	0.84	0.07	96.47
cf195_cpx122_mi1	58.35	4.20	0.87	18.03	8.48	2.81	0.50	0.10	3.83	0.13	0.67	0.08	98.06
cf195_cpx122_mi2	58.26	4.08	0.81	18.12	8.94	2.83	0.44	0.12	3.66	0.13	0.66	0.09	98.14
cf195_cpx123_mi3	59.68	5.03	0.51	16.97	7.43	2.33	0.53	0.12	3.85	0.10	0.94	0.05	97.55
cf195_cpx137_mi5	58.71	4.42	0.70	17.71	8.42	2.24	0.49	0.11	3.37	0.11	0.77	0.07	97.14
cf195_cpx159_mi1	57.35	4.76	1.69	16.88	6.82	4.34	0.47	0.17	4.07	0.15	0.87	0.04	97.61
cf195_cpx159_mi4	57.83	4.85	0.66	17.10	7.18	2.59	0.50	0.20	3.91	0.15	0.89	0.05	95.90
cf195_cpx188_mi1	58.59	4.77	0.68	17.52	8.25	2.52	0.47	0.13	3.38	0.11	0.78	0.05	97.24
cf195_gcp39_m_1	58.76	4.71	0.58	18.11	8.46	2.43	0.40	0.18	3.79	0.13	0.75	0.03	98.33
cf195_gcp39_m_1	58.55	4.85	0.75	18.58	7.98	2.39	0.45	0.14	3.13	0.11	0.92	0.08	97.91
cf195_gcp39_m_2	54.71	4.14	1.65	15.87	7.33	4.10	0.53	0.16	3.87	0.10	0.69	0.06	93.20
cf195_gcp39_m_1	58.12	4.84	0.68	17.02	7.25	2.20	0.42	0.11	3.30	0.11	0.95	0.07	95.06
cf195_gcp39_m_2	55.00	4.86	0.74	16.77	8.18	2.34	0.42	0.04	3.32	0.10	1.01	0.08	92.86
cf195_gcp39_m_2	55.85	4.15	0.74	17.21	7.98	2.53	0.41	0.05	3.11	0.12	0.72	0.07	92.96

Table A4.1 | Major and trace element compositions of clinopyroxene-hosted melt inclusions from Monte Nuovo. All elements were measured by EPMA. Concentrations are in wt%.

Astroni 1 clinopyroxenes-hosted melt inclusions													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
CF69_cpx_95_mi_1	55.98	4.39	0.69	18.53	8.55	2.31	0.37	0.13	3.41	0.15	0.72	-	95.24
CF69_cpx_4_mi_1	58.85	4.62	0.61	18.42	8.41	2.21	0.46	0.12	3.26	0.09	0.88	-	97.94
CF69_cpx_7_mi_2	57.63	4.37	0.52	17.94	8.45	2.16	0.41	0.14	3.40	0.09	1.02	-	96.14
CF69_cpx_17_mi_1	57.82	4.44	0.51	17.83	8.35	2.39	0.42	0.16	3.15	0.07	0.93	-	96.08
CF69_cpx_18_mi_1	57.66	4.24	0.70	18.28	9.15	2.42	0.46	0.08	3.02	0.11	0.74	-	96.86
CF69_cpx_18_mi_2	57.54	4.08	0.64	18.07	8.39	2.16	0.37	0.10	3.38	0.10	0.81	-	95.64
CF69_cpx_22_mi_1	57.70	4.39	0.65	17.90	8.08	2.47	0.45	0.10	3.36	0.12	0.96	-	96.17
CF69_cpx_22_mi_2	57.59	4.57	0.61	18.14	8.27	2.47	0.50	0.20	3.35	0.09	0.92	-	96.72
CF69_cpx_22_mi_3	58.38	4.36	0.66	18.33	8.19	2.44	0.43	0.18	3.36	0.14	0.91	-	97.37
CF69_cpx_23_mi_1	58.27	4.38	0.47	17.97	8.34	2.17	0.44	0.14	3.44	0.12	0.91	0.07	96.72
CF69_cpx_23_mi_2	59.17	4.25	0.42	17.84	8.36	2.19	0.49	0.19	3.65	0.10	1.00	0.06	97.72
CF69_cpx_39_mi_1	57.87	4.58	0.49	17.89	8.55	2.30	0.38	0.07	3.19	0.10	0.92	-	96.34
CF69_cpx_40_mi_1	55.71	4.29	0.57	17.33	7.59	2.41	0.48	0.20	3.55	0.10	0.93	0.08	93.24
CF69_cpx_40_mi_2	56.86	4.54	0.48	17.59	8.20	2.23	0.43	0.16	3.24	0.11	0.96	0.08	94.89
CF69_cpx_40_mi_3	57.14	4.20	0.52	17.72	8.17	2.20	0.38	0.18	3.42	0.05	0.93	0.08	94.99
CF69_cpx_40_mi_4	56.73	4.23	0.49	17.45	8.19	2.24	0.46	0.12	3.31	0.10	0.96	0.07	94.34
CF69_cpx_55_mi_1	56.74	4.26	0.54	18.07	8.89	2.17	0.41	0.04	3.15	0.08	0.87	0.07	95.30
CF69_cpx_55_mi_2	56.99	4.52	0.53	17.82	8.50	2.15	0.44	0.13	3.37	0.10	0.93	0.07	95.54
CF69_cpx_62_mi_1	55.85	4.87	0.59	17.25	8.47	2.20	0.42	0.12	3.35	0.10	0.95	-	94.16
CF69_cpx_66_mi_1	54.97	4.15	0.61	17.60	8.55	2.43	0.47	0.09	3.76	0.14	0.75	0.11	93.63
CF69_cpx_66_mi_2	56.47	3.87	0.59	17.96	8.89	2.48	0.50	0.08	3.63	0.14	0.73	-	95.35
CF69_cpx_66_mi_3	56.56	4.02	0.72	18.24	8.83	2.62	0.47	0.12	4.20	0.13	0.69	-	96.60
CF69_cpx_68_mi_1	57.49	4.85	0.42	17.64	7.85	2.42	0.47	0.20	3.39	0.08	1.00	0.03	95.84
CF69_cpx_68_mi_2	56.56	4.37	0.52	17.63	8.43	2.23	0.47	0.05	3.42	0.10	0.91	-	94.69
CF69_cpx_70_mi_1	55.82	4.24	0.51	17.68	8.19	2.25	0.52	0.10	3.46	0.07	0.89	-	93.75
CF69_cpx_70_mi_2	58.12	4.62	0.45	18.30	8.60	2.26	0.44	0.11	3.15	0.08	0.93	0.05	97.10
CF69_cpx_75_mi_1	57.20	4.32	0.67	17.79	8.33	2.32	0.48	0.12	3.15	0.11	0.95	0.08	95.53
CF69_cpx_75_mi_2	54.40	3.45	0.64	17.72	9.17	2.32	0.32	0.13	3.11	0.09	0.76	0.07	92.18
CF69_cpx_75_mi_3	56.81	4.33	0.62	17.71	8.24	2.39	0.47	0.11	3.54	0.14	0.87	0.09	95.32
CF69_cpx_82_mi_1	56.78	4.20	0.50	17.90	8.35	2.07	0.45	0.19	3.40	0.13	0.91	0.07	94.96
CF69_cpx_83_mi_1	56.29	4.33	0.43	16.94	7.99	2.43	0.45	0.20	3.48	0.10	0.90	0.06	93.58
CF69_cpx_87_mi_1	56.20	4.86	0.45	18.43	8.34	2.49	0.54	0.09	3.88	0.13	0.72	0.11	96.25
CF69_cpx_87_mi_2	55.92	4.12	0.63	18.09	9.02	2.49	0.51	0.05	3.54	0.19	0.71	0.12	95.38
CF69_cpx_88_mi_1	57.80	4.05	0.50	18.20	8.58	2.18	0.35	0.10	2.86	0.06	0.87	-	95.55
CF69_cpx_88_mi_2	56.19	4.39	0.66	17.78	8.32	2.19	0.42	0.13	3.14	0.05	0.96	-	94.23
CF69_cpx_88_mi_3	58.21	4.23	0.53	18.19	8.44	2.25	0.30	0.01	2.52	0.08	0.80	-	95.57
CF69_cpx_90_mi_1	57.21	4.05	0.63	18.50	8.69	2.32	0.48	0.10	3.16	0.17	0.80	-	96.10
CF69_cpx_91_mi_1	58.21	4.60	0.51	17.67	8.37	2.03	0.48	0.20	3.40	0.08	1.03	0.07	96.65
CF69_cpx_91_mi_2	58.66	5.31	0.48	17.28	7.38	2.04	0.51	0.16	3.35	0.08	1.10	-	96.37
CF69_cpx_91_mi_3	57.51	4.69	0.51	17.36	8.48	2.08	0.48	0.18	3.26	0.13	1.02	-	95.70
CF69_cpx_91_mi_4	57.47	4.55	0.51	17.06	8.28	2.13	0.48	0.19	3.24	0.08	0.98	-	94.99
CF69_cpx_92_mi_1	57.38	4.35	0.76	18.60	8.44	2.47	0.41	0.11	2.85	0.17	0.84	0.04	96.43
CF69_cpx_92_mi_2	58.67	4.48	0.55	18.48	7.67	2.51	0.32	0.08	2.82	0.10	0.82	0.06	96.56
CF69_cpx_93_mi_1	57.55	4.58	0.52	17.51	8.05	2.51	0.48	0.19	3.61	0.07	0.98	-	96.06
CF69_cpx_93_mi_2	57.78	4.41	0.56	17.66	8.07	2.37	0.58	0.14	3.52	0.10	0.98	0.05	96.23
CF69_cpx_97_mi_1	55.28	4.51	0.49	17.09	8.08	2.17	0.32	0.11	3.08	0.08	0.81	0.09	92.10
CF69_cpx_97_mi_2	56.92	4.62	0.48	17.93	8.36	2.28	0.42	0.08	3.20	0.09	0.77	-	95.15
CF69_cpx_97_mi_3	57.73	4.46	0.54	17.91	8.27	2.34	0.45	0.12	3.38	0.08	0.90	0.07	96.25
CF69_cpx_97_mi_4	57.20	4.43	0.51	17.98	8.39	2.38	0.36	0.22	3.16	0.08	0.95	-	95.67
CF69_cpx_100_mi_1	56.98	3.11	0.78	17.81	8.87	2.55	0.41	0.12	3.50	0.13	0.75	0.09	95.10
CF69_cpx_100_mi_2	55.11	4.30	0.62	17.10	8.00	2.36	0.46	0.21	3.29	0.07	0.90	-	92.42

	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
CF69_cpx_100_mi_3	55.80	4.30	0.64	17.30	7.84	2.20	0.42	0.13	3.23	0.12	0.91	0.06	92.93
CF69_cpx_101_mi_1	57.39	4.78	0.40	16.85	7.62	2.43	0.53	0.26	3.47	0.08	0.92	0.05	94.77
CF69_cpx_102_mi_1	56.33	4.02	0.36	16.21	7.86	1.79	0.62	0.21	3.53	0.08	0.88	0.07	91.96
CF69_cpx_102_mi_2	58.12	4.14	0.40	16.01	7.66	1.76	0.63	0.12	3.69	0.12	0.84	0.06	93.53
CF69_cpx_104_mi_1	57.53	4.35	0.54	18.23	8.34	2.24	0.46	0.03	3.57	0.14	0.86	-	96.29
CF69_cpx_106_mi_1	56.71	4.36	0.45	17.32	8.05	2.52	0.56	0.18	3.87	0.10	0.96	0.08	95.16
CF69_cpx_106_mi_2	57.80	5.10	0.45	17.55	7.11	2.93	0.61	0.22	4.09	0.07	0.94		96.88
CF69_cpx_108_mi_1	57.46	4.82	0.55	17.21	7.02	2.34	0.59	0.17	3.46	0.08	1.10	0.04	94.84
CF69_cpx_108_mi_2	56.79	4.78	0.55	16.89	7.04	2.49	0.50	0.15	3.65	0.09	1.08	0.04	94.06
CF69_cpx_109_mi_1	58.26	4.47	0.41	16.49	7.98	2.13	0.59	0.19	3.65	0.06	0.87	-	95.13
CF69_cpx_111_mi_1	56.92	4.50	0.52	17.52	8.28	2.25	0.47	0.15	3.38	0.12	0.94	0.08	95.13
CF69_cpx_111_mi_2	57.37	4.54	0.55	17.83	8.28	2.26	0.48	0.11	3.31	0.10	0.92	0.08	95.82
CF69_cpx_111_mi_3	56.89	4.28	0.48	17.60	8.31	2.24	0.44	0.08	3.17	0.09	0.90	0.05	94.52
CF69_cpx_111_mi_4	55.58	4.28	0.49	18.44	7.37	3.26	0.36	0.11	2.97	0.12	0.84	-	93.83
CF69_cpx_111_mi_5	54.66	4.34	0.59	16.53	8.01	2.19	0.51	0.09	3.20	0.11	0.92	-	91.15
CF69_cpx_112_mi_1	55.57	4.46	0.50	16.95	8.13	2.31	0.43	0.14	3.35	0.11	0.95	-	92.89
CF69_cpx_113_mi_1	56.74	4.76	0.55	17.51	8.57	2.17	0.45	0.15	3.19	0.08	0.93	0.06	95.17
CF69_cpx_116_mi_1	56.44	3.65	0.78	18.40	8.84	2.37	0.51	0.02	3.27	0.15	0.73	-	95.16
CF69_cpx_120_mi_1	57.45	4.21	0.61	17.62	8.55	2.22	0.47	0.19	3.23	0.12	0.78	0.09	95.53
CF69_cpx_122_mi_1	55.11	4.53	0.54	16.80	8.38	2.24	0.44	0.18	3.19	0.12	0.93	0.07	92.51
CF69_cpx_122_mi_2	54.54	3.78	0.64	17.07	8.84	2.22	0.47	0.10	3.50	0.16	0.70	0.10	92.10
CF69_cpx_122_mi_3	55.82	4.59	0.52	17.12	8.43	2.18	0.43	0.18	3.48	0.09	0.96	0.06	93.86
CF69_cpx_123_mi_1	56.97	3.75	0.76	17.89	8.37	2.36	0.46	0.08	3.31	0.11	0.81	-	94.87
CF69_cpx_125_mi_1	55.61	4.80	0.50	17.25	8.33	2.26	0.49	0.12	3.14	0.05	1.01	0.07	93.64
CF69_cpx_127_mi_1	56.55	4.22	0.58	17.65	8.28	2.34	0.45	0.10	3.84	0.15	0.82	0.08	95.07
CF69_cpx_127_mi_2	56.29	3.92	0.58	17.60	8.27	2.43	0.49	0.15	3.56	0.13	0.84	-	94.27
CF69_cpx_127_mi_3	57.17	4.07	0.54	17.63	8.36	2.31	0.49	0.14	3.60	0.16	0.88	0.08	95.44
CF69_cpx_127_mi_4	57.25	4.30	0.58	18.42	8.23	2.43	0.43	0.13	3.57	0.14	0.77	-	96.24
CF69_cpx_130_mi_1	56.80	4.51	0.55	17.67	8.37	2.30	0.51	0.11	3.40	0.10	0.93	0.06	95.31
CF69_cpx_130_mi_2	55.84	4.43	0.53	17.29	8.10	2.17	0.39	0.20	3.10	0.12	0.84	-	92.99
CF69_cpx_133_mi_1	56.56	4.50	0.78	17.62	8.13	2.63	0.37	0.09	3.01	0.08	0.80	0.05	94.62
CF69_cpx_133_mi_2	56.43	3.92	0.90	17.81	8.61	2.40	0.50	0.13	3.16	0.13	0.86	0.09	94.94
CF69_cpx_134_mi_1	55.07	5.15	0.46	17.21	8.47	2.10	0.47	0.17	3.20	0.10	0.85	0.06	93.32
CF69_cpx_134_mi_2	54.90	4.87	0.48	17.36	8.55	2.22	0.42	0.07	3.27	0.09	0.90	-	93.12
CF69_cpx_134_mi_3	54.39	4.35	0.55	16.98	8.04	2.29	0.43	0.18	3.22	0.08	0.90	0.07	91.46
CF69_cpx_136_mi_1	55.68	4.46	0.50	17.53	8.38	2.49	0.53	0.21	3.55	0.07	0.96	-	94.35
CF69_cpx_138_mi_1	54.14	4.27	0.47	17.03	8.13	2.08	0.48	0.13	3.20	0.10	0.94	0.06	91.02
CF69_cpx_138_mi_2	55.39	4.62	0.42	17.09	8.48	2.01	0.40	0.13	3.34	0.06	0.97	-	92.90
CF69_cpx_138_mi_3	56.61	4.78	0.46	17.47	8.48	2.27	0.48	0.10	3.27	0.06	0.90	-	94.87
CF69_cpx_138_mi_4	57.51	4.63	0.46	17.17	8.16	2.30	0.52	0.17	3.74	0.08	0.98	0.07	95.79
CF69_cpx_138_mi_5	58.13	4.49	0.47	17.52	8.35	2.22	0.51	0.11	3.69	0.04	0.98	-	96.53
CF69_cpx_138_mi_6	57.56	4.81	0.37	16.31	7.65	2.33	0.47	0.13	3.66	0.03	0.94	0.07	94.33
CF69_cpx_141_mi_1	56.94	3.82	0.59	17.41	8.47	2.47	0.45	0.13	3.74	0.15	0.74	0.08	95.00
CF69_cpx_141_mi_2	56.64	3.96	0.65	17.61	8.28	2.35	0.49	0.20	3.61	0.10	0.81	-	94.68
CF69_cpx_141_mi_3	56.84	4.32	0.67	18.01	8.27	2.37	0.56	0.17	3.70	0.11	0.80	0.10	95.92
CF69_cpx_145_mi_1	55.07	3.93	0.60	17.48	8.06	2.47	0.45	0.09	3.60	0.17	0.82	0.08	92.81
CF69_cpx_145_mi_2	55.26	3.77	0.63	17.25	8.63	2.59	0.47	0.14	3.67	0.13	0.69	-	93.23
CF69_cpx_148_mi_1	55.61	4.22	0.56	17.15	8.14	2.26	0.41	0.21	3.27	0.08	0.90	-	92.81
CF69_cpx_148_mi_2	56.34	4.41	0.49	17.55	8.41	2.30	0.44	0.14	3.59	0.07	0.92	-	94.66
CF69_cpx_151_mi_1	55.50	3.98	0.59	17.46	8.31	2.16	0.45	0.11	3.39	0.10	0.75	-	92.80
CF69_cpx_153_mi_1	55.27	3.80	0.63	17.52	8.75	2.43	0.42	0.06	3.58	0.15	0.73	-	93.34
CF69_cpx_156_mi_1	59.12	4.59	0.44	17.00	8.03	2.02	0.46	0.13	3.50	0.09	0.93	-	96.30

	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
CF69_cpx_156_mi_2	58.52	4.56	0.45	17.12	8.03	2.23	0.48	0.16	3.53	0.09	0.91	-	96.07
CF69_cpx_156_mi_3	57.45	4.50	0.49	17.03	8.11	2.19	0.48	0.16	3.61	0.08	0.92	-	95.01
CF69_cpx_158_mi_1	55.09	4.27	0.73	17.74	8.86	2.11	0.41	0.12	2.73	0.14	0.79	0.08	93.05
CF69_cpx_161_mi_1	56.60	4.85	0.47	17.65	8.39	2.32	0.45	0.14	3.43	0.10	0.94	-	95.35
CF69_cpx_161_mi_2	55.96	4.34	0.54	17.78	8.35	2.20	0.38	0.06	2.65	0.08	0.82	-	93.16
CF69_cpx_162_mi_1	54.15	4.50	0.66	17.45	8.11	2.42	0.42	0.13	3.12	0.09	1.01	-	92.05
CF69_cpx_163_mi_1	55.63	3.58	0.99	17.14	8.52	3.26	0.49	0.10	4.16	0.17	0.69	-	94.73
CF69_cpx_176_mi_1	54.94	4.10	0.51	17.25	8.64	2.21	0.44	0.10	3.00	0.13	0.76	-	92.10
CF69_cpx_178_mi_1	56.51	4.26	0.78	18.03	8.28	2.53	0.43	0.15	2.98	0.17	0.74	-	94.86
CF69_cpx_179_mi_1	56.72	4.54	0.58	17.71	7.87	2.29	0.41	0.08	3.62	0.11	0.84	-	94.77
CF69_cpx_180_mi_1	55.20	4.30	0.52	17.33	8.03	2.30	0.45	0.07	3.32	0.08	0.96	0.05	92.60
CF69_cpx_180_mi_2	56.74	4.73	0.63	18.07	8.25	2.34	0.49	0.14	3.33	0.12	0.92	-	95.75
CF69_cpx_181_mi_1	54.87	3.84	0.71	18.20	8.77	2.35	0.46	0.11	3.13	0.13	0.82	0.09	93.47
CF69_cpx_181_mi_2	55.53	3.67	0.82	18.35	9.05	2.33	0.55	0.07	3.22	0.21	0.72	0.09	94.62
CF69_cpx_181_mi_3	54.09	3.85	0.49	17.45	8.18	2.32	0.36	0.05	2.90	0.11	0.78	-	90.59
CF69_cpx_181_mi_4	55.89	3.72	0.67	18.27	8.57	2.16	0.47	0.02	3.63	0.14	0.85	-	94.39
CF69_cpx_182_mi_1	55.35	3.76	0.71	17.52	8.53	2.64	0.48	0.12	3.90	0.20	0.74	-	93.94
CF69_cpx_182_mi_2	55.59	3.87	0.77	17.53	8.48	2.70	0.50	0.17	3.39	0.12	0.73	-	93.85
CF69_cpx_183_mi_1	56.37	4.31	0.51	16.71	8.03	2.21	0.49	0.10	3.52	0.11	0.91	-	93.27
CF69_cpx_184_mi_1	55.05	4.53	0.66	18.20	8.15	2.27	0.41	0.11	2.99	0.07	0.91	-	93.36
CF69_cpx_187_mi_1	56.76	4.29	0.52	18.03	8.92	2.03	0.44	0.20	3.21	0.08	0.73	0.09	95.27
CF69_cpx_189_mi_1	56.34	4.74	0.40	18.11	8.51	2.32	0.41	0.06	3.21	0.14	0.94	-	95.19
CF69_cpx_189_mi_2	54.60	5.24	0.56	19.10	8.28	2.63	0.47	0.11	3.56	0.11	1.04	-	95.70
CF69_cpx_192_mi_1	54.63	3.91	0.44	17.43	8.64	2.47	0.43	0.10	3.55	0.14	0.71	-	92.44
CF69_cpx_192_mi_2	53.69	3.61	0.53	16.83	8.63	2.23	0.52	0.09	3.37	0.14	0.70	-	90.34
CF69_cpx_192_mi_3	55.60	4.08	0.52	17.86	8.34	2.56	0.50	0.13	3.67	0.15	0.82	-	94.21
CF69_cpx_201_mi_1	55.59	4.35	0.54	17.61	8.32	2.52	0.56	0.16	3.48	0.10	0.96	-	94.19
CF69_cpx_205_mi_1	56.67	4.38	0.73	17.26	8.31	2.14	0.54	0.17	3.28	0.17	0.97	-	94.62
CF69_cpx_206_mi_1	55.23	5.06	0.82	16.27	6.91	2.96	0.61	0.20	3.75	0.05	0.97	-	92.83

Table A4.2 | Major and trace element compositions of clinopyroxene-hosted melt inclusions from Astroni 1. All elements were measured by EPMA. Concentrations are in wt%.

Astroni 1 biotite-hosted melt inclusions													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
CF69_bi_11_mi1	55.21	4.58	0.64	17.21	8.28	2.16	0.63	0.18	3.55	0.06	0.95	-	93.44
CF69_bi_25_mi1	56.30	4.41	0.52	17.31	8.28	2.20	0.47	0.18	3.34	0.10	0.93	-	94.05
CF69_bi_30_mi1	54.22	4.28	0.47	16.71	8.16	2.14	0.50	0.15	3.54	0.07	0.93	-	91.17
CF69_bi_46_mi1	56.55	4.38	0.59	17.74	8.44	2.24	0.53	0.16	3.55	0.10	0.88	-	95.16
CF69_bi_46_mi2	56.62	4.82	0.60	17.65	8.27	2.19	0.53	0.13	3.90	0.09	0.92	-	95.71
CF69_bi_46_mi3	55.89	4.37	0.66	17.40	8.16	2.19	0.54	0.12	3.45	0.15	0.96	-	93.89
CF69_bi_47_mi1	55.43	4.54	0.39	17.22	8.26	2.19	0.43	0.19	3.36	0.09	0.97	-	93.06
CF69_bi_49_mi1	57.58	4.34	0.52	18.09	8.38	2.21	0.60	0.21	3.61	0.09	0.90	-	96.54
CF69_bi_79_mi1	57.08	4.58	0.52	17.75	8.36	2.23	0.50	0.09	3.62	0.10	0.92	-	95.76
CF69_bi_86_mi1	53.38	4.20	0.56	17.49	8.70	3.03	0.37	0.11	3.83	0.18	0.75	-	92.60
CF69_bi_104_mi1	53.38	4.66	0.53	16.82	8.26	2.32	0.51	0.10	3.39	0.10	0.92	-	90.99
CF69_bi_122_mi1	55.33	4.51	0.55	17.14	8.07	2.27	0.51	0.12	3.56	0.13	0.90	-	93.10
CF69_bi_124_mi1	56.68	4.82	0.51	17.70	8.25	2.26	0.40	0.23	3.45	0.10	0.88	-	95.29
CF69_bi_142_mi1	55.17	4.21	0.55	17.94	8.71	3.02	0.37	0.19	3.45	0.18	0.84	-	94.62
CF69_bi_150_mi1	56.97	4.61	0.54	17.58	8.25	2.35	0.42	0.23	3.42	0.09	1.00	-	95.48
CF69_bi_151_mi1	57.28	4.49	0.55	17.63	8.51	2.26	0.52	0.13	3.55	0.10	0.88	-	95.91
CF69_bi_169_mi1	55.47	4.39	0.51	17.49	8.26	2.28	0.39	0.07	3.27	0.15	0.87	-	93.17
CF69_bi_182_mi1	53.99	4.30	1.06	17.01	7.90	2.10	0.61	0.16	3.70	0.11	0.94	-	91.89
CF69_bi_187_mi1	54.85	4.49	0.49	17.05	8.27	2.23	0.45	0.23	3.33	0.12	0.94	-	92.45
CF69_bi_5_mi1	55.56	4.54	0.49	17.46	8.30	2.17	0.52	0.18	3.41	0.12	0.94	-	93.69
CF69_bi_17_mi1	55.19	4.62	0.50	17.32	8.23	2.25	0.45	0.14	3.47	0.12	0.95	-	93.25
CF69_bi_26_mi1	55.80	4.29	0.53	17.27	8.13	2.34	0.42	0.16	3.28	0.08	0.90	-	93.19
CF69_bi_26_mi2	56.23	4.34	0.50	17.44	8.17	2.17	0.46	0.10	3.12	0.13	0.86	-	93.52
CF69_bi_26_mi3	56.24	4.48	0.53	17.75	8.37	2.36	0.47	0.17	3.02	0.08	0.85	-	94.32
CF69_bi_30_mi2	55.87	4.42	0.49	17.55	8.27	2.21	0.53	0.18	3.44	0.10	0.96	-	94.01
CF69_bi_27_mi1	57.08	4.40	0.57	18.22	8.31	2.36	0.41	0.16	3.39	0.11	0.84	-	95.84
CF69_bi_48_mi1	56.45	4.61	0.51	17.65	8.51	2.25	0.53	0.13	3.52	0.14	0.90	-	95.19

Table A4.3 | Major and trace element compositions of biotite-hosted melt inclusions from Astroni 1. All elements were measured by EPMA. Concentrations are in wt%.

Fondi di Baia clinopyroxene-hosted melt inclusions													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
CF88_cpx99_mi1_2	56.03	4.74	1.36	15.52	6.23	4.53	0.51	0.28	3.63	0.04	0.89	0.01	93.79
CF88_cpx123_mi1_1	58.93	5.47	0.05	17.30	7.37	1.19	0.42	0.09	2.78	0.05	1.11	0.01	94.77
CF88_cpx_142_mi_1	57.06	5.10	1.59	15.63	5.80	5.20	0.41	0.30	4.18	0.04	0.83	-	96.15
CF88_cpx_154_mi_1	58.00	5.44	0.08	17.18	7.10	1.17	0.38	0.24	2.34	0.04	1.02	-	92.99

Table A4.4 | Major and trace element compositions of clinopyroxene-hosted melt inclusions from Fondi di Baia. All elements were measured by EPMA. Concentrations are in wt%.

Pisani 1 clinopyroxene-hosted melt inclusions													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
CF25_cpx86_mi3_1	52.97	3.53	1.34	17.97	8.20	3.43	0.62	0.02	4.70	0.45	0.60	0.24	94.05
CF25_cpx129_mi3_1	55.86	3.36	1.00	17.53	8.14	3.57	0.59	0.21	4.76	0.24	0.69	0.09	96.06
cf25_cpx54_m_1	53.83	2.94	2.69	15.06	7.17	5.75	0.44	0.17	5.13	0.18	0.63	0.10	94.08
cf25_cpx54_m_2	57.78	3.35	1.07	17.36	8.32	3.14	0.45	0.12	4.70	0.22	0.78	0.11	97.41
cf25_cpx54_m_3	55.81	3.46	1.17	17.89	7.88	3.58	0.63	0.10	4.91	0.25	0.78	0.11	96.58
cf25_cpx69_m_1	57.23	3.38	1.38	19.14	7.68	3.78	0.58	0.06	4.49	0.28	0.80	0.19	98.99
cf25_cpx118_m_1	50.57	3.02	2.67	15.24	6.20	6.55	0.78	0.11	5.41	0.17	0.56	0.10	91.38
cf25_cpx118_m_3	52.47	3.55	1.05	17.60	7.70	3.65	0.64	0.13	5.03	0.28	0.71	0.13	92.94
cf25_cpx129_m_1	57.52	3.57	0.97	18.25	7.98	3.57	0.58	0.22	5.23	0.18	0.77	0.11	98.97
cf25_cpx129_m_2	55.12	3.55	1.07	18.01	7.99	3.58	0.56	0.22	5.07	0.21	0.83	0.10	96.30

Table A4.5 | Major and trace element compositions of clinopyroxene-hosted melt inclusions from Pisani 1. All elements were measured by EPMA. Concentrations are in wt%.

Pomici Principali clinopyroxene-hosted melt inclusions													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
CF6_cpx15_mi1_1	56.63	3.71	0.99	18.17	9.00	3.56	0.51	0.16	4.14	0.12	0.65	0.09	97.73
CF6_cpx29_mi1_1	57.09	4.06	0.82	18.24	9.28	3.16	0.41	0.09	3.67	0.14	0.74	0.12	97.84
CF6_cpx98_mi1_1	56.58	3.70	0.83	18.19	9.22	3.18	0.45	0.16	3.92	0.14	0.73	0.11	97.21
CF6_cpx110_mi1_1	56.59	3.83	0.54	18.21	9.18	2.95	0.47	0.17	3.94	0.17	0.67	0.14	96.84
CF6_cpx121_mi2_1	57.57	3.39	0.77	18.45	9.08	3.17	0.48	0.04	3.82	0.12	0.73	0.10	97.71
CF6_cpx192_mi1_1	57.05	3.24	0.72	18.11	8.84	3.14	0.46	0.14	3.89	0.12	0.72	0.12	96.55
cf6_bcp_x_103_1	56.53	3.74	0.86	18.55	9.27	3.01	0.39	0.08	3.12	0.14	0.75	0.11	96.55
cf6_bcp_x_103_2	56.69	3.45	0.93	18.54	9.18	3.02	0.48	0.12	3.33	0.10	0.76	0.11	96.72
cf6_bcp_x_117_1	54.48	2.85	2.99	15.67	7.43	6.56	0.44	0.21	4.66	0.07	0.55	0.08	95.97
cf6_bcp_x_117_2	55.14	3.58	0.58	18.00	9.17	2.66	0.46	0.07	3.55	0.12	0.81	0.11	94.23
cf6_bcp_x_120_1	56.65	3.51	0.77	18.64	9.32	2.67	0.34	0.17	3.44	0.15	0.83	0.12	96.61
cf6_bcp_x_121_1	56.38	3.90	1.93	15.84	6.80	6.21	0.71	0.24	4.73	0.07	0.73	0.06	97.60
cf6_bcp_x_128_1	51.93	2.78	1.88	18.74	7.80	6.45	0.51	0.06	4.07	0.64	0.69	0.21	95.76
cf6_bcp_x_132_1	54.94	3.14	2.36	16.75	7.69	5.58	0.48	0.14	4.27	0.16	0.75	0.16	96.43
cf6_bcp_x_137_1	56.41	3.67	0.53	18.55	9.23	2.97	0.50	0.16	3.99	0.14	0.86	0.14	97.15
cf6_bcp_x_137_2	56.34	3.95	0.54	18.15	9.10	3.06	0.55	0.14	3.90	0.11	0.86	0.11	96.81
cf6_bcp_x_140_1	56.55	3.66	0.92	18.04	9.15	3.31	0.46	0.11	3.40	0.11	0.85	0.11	96.67
cf6_bcp_x_147_1	54.24	2.92	2.33	15.93	7.52	5.81	0.49	0.22	4.28	0.13	0.75	0.12	94.75
cf6_bcp_x_164_1	56.56	3.45	0.73	18.18	9.03	3.11	0.49	0.17	4.13	0.13	0.83	0.13	96.95
cf6_bcp_x_165_1	54.29	2.85	2.94	15.68	7.19	7.36	0.60	0.16	4.79	0.11	0.61	0.09	96.65
cf6_bcp_x_167_1	56.56	3.54	0.83	18.41	9.00	3.17	0.44	0.17	3.56	0.15	0.84	0.13	96.81
cf6_bcp_x_195_1	51.86	2.81	3.18	14.72	6.99	7.11	0.46	0.10	4.26	0.09	0.57	0.07	92.22
cf6_bcp_x_36_1	52.77	3.14	2.94	17.93	6.72	6.06	0.64	0.16	5.82	0.32	0.58	0.16	97.25

Table A4.6 | Major and trace element compositions of clinopyroxene-hosted melt inclusions from Pomici Principali. All elements were measured by EPMA. Concentrations are in wt%.

Minopoli 1 clinopyroxene-hosted melt inclusions													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
CF13_cpx29_mi1_1	49.19	2.61	3.26	18.29	5.78	7.30	0.98	0.12	7.42	0.66	0.48	0.22	96.11
CF13_cpx142_mi1_1	49.92	3.54	2.23	18.30	7.45	5.83	0.86	0.17	7.02	0.63	0.51	0.25	96.56
CF13_cpx195_mi1_1	53.20	2.91	2.73	17.58	7.55	4.96	0.88	0.11	7.17	0.43	0.51	0.11	98.06
cf13_bcp_x_210_1	53.29	3.09	2.72	17.52	5.85	6.04	0.72	0.11	6.15	0.55	0.81	0.11	97.00
cf13_bcp_x_202_1	52.88	3.37	2.06	17.91	6.30	5.87	1.11	0.19	6.67	0.15	0.50	0.12	97.89
cf13_bcp_x_188_1	50.53	3.41	1.75	17.77	6.97	5.00	0.86	0.10	6.31	0.53	0.41	0.21	94.22
cf13_bcp_x_188_2	49.60	2.91	2.95	16.06	5.83	7.61	0.90	0.20	6.34	0.55	0.30	0.14	93.93
cf13_bcp_x_179_1	52.99	2.77	1.95	17.72	6.92	4.63	0.87	0.23	7.59	0.27	0.66	0.14	97.17
cf13_bcp_x_140_1	53.36	2.36	3.56	16.98	5.82	6.35	0.66	0.11	4.85	0.68	0.59	0.27	95.53
cf13_bcp_x_135_1	54.30	3.44	2.07	18.35	7.62	5.35	0.83	0.14	4.82	0.63	0.77	0.10	98.47
cf13_bcp_x_81_1	54.59	2.42	2.55	15.66	5.89	7.06	0.64	0.19	6.36	0.07	0.57	0.02	96.85
cf13_bcp_x_55_1	52.65	2.96	2.29	17.30	6.50	5.63	0.92	0.18	6.90	0.44	0.67	0.20	96.84
cf13_bcp_x_49_1	48.99	2.15	3.43	17.90	5.41	7.54	1.00	0.20	7.90	0.65	0.58	0.24	96.04
cf13_bcp_x_49_2	49.23	2.40	3.62	17.53	5.09	7.79	0.98	0.20	7.93	0.65	0.55	0.28	96.28
cf13_bcp_x_52_1	54.10	2.90	2.60	16.63	6.93	5.86	0.66	0.12	5.39	0.25	0.52	0.15	96.72
cf13_bcp_x_22_1	49.43	3.13	2.85	18.79	6.43	6.75	0.89	0.09	6.84	0.61	0.58	0.24	96.74
cf13_cpx196_m_1	45.40	2.16	3.41	16.19	4.80	6.85	0.86	0.09	7.14	0.52	0.46	0.32	88.34
cf13_cpx209_m_1	51.06	3.17	2.49	17.96	7.35	5.05	0.72	0.15	6.05	0.51	0.81	0.19	95.52
cf13_cpx147_m_1	50.02	2.59	3.21	17.74	6.18	6.56	0.65	0.17	6.51	0.63	0.62	0.24	95.16
cf13_cpx119_m_1	48.34	2.32	3.57	17.55	4.88	7.51	0.83	0.18	7.82	0.70	0.55	0.28	94.50
cf13_cpx119_m_2	49.22	2.30	3.41	17.69	5.28	7.74	0.89	0.10	6.49	0.65	0.59	0.29	94.64
cf13_cpx90_m_1	47.23	2.08	4.78	17.23	4.00	9.54	0.90	0.18	6.11	0.50	0.44	0.49	93.58
cf13_cpx90_m_2	48.03	2.35	4.05	17.84	4.89	7.79	0.77	0.10	6.81	0.67	0.60	0.49	94.13
cf13_cpx44_m_1	52.41	3.00	2.08	17.42	7.27	5.17	0.99	0.03	7.02	0.58	0.66	0.03	96.84
cf13_cpx44_m_2	49.75	2.57	3.26	16.40	6.61	6.65	0.60	0.07	5.63	0.46	0.45	0.19	93.01
cf13_cpx31_m_1	49.69	2.08	3.49	17.41	5.38	8.14	0.78	0.14	6.13	0.56	0.51	0.28	94.75
cf13_cpx16_m_1	51.15	2.77	2.33	17.29	6.84	5.51	0.89	0.16	6.59	0.59	0.61	0.24	95.02

Table A4.7 | Major and trace element compositions of clinopyroxene-hosted melt inclusions from Minopoli 1. All elements were measured by EPMA. Concentrations are in wt%.

Appendix 4.2. Matrix glass EPMA data

Monte Nuovo matrix glasses													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
mg_cf195_1_1	56.50	6.88	0.21	18.28	6.88	1.81	0.49	0.24	3.08	0.01	0.90	0.00	95.28
mg_cf195_2_1	57.19	7.88	0.25	18.79	7.23	1.51	0.50	0.37	3.30	0.00	0.97	0.01	98.00
mg_cf195_2_2	57.52	7.42	0.20	18.94	7.22	1.61	0.46	0.33	2.78	0.04	1.10	-	97.63
mg_cf195_3_1	58.62	7.56	0.28	19.04	7.25	1.66	0.39	0.20	2.74	0.00	0.97	0.00	98.71
mg_cf195_4_1	57.66	7.69	0.17	18.69	7.20	1.69	0.45	0.20	2.89	0.05	1.05	0.01	97.73
mg_cf195_4_2	57.48	7.29	0.18	18.87	7.30	1.75	0.43	0.28	3.19	0.07	1.17	0.01	98.03
mg_cf195_4_3	57.82	7.29	0.22	18.93	7.11	1.64	0.40	0.22	2.94	0.02	1.02	-	97.61
mg_cf195_4_4	58.09	7.43	0.25	18.98	7.09	1.84	0.38	0.18	2.88	0.00	0.90	-	98.05

Table A4.8 | Major and trace element compositions of matrix glasses from Monte Nuovo. All elements were measured by EPMA. Concentrations are in wt%.

Astroni 1 matrix glasses													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
mg_cf69_1_1	58.42	4.88	0.67	17.82	8.39	2.35	0.60	0.13	3.86	0.10	0.97	0.00	98.18
mg_cf69_2_1	59.14	3.90	0.54	18.37	8.61	2.29	0.48	0.16	3.27	0.04	0.91	0.02	97.75
mg_cf69_3_1	57.69	4.38	0.50	17.85	8.47	2.28	0.42	0.17	3.31	0.09	0.91	0.02	96.08
mg_cf69_4_1	55.52	4.08	0.47	16.66	7.79	2.21	0.38	0.13	3.01	0.12	0.91	0.01	91.28
mg_cf69_5_1	57.35	4.61	0.50	17.70	8.33	2.23	0.50	0.08	2.93	0.08	0.76	0.01	95.08
mg_cf69_5_2	59.43	4.67	0.49	18.09	8.44	2.45	0.46	0.16	3.42	0.09	0.94	-	98.64
mg_cf69_6_1	58.83	4.50	0.58	18.11	8.56	2.36	0.37	0.07	3.41	0.05	0.92	-	97.76
mg_cf69_6_2	56.85	4.51	0.56	17.37	8.25	2.09	0.43	0.17	3.07	0.13	0.89	0.02	94.33
mg_cf69_7_1	56.77	4.68	0.50	17.41	8.26	2.14	0.42	0.19	3.19	0.06	0.95	0.04	94.60
mg_cf69_7_2	57.43	4.11	0.48	17.42	8.15	2.20	0.45	0.19	3.11	0.08	0.84	0.02	94.47
mg_cf69_7_3	59.86	3.38	0.32	18.64	9.13	2.33	0.34	0.09	2.27	0.13	0.59	0.01	97.09
mg_cf69_8_1	58.84	4.26	0.48	18.19	8.65	2.10	0.40	0.18	3.06	0.09	0.86	-	97.10
mg_cf69_8_2	56.36	4.24	0.45	17.89	8.37	2.38	0.46	0.12	3.17	0.10	0.86	-	94.39
mg_cf69_8_3	56.77	3.36	0.47	17.80	8.28	2.34	0.42	0.14	2.98	0.08	0.89	-	93.55
mg_cf69_8_4	56.79	2.87	0.52	18.09	8.09	2.41	0.48	0.14	3.37	0.10	0.85	0.02	93.74
mg_cf69_9_1	58.68	4.52	0.59	18.01	8.67	2.49	0.45	0.20	3.33	0.13	0.92	0.03	98.02
mg_cf69_9_2	61.20	3.66	0.29	18.75	10.18	1.93	0.34	0.12	2.01	0.10	0.52	-	99.10
mg_cf69_9_3	58.28	4.62	0.58	18.21	8.60	2.32	0.44	0.11	3.34	0.07	0.88	-	97.45

Table A4.9 | Major and trace element compositions of matrix glasses from Astroni 1. All elements were measured by EPMA. Concentrations are in wt%.

Fondi di Baia matrix glasses													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
mg_cf88_1_2	58.39	4.95	0.34	16.03	6.79	2.14	0.54	0.26	4.29	0.05	1.15	0.00	94.93
mg_cf88_1_3	58.76	4.63	0.24	17.25	7.39	2.15	0.39	0.20	3.02	0.02	0.84	0.00	94.89
mg_cf88_1_4	61.44	4.60	0.17	17.51	8.40	1.96	0.29	0.13	2.09	0.05	0.56	0.00	97.21

Table A4.10 | Major and trace element compositions of matrix glasses from Fondi di Baia. All elements were measured by EPMA. Concentrations are in wt%.

Pisani 1 matrix glasses													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
mg_cf25_1_1	54.29	3.31	1.80	19.05	7.01	4.57	0.70	0.11	5.64	0.34	0.52	0.04	97.38
mg_cf25_1_2	55.39	2.49	1.93	18.02	7.80	5.02	0.74	0.16	6.35	0.48	0.52	-	98.90
mg_cf25_2_1	56.27	3.34	1.53	17.82	8.13	4.27	0.65	0.09	5.41	0.42	0.76	0.04	98.74
mg_cf25_4_1	55.42	3.08	2.08	17.90	7.11	5.52	0.75	0.13	6.21	0.50	0.56	0.01	99.29
mg_cf25_4_2	54.66	3.17	1.96	18.21	7.27	5.35	0.81	0.06	6.07	0.49	0.61	0.03	98.68

Table A4.11 | Major and trace element compositions of matrix glasses from Pisani 1. All elements were measured by EPMA. Concentrations are in wt%.

Pomici Principali matrix glasses													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
mg_cf6_1_1	53.53	2.86	2.39	16.94	7.18	5.61	1.06	0.17	6.96	0.61	0.61	0.01	97.93
mg_cf6_1_2	53.43	3.15	2.35	16.79	7.17	5.82	1.04	0.19	6.98	0.68	0.63	-	98.24
mg_cf6_1_3	53.34	2.91	2.40	17.06	7.47	5.65	1.01	0.18	6.94	0.76	0.55	0.00	98.29
mg_cf6_1_4	49.92	3.01	2.19	15.73	6.65	5.47	0.97	0.13	6.74	0.59	0.73	0.00	92.14
mg_cf6_1_5	53.38	2.96	2.14	18.49	6.64	6.27	0.92	0.17	7.02	0.59	0.50	0.01	99.07
mg_cf6_1_6	53.59	2.90	2.27	17.39	6.82	5.55	0.99	0.16	6.96	0.66	0.68	-	97.98

Table A4.12 | Major and trace element compositions of matrix glasses from Pomici Principali. All elements were measured by EPMA. Concentrations are in wt%.

Minopoli 1 matrix glasses													
	SiO ₂	NaO	MgO	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	FeOt	P ₂ O ₅	Cl	SO ₂	Total
mg_cf13_1_1	56.31	3.71	1.03	17.98	8.90	3.64	0.45	0.13	4.24	0.17	0.69	0.03	97.29
mg_cf13_1_2	55.90	3.21	0.92	17.96	8.94	3.43	0.47	0.19	4.13	0.12	0.75	0.02	96.05
mg_cf13_3_1	56.52	3.25	0.98	18.45	9.16	3.68	0.47	0.12	4.18	0.16	0.71	0.02	97.70
mg_cf13_4_1	55.79	3.45	1.03	17.74	9.00	3.86	0.50	0.04	4.18	0.22	0.69	0.01	96.51
mg_cf13_5_1	51.34	2.85	0.90	16.38	8.07	3.23	0.46	0.10	3.94	0.25	0.85	0.03	88.40
mg_cf13_5_2	56.16	3.67	1.00	17.99	8.98	3.69	0.42	0.17	4.24	0.14	0.73	-	97.20
mg_cf13_10_1	56.31	3.71	1.03	17.98	8.90	3.64	0.45	0.13	4.24	0.17	0.69	0.03	97.29

Table A4.13 | Major and trace element compositions of matrix glasses from Minopoli 1. All elements were measured by EPMA. Concentrations are in wt%.

Appendix 4.3. Melt inclusion SIMS data

Monte Nuovo clinopyroxene-hosted melt inclusions			
	MgO	H ₂ O	F
cf195_cpx123_mi3	0.51	2.28	0.23
cf195_cpx64_mi1-1	0.77	3.48	0.22
cf195_cpx122_mi2	0.81	1.04	0.22
cf195_cpx122_mi1	0.87	2.44	0.25
cf195_cpx137_mi5	0.70	2.54	0.28
cf195_cpx110_mi1	0.76	3.47	0.22
cf195_cpx113_mi6	0.55	2.82	0.25
cf195_cpx113_mi7	0.59	2.45	0.28
cf195_cpx188_mi1	0.68	2.38	0.32
cf195_cpx159_mi4	0.66	3.71	0.24
cf195_cpx86_mi3	0.74	5.56	0.22
cf195_cpx86_mi2	0.75	2.84	0.23

Table A4.15 | Volatile element compositions of clinopyroxene-hosted melt inclusions from Monte Nuovo. Water and F were measured by SIMS. MgO (measured by EPMA) is a fractionation index, used in Figure 6.7. Concentrations are in wt%.

Astroni 1 clinopyroxene-hosted melt inclusions			
	MgO	H ₂ O	F
cf69_cpx92_mi1-12	0.76	2.21	0.30
cf69_cpx116_mi1-1	0.78	2.33	0.22
cf69_cpx113_mi1-1	0.55	2.62	0.25
cf69_cpx127_mi3-1	0.54	2.57	0.20
cf69_cpx127_mi1-1	0.58	2.51	0.20
cf69_cpx130_mi1-1	0.55	2.43	0.28
cf69_cpx138_mi2-1	0.42	2.69	0.27
cf69_cpx156_mi2-1	0.45	2.30	0.26
cf69_cpx182_mi2-1	0.77	2.51	0.21
cf69_cpx182_mi1-1	0.71	2.39	0.19
cf69_cpx22_mi1-12	0.65	2.37	0.28
cf69_cpx23_mi2-12	0.42	2.22	0.28
cf69_cpx55_mi1-12	0.54	2.12	0.26
cf69_cpx55_mi2-12	0.53	2.56	0.25
cf69_cpx66_mi1-12	0.61	2.21	0.21
cf69_cpx66_mi3-12	0.72	2.58	0.23
cf69_cpx82_mi1-12	0.50	2.29	0.28
cf69_cpx91_mi1-12	0.51	2.27	0.31
cf69_cpx97_mi3-12	0.54	2.00	0.25

Table A4.16 | (previous page) Volatile element compositions of clinopyroxene-hosted melt inclusions from Astroni 1. Water and F were measured by SIMS. MgO (measured by EPMA) is a fractionation index, used in Figure 6.7. Concentrations are in wt%.

Pisani 1 clinopyroxene-hosted melt inclusions			
	MgO	H ₂ O	F
cf25_cpx86_mi3	1.34	2.17	0.19
cf25_cpx54_mi3	1.17	2.37	0.21
cf25_cpx69_mi1	1.38	4.04	0.25
cf25_cpx118_mi3	1.05	2.30	0.23
cf25_cpx129_mi1	0.97	2.12	0.24
cf25_cpx129_mi3	1.00	2.23	0.19
cf25_cpx129_mi2	1.07	2.32	0.23

Table A4.17 | Volatile element compositions of clinopyroxene-hosted melt inclusions from Pisani 1. Water and F were measured by SIMS. MgO (measured by EPMA) is a fractionation index, used in Figure 6.7. Concentrations are in wt%.

Pomici Principali clinopyroxene-hosted melt inclusions			
	MgO	H ₂ O	F
cf6_cpx98_mi1	0.83	3.84	0.22
cf6_cpx29_mi1	0.82	1.26	0.23
cf6_cpx121_mi2	0.77	1.98	0.22
cf6_cpx110_mi1	0.54	2.52	0.25
cf6_cpx137_mi2	0.54	2.35	0.24
cf6_cpx167_mi1	0.83	2.69	0.27
cf6_cpx192_mi1	0.72	3.35	0.28

Table A4.18 | Volatile element compositions of clinopyroxene-hosted melt inclusions from Pomici Principali. Water and F were measured by SIMS. MgO (measured by EPMA) is a fractionation index, used in Figure 6.7. Concentrations are in wt%.

Minopoli 1 clinopyroxene-hosted melt inclusions			
	MgO	H ₂ O	F
cf13_cpx119_mi1	3.58	2.63	0.31
cf13_cpx55_mi1	2.29	2.26	0.33
cf13_cpx49_mi2	3.62	2.53	0.44
cf13_cpx29_mi1	3.26	1.87	0.29
cf13_cpx142_mi1	2.23	1.30	0.30
cf13_cpx140_mi1	3.56	3.05	0.28
cf13_cpx135_mi1	2.07	1.25	0.22

Table A4.19 | Volatile element compositions of clinopyroxene-hosted melt inclusions from Minopoli 1. Water and F were measured by SIMS. MgO (measured by EPMA) is a fractionation index, used in Figure 6.7. Concentrations are in wt%.

Appendix 4.4. Matrix glass SIMS data

Monte Nuovo matrix glasses			
	MgO	H ₂ O	F
mg_CF195_4_1	0.17	1.02	0.82
mg_CF195_4_2	0.18	1.04	0.68
mg_CF195_3_1	0.28	0.94	0.73
mg_CF195_2_1	0.25	0.72	0.65
mg_cf195_1_1	0.21	0.84	1.21

Table A4.20 | Volatile element compositions of matrix glasses from Monte Nuovo. Water and F were measured by SIMS. MgO (measured by EPMA) is a fractionation index, used in Figure 6.8. Concentrations are in wt%.

Astroni 1 matrix glasses			
	MgO	H ₂ O	F
mg_CF69_2_1	0.54	0.71	0.25
mg_CF69_9_1	0.52	0.91	0.26
mg_CF69_6_1	0.58	1.26	0.25
mg_CF69_5_1	0.49	0.20	0.22
mg_CF69_8_1	0.45	0.63	0.09
mg_cf69_9_2	0.59	0.95	0.29
mg_cf69_3_1	0.50	0.67	0.26

Table A4.21 | Volatile element compositions of matrix glasses from Astroni 1. Water and F were measured by SIMS. MgO (measured by EPMA) is a fractionation index, used in Figure 6.8. Concentrations are in wt%.

Fondi di Baia matrix glass			
	MgO	H ₂ O	F
mg_cf88_1_2	0.34	0.77	0.23

Table A4.22 | Volatile element compositions of matrix glass from Fondi di Baia. Water and F were measured by SIMS. MgO (measured by EPMA) is a fractionation index, used in Figure 6.8. Concentrations are in wt%.

Pisani 1 matrix glasses			
	MgO	H ₂ O	F
mg_cf25_2_1-12	1.53	0.09	0.22
mg_cf25_4_2-12	1.96	0.32	0.27
mg_cf25_4_1-12	2.08	0.04	0.31
mg_cf25_2_1-12	1.53	0.13	0.20

Table A4.23 | Volatile element compositions of matrix glass from Pisani 1. Water and F were measured by SIMS. MgO (measured by EPMA) is a fractionation index, used in Figure 6.8. Concentrations are in wt%.

Pomici Principali matrix glasses			
	MgO	H ₂ O	F
mg_cf6_1_3	0.98	1.05	0.26
mg_cf6_1_2	0.92	0.06	0.27
mg_cf6_1_1	1.03	0.28	0.24
mg_cf6_1_4	1.03	0.28	0.24
mg_cf6_1_5	0.90	0.30	0.14

Table A4.24 | Volatile element compositions of matrix glass from Pomici Principali. Water and F were measured by SIMS. MgO (measured by EPMA) is a fractionation index, used in Figure 6.8. Concentrations are in wt%.

Minopoli 1 matrix glasses			
	MgO	H ₂ O	F
mg_cf13_10_1	2.28	0.04	0.33
mg_cf13_4_1	2.19	0.10	0.30
mg_cf13_5_1	2.14	0.17	0.34
mg_cf13_3_1	2.40	0.10	0.29
mg_cf13_1_1	2.35	0.10	0.31

Table A4.25 | Volatile element compositions of matrix glass from Minopoli 1. Water and F were measured by SIMS. MgO (measured by EPMA) is a fractionation index, used in Figure 6.8. Concentrations are in wt%.

Appendix 5

Full dataset of Campi Flegrei apatite compositions

This appendix presents a complete dataset of clinopyroxene- and biotite-hosted apatite inclusion and apatite microphenocryst compositions from the eight studied eruptions of Campi Flegrei. These data are used in Chapter 6 to investigate magmatic fluid systematics and constrain the pre-eruptive volatile contents of the different eruptions.

Many of the samples used in this study are from Smith *et al.*, (2011). See Section 6.2. and Smith *et al.*, (2011) for sampling locations.

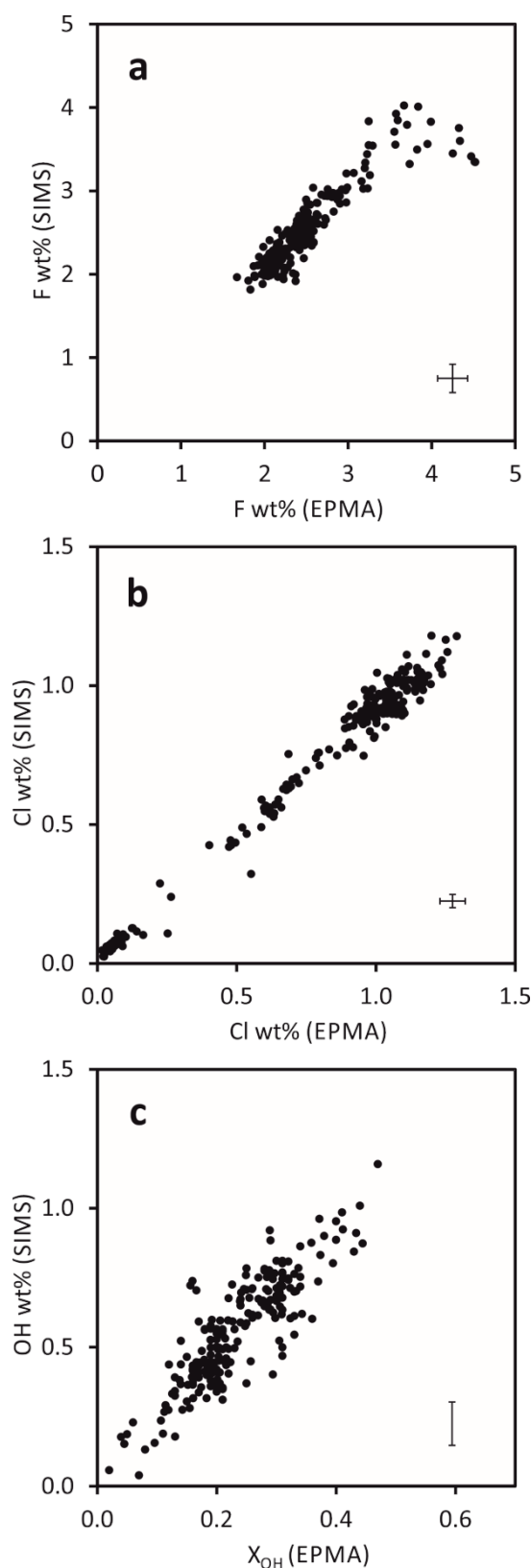


Figure A5.1 | The relationship between apatite compositions measured by EPMA and SIMS. Analyses include apatite inclusions and microphenocrysts. Error bars represent average precision with ± 1 s.d. (EPMA) or a 95% confidence interval (SIMS); otherwise uncertainties are less than the size of the data points. X_{OH} was calculated 'by difference' for EPMA analyses and error bars cannot be quantified, due to the potential for composition-dependant electron-beam induced F migration (Chapter 3).

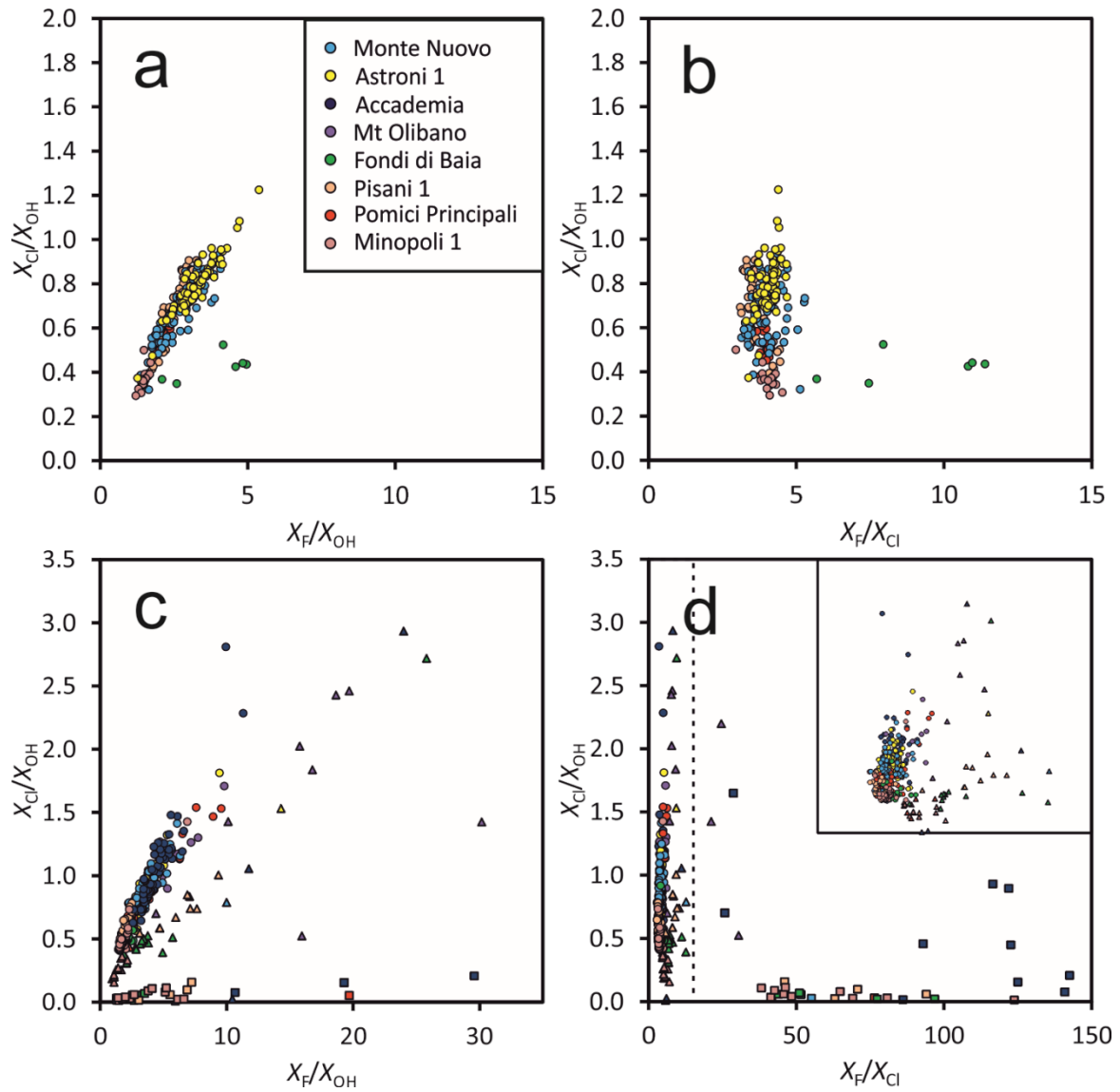


Figure A5.2 | The volatile compositions of Campi Flegrei apatites, measured by EPMA. a,b, Clinopyroxene- and biotite-hosted apatite inclusions. **c,d,** Apatite microphenocrysts from the high- (circles), medium- (triangles) and low-Cl (squares) populations. The inset in **d** shows an expansion of the area marked by the black dashed line. Inclusion data were filtered to remove crystals in contact with glass (matrix or melt inclusions), which may have re-equilibrated volatiles post-entrapment. Data are in X_{Cl}/X_{OH} versus X_F/X_{OH} (**a,c**) and X_{Cl}/X_{OH} versus X_F/X_{Cl} (**b,d**) space. Error bars cannot be quantified, due to the potential for composition-dependant electron-beam induced F migration (Chapter 3) and the necessity for calculation of OH ‘by difference’. Data show considerable scatter, particularly in near end-member FAp compositions (typically in lava dome samples). However, the general high-, medium- and low-Cl apatite population trends agree well with SIMS data. End-member FAp microphenocrysts from lava dome eruptions are not shown, as $X_{Cl} \approx X_{OH} \approx 0$ within uncertainty and mole fraction ratios can therefore not be calculated.

Appendix 5.1. Apatite inclusion EPMA data

Monte Nuovo clinopyroxene-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
cf195_bcp_x_10_ap_1	40.41	0.63	53.27	0.60	2.46	1.10	96.89
cf195_bcp_x_10_ap_2	40.63	0.78	53.52	0.53	2.34	1.07	97.36
cf195_bcp_x_10_ap_3	40.91	0.69	54.31	0.42	2.42	1.05	98.24
cf195_bcp_x_102_ap_1	40.76	0.68	53.60	0.48	2.46	0.88	97.27
cf195_bcp_x_102_ap_2	39.01	2.17	53.26	0.70	2.38	0.93	96.91
cf195_bcp_x_102_ap_3	40.85	0.75	53.26	0.42	2.59	0.89	97.08
cf195_bcp_x_103_ap_1	40.39	0.96	52.91	0.14	2.32	0.91	96.12
cf195_bcp_x_118_ap_1	40.25	1.06	53.12	0.67	2.12	1.10	96.95
cf195_bcp_x_121_ap_1	40.21	0.67	53.76	0.49	2.48	0.95	96.95
cf195_bcp_x_121_ap_3	40.54	0.81	53.75	0.16	2.38	1.04	97.14
cf195_bcp_x_123_ap_1	38.58	1.98	52.23	0.21	2.36	1.09	94.92
cf195_bcp_x_128_ap_1	40.73	0.79	53.18	0.34	2.40	1.14	97.02
cf195_bcp_x_13_ap_1	40.11	0.77	52.90	0.45	2.34	1.13	96.19
cf195_bcp_x_133_ap_1	40.57	0.48	53.63	0.57	2.02	1.07	97.04
cf195_bcp_x_133_ap_2	40.79	0.68	53.13	0.45	1.99	1.14	96.90
cf195_bcp_x_140_ap_2	41.16	0.39	54.24	0.41	2.15	1.12	98.08
cf195_bcp_x_146_ap_1	41.56	0.58	53.92	0.39	2.21	1.11	98.35
cf195_bcp_x_148_ap_1	41.37	0.52	53.97	0.47	2.11	1.09	98.16
cf195_bcp_x_153_ap_1	40.60	0.71	53.61	0.68	2.23	1.06	97.45
cf195_bcp_x_159_ap_1	40.71	0.74	53.82	0.15	2.26	1.12	97.35
cf195_bcp_x_170_ap_2	40.76	0.72	53.39	0.62	2.33	1.06	97.37
cf195_bcp_x_173_ap_1	39.65	1.32	53.03	0.12	1.87	0.96	95.75
cf195_bcp_x_19_ap_2	41.20	0.57	54.00	0.51	2.36	1.08	98.19
cf195_bcp_x_200_ap_1	40.56	0.80	53.88	0.51	2.33	1.05	97.62
cf195_bcp_x_207_ap_1	41.07	0.60	53.99	0.43	2.30	1.11	98.01
cf195_bcp_x_208_ap_1	40.80	0.76	54.25	0.50	1.99	0.99	98.01
cf195_bcp_x_216_ap2	39.92	1.11	52.85	0.13	2.26	1.04	95.85
cf195_bcp_x_223_ap2	40.61	0.74	53.91	0.34	2.38	1.05	97.49
cf195_bcp_x_225_ap1	41.03	0.70	53.63	0.15	2.30	0.96	97.28
cf195_bcp_x_236_ap2	40.72	0.80	53.44	0.43	2.24	1.12	97.31
cf195_bcp_x_240_ap2	40.41	0.85	53.22	0.25	2.24	1.11	96.63
cf195_bcp_x_248_ap1	39.36	1.16	53.67	0.93	2.29	1.23	97.16
cf195_bcp_x_250_ap2	41.44	0.53	54.61	0.36	2.52	1.07	98.89
cf195_bcp_x_250_ap3	39.93	1.16	53.31	0.70	2.44	1.02	96.98
cf195_bcp_x_250_ap4	38.59	1.46	52.53	1.16	2.41	1.10	95.70
cf195_bcp_x_37_ap_2	41.14	0.64	54.00	0.58	2.28	1.03	98.20
cf195_bcp_x_51_ap_3	40.95	0.82	53.89	0.48	2.10	1.12	98.00
cf195_bcp_x_63_ap_1	41.29	0.61	53.85	0.39	2.02	1.08	97.93
cf195_bcp_x_63_ap_2	41.01	0.64	53.60	0.58	2.05	1.13	97.69
cf195_bcp_x_68_ap_1	39.97	1.13	53.15	0.60	2.06	1.15	96.73

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
cf195_bcp_x_80_ap_1	41.30	0.45	53.87	0.36	2.41	1.03	97.86
cf195_bcp_x_80_ap_2	41.20	0.52	54.08	0.42	2.39	1.01	98.08
cf195_bcp_x_80_ap_4	41.35	0.50	54.13	0.36	2.39	1.04	98.21
cf195_bcp_x_80_ap_5	41.06	0.66	53.72	0.40	2.22	1.09	97.72
cf195_bcp_x_80_ap_6	40.93	0.66	54.12	0.29	2.37	1.03	97.87
cf195_bcp_x_83_ap_4	41.02	0.82	53.24	0.19	2.38	1.13	97.24
cf195_bcp_x_83_ap_5	41.00	0.72	53.26	0.18	2.40	1.16	97.17
cf195_bcp_x_83_ap_6	40.33	0.63	53.06	0.51	2.30	1.13	96.47
cf195_bcp_x_85_ap_2	41.10	0.72	53.72	0.35	2.24	1.11	97.80
cf195_bcp_x_85_ap_4	41.17	0.73	53.62	0.29	2.07	1.11	97.65
cf195_cc_ap_3	41.70	0.49	54.68	0.50	2.23	1.00	99.16
cf195_cc_ap_7	41.30	0.46	54.32	0.42	2.20	0.96	98.23
cf195_gcp_x_107_ap_1	41.36	0.59	54.23	0.45	2.43	1.02	98.51
cf195_gcp_x_118_ap_1	41.74	0.51	54.12	0.48	2.19	1.11	98.73
cf195_gcp_x_129_ap_1	39.87	0.69	54.13	0.65	2.26	1.05	97.18
cf195_gcp_x_129_ap_2	41.25	0.56	53.91	0.43	2.04	1.11	97.97
cf195_gcp_x_138_ap_1	41.84	0.55	54.23	0.40	2.55	1.01	98.93
cf195_gcp_x_150_ap_2	40.89	0.63	53.70	0.71	2.43	1.07	97.85
cf195_gcp_x_158_ap_1	42.15	0.63	54.04	0.13	2.27	1.13	98.88
cf195_gcp_x_159_ap_2	41.92	0.57	53.82	0.36	2.50	0.99	98.53
cf195_gcp_x_17_ap_1	41.68	0.60	54.41	0.44	2.58	0.99	99.04
cf195_gcp_x_43_ap_1	41.12	0.76	53.61	0.76	2.10	1.16	98.14
cf195_gcp_x_57_ap_1	41.87	0.64	54.22	0.15	2.50	1.01	98.76
cf195_gcp_x_57_ap_2	41.78	0.67	54.22	0.10	2.55	1.06	98.72
cf195_gcp_x_64_ap_1	40.78	0.68	53.76	0.13	2.44	0.94	97.15
cf195_gcp_x_96_ap_3	40.93	0.75	53.72	0.69	2.25	1.16	98.05
cf195_gcp_x_96_ap_5	41.85	0.66	54.26	0.28	2.29	1.14	99.00
cf195_gcp_x_110_ap_2	39.50	0.76	54.29	0.55	2.47	1.02	96.98
cf195_gcp_x_121_ap_1	38.94	1.67	53.54	1.13	2.47	1.13	97.28
cf195_gcp_x_122_ap_1	41.46	0.68	54.50	0.44	2.16	1.37	99.21
cf195_gcp_x_133_ap_1	41.16	1.06	53.61	0.37	2.55	0.88	97.99
cf195_gcp_x_138_ap_2	41.71	0.63	54.80	0.50	2.66	1.03	99.61
cf195_gcp_x_150_ap_1	41.38	0.63	54.05	0.36	2.64	1.06	98.42
cf195_gcp_x_150_ap_3	40.62	0.97	53.22	0.12	2.46	0.97	96.77
cf195_gcp_x_153_ap_1	41.28	0.93	53.18	0.24	2.47	1.18	97.68
cf195_gcp_x_159_ap_1	40.56	0.70	53.49	0.64	2.40	1.01	97.25
cf195_gcp_x_171_ap_2	41.59	0.82	53.83	0.17	2.19	1.16	98.35
cf195_gcp_x_45_ap_1	41.05	0.32	54.04	0.12	1.94	0.40	96.62
cf195_gcp_x_47_ap_1	41.40	0.49	53.86	0.27	2.53	0.97	97.88
cf195_gcp_x_47_ap_2	40.15	0.66	54.08	0.45	2.51	1.06	97.28
cf195_gcp_x_47_ap_3	40.84	0.67	53.96	0.80	2.32	1.19	98.29
cf195_gcp_x_47_ap_4	40.68	0.72	53.91	0.66	2.26	1.17	97.93
cf195_gcp_x_58_ap_1	41.36	0.51	54.09	0.59	2.51	0.93	98.36

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>cf195_gcp_x_76_ap_1</i>	41.33	0.68	54.10	0.59	2.45	1.18	98.76
<i>cf195_gcp_x_80_ap_1</i>	41.33	0.59	54.12	0.64	1.97	1.00	98.38
<i>cf195_gcp_x_84_ap_1</i>	42.08	0.45	53.85	0.45	2.50	1.09	98.80
<i>cf195_gcp_x_91_ap_1</i>	41.19	0.64	53.76	0.57	2.22	1.14	98.08
<i>cf195_gcp_x_91_ap_2</i>	41.04	0.72	53.81	0.50	2.08	1.15	97.94
<i>cf195_gcp_x_96_ap_1</i>	40.94	0.64	53.80	0.55	2.32	1.14	97.88
<i>cf195_gcp_x_96_ap_2</i>	41.24	0.73	53.86	0.41	2.27	1.12	98.16
<i>cf195_gcp_x_96_ap_4</i>	41.93	0.62	54.16	0.57	2.26	1.16	99.24
<i>cf195_gcp_x_96_ap_6</i>	40.85	1.13	53.36	0.41	2.19	1.11	97.63
<i>cf195_bcp_x_103_ap_2</i>	41.16	0.65	53.63	0.18	2.31	1.12	97.56
<i>cf195_bcp_x_108_ap_1</i>	40.50	0.93	53.65	0.10	1.91	1.03	96.89
<i>cf195_bcp_x_11_ap_1</i>	40.54	0.62	53.82	0.58	2.18	1.01	97.35
<i>cf195_bcp_x_121_ap_2</i>	40.91	0.64	53.79	0.48	2.36	1.11	97.75
<i>cf195_bcp_x_128_ap_2</i>	41.11	0.64	53.49	0.18	2.34	1.14	97.38
<i>cf195_bcp_x_128_ap_3</i>	40.78	0.61	53.55	0.46	2.18	1.15	97.32
<i>cf195_bcp_x_128_ap_4</i>	41.02	0.72	53.80	0.25	2.43	0.92	97.57
<i>cf195_bcp_x_132_ap_1</i>	40.69	1.15	54.06	0.65	2.79	0.79	98.32
<i>cf195_bcp_x_132_ap_2</i>	41.36	0.49	54.19	0.35	2.60	0.78	98.09
<i>cf195_bcp_x_137_ap_1</i>	40.96	0.60	53.84	0.55	2.50	1.00	97.83
<i>cf195_bcp_x_138_ap_1</i>	40.62	0.91	52.82	0.12	2.05	1.16	96.35
<i>cf195_bcp_x_138_ap_2</i>	37.22	2.19	51.94	1.04	2.14	1.37	94.51
<i>cf195_bcp_x_140_ap_1</i>	41.24	0.58	54.14	0.51	2.14	1.13	98.35
<i>cf195_bcp_x_143_ap_1</i>	41.81	0.43	53.81	0.13	2.25	1.08	98.06
<i>cf195_bcp_x_143_ap_2</i>	41.42	0.44	53.96	0.13	2.38	1.19	97.98
<i>cf195_bcp_x_144_ap_1</i>	41.29	0.47	54.23	0.39	2.35	1.06	98.27
<i>cf195_bcp_x_147_ap_1</i>	39.92	1.05	53.54	0.90	2.37	1.07	97.31
<i>cf195_bcp_x_147_ap_2</i>	40.21	0.88	53.60	0.92	2.40	1.07	97.53
<i>cf195_bcp_x_148_ap_2</i>	41.74	0.47	54.15	0.39	2.09	1.05	98.53
<i>cf195_bcp_x_150_ap_1</i>	40.90	0.56	53.91	0.52	2.05	1.10	97.71
<i>cf195_bcp_x_151_ap_1</i>	42.06	0.35	54.43	0.36	2.36	1.05	99.07
<i>cf195_bcp_x_153_ap_2</i>	40.99	0.63	53.88	0.49	2.28	1.06	97.85
<i>cf195_bcp_x_153_ap_3</i>	40.35	0.85	53.81	0.53	2.37	1.06	97.44
<i>cf195_bcp_x_170_ap_1</i>	40.16	0.65	52.76	0.69	2.37	0.87	95.98
<i>cf195_bcp_x_172_ap_1</i>	38.45	0.53	53.85	0.43	2.43	1.04	95.17
<i>cf195_bcp_x_180_ap_1</i>	40.76	0.58	53.59	0.55	2.34	1.08	97.39
<i>cf195_bcp_x_187_ap_1</i>	40.63	0.75	53.75	0.43	2.28	1.12	97.49
<i>cf195_bcp_x_187_ap_2</i>	41.03	0.64	54.19	0.53	2.12	1.14	98.28
<i>cf195_bcp_x_188_ap_1</i>	40.89	0.67	53.94	0.40	2.49	0.89	97.68
<i>cf195_bcp_x_191_ap_1</i>	40.57	0.61	53.87	0.35	2.43	0.99	97.25
<i>cf195_bcp_x_191_ap_2</i>	40.73	0.80	53.70	0.57	2.34	1.00	97.63
<i>cf195_bcp_x_191_ap_3</i>	41.26	0.64	53.99	0.61	2.34	1.00	98.33
<i>cf195_bcp_x_194_ap_2</i>	40.80	0.99	54.05	0.40	2.41	1.14	98.23
<i>cf195_bcp_x_197_ap_1</i>	40.13	0.74	53.95	0.64	2.52	1.02	97.38

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>cf195_bcp_x_199_ap_1</i>	40.22	0.94	53.50	0.64	2.41	1.09	97.24
<i>cf195_bcp_x_200_ap_2</i>	41.16	0.69	53.69	0.29	2.23	1.12	97.74
<i>cf195_bcp_x_200_ap_3</i>	41.18	0.60	54.07	0.14	2.20	1.09	97.86
<i>cf195_bcp_x_203_ap_1</i>	41.44	0.67	53.57	0.15	2.79	0.52	97.33
<i>cf195_bcp_x_203_ap_2</i>	41.15	0.56	54.07	0.12	2.57	0.49	97.30
<i>cf195_bcp_x_208_ap_2</i>	40.68	0.72	53.65	0.21	1.90	0.97	96.89
<i>cf195_bcp_x_208_ap_3</i>	40.15	1.02	53.16	0.17	1.94	0.97	96.16
<i>cf195_bcp_x_213_ap1</i>	41.53	0.44	54.49	0.45	2.50	0.97	98.76
<i>cf195_bcp_x_216_ap1</i>	40.69	0.76	53.63	0.64	2.30	1.07	97.61
<i>cf195_bcp_x_22_ap_1</i>	41.19	0.56	54.63	0.51	2.46	1.15	98.90
<i>cf195_bcp_x_223_ap1</i>	41.06	0.51	54.05	0.36	2.39	1.02	97.84
<i>cf195_bcp_x_225_ap3</i>	40.08	0.86	53.55	0.55	2.20	1.16	96.98
<i>cf195_bcp_x_228_ap1</i>	40.03	0.91	53.76	0.84	2.30	1.04	97.39
<i>cf195_bcp_x_228_ap2</i>	40.90	0.60	54.49	0.50	2.41	0.99	98.32
<i>cf195_bcp_x_23_ap_1</i>	40.82	0.81	53.48	0.24	2.30	1.08	97.25
<i>cf195_bcp_x_23_ap_2</i>	40.24	0.80	53.47	0.45	2.28	1.10	96.86
<i>cf195_bcp_x_235_ap2</i>	39.65	0.92	52.38	0.18	2.60	0.97	95.03
<i>cf195_bcp_x_236_ap1</i>	41.12	0.57	53.86	0.67	2.23	1.16	98.16
<i>cf195_bcp_x_236_ap3</i>	40.85	0.68	54.00	0.59	2.27	1.11	98.04
<i>cf195_bcp_x_240_ap1</i>	41.43	0.42	54.15	0.37	2.32	1.12	98.30
<i>cf195_bcp_x_240_ap3</i>	41.53	0.48	53.87	0.46	2.26	1.10	98.23
<i>cf195_bcp_x_250_ap1</i>	40.87	0.79	53.01	0.13	2.65	1.01	96.75
<i>cf195_bcp_x_250_ap5</i>	39.99	0.56	52.68	0.47	2.37	0.97	95.50
<i>cf195_bcp_x_257_ap1</i>	41.58	0.44	54.45	0.40	2.47	0.98	98.71
<i>cf195_bcp_x_30_ap_1</i>	39.81	1.40	51.97	0.08	2.47	1.02	95.15
<i>cf195_bcp_x_35_ap_1</i>	40.12	0.90	53.12	0.78	2.69	0.70	96.57
<i>cf195_bcp_x_37_ap_1</i>	40.80	0.69	54.28	0.61	2.28	1.11	98.30
<i>cf195_bcp_x_42_ap_1</i>	40.51	0.65	53.22	0.59	2.08	1.14	96.84
<i>cf195_bcp_x_42_ap_2</i>	40.90	0.57	53.84	0.60	2.31	1.15	97.88
<i>cf195_bcp_x_42_ap_3</i>	39.63	1.00	52.43	0.61	2.22	1.12	95.57
<i>cf195_bcp_x_42_ap_4</i>	40.72	0.59	53.90	0.63	2.08	1.16	97.73
<i>cf195_bcp_x_42_ap_6</i>	41.02	0.43	53.50	0.47	2.26	1.12	97.33
<i>cf195_bcp_x_42_ap_7</i>	41.62	0.41	54.04	0.40	2.21	1.14	98.39
<i>cf195_bcp_x_42_ap_8</i>	41.20	0.41	53.87	0.37	2.21	1.11	97.74
<i>cf195_bcp_x_51_ap_1</i>	41.78	0.43	54.59	0.37	2.17	0.90	98.84
<i>cf195_bcp_x_51_ap_2</i>	41.29	0.59	54.48	0.41	2.18	0.97	98.52
<i>cf195_bcp_x_55_ap_1</i>	40.80	0.60	54.15	0.65	2.19	1.17	98.14
<i>cf195_bcp_x_55_ap_2</i>	40.39	0.74	53.28	0.42	2.27	1.19	96.82
<i>cf195_bcp_x_62_ap_1</i>	39.75	1.15	53.41	0.85	2.47	1.05	97.09
<i>cf195_bcp_x_62_ap_2</i>	41.42	0.56	53.69	0.31	2.59	0.98	97.87
<i>cf195_bcp_x_62_ap_3</i>	41.74	0.52	53.37	0.42	2.61	1.00	97.98
<i>cf195_bcp_x_80_ap_3</i>	41.09	0.68	53.70	0.70	2.28	1.09	98.07
<i>cf195_bcp_x_80_ap_7</i>	41.48	0.60	54.14	0.25	2.39	1.04	98.35

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>cf195_bcp_x_80_ap_8</i>	40.44	0.81	53.35	0.45	2.21	1.08	96.91
<i>cf195_bcp_x_83_ap_1</i>	41.41	0.53	53.39	0.16	2.42	1.08	97.42
<i>cf195_bcp_x_83_ap_2</i>	41.26	0.53	53.11	0.18	2.67	0.53	96.55
<i>cf195_bcp_x_83_ap_3</i>	41.93	0.37	53.36	0.21	2.21	1.09	97.74
<i>cf195_bcp_x_85_ap_1</i>	40.35	0.54	53.34	0.34	2.19	1.10	96.44
<i>cf195_bcp_x_85_ap_3</i>	40.90	0.46	53.19	0.42	2.30	1.13	96.91
<i>cf195_bcp_x_87_ap_1</i>	41.36	0.56	53.73	0.23	2.20	1.08	97.74
<i>cf195_bcp_x_95_ap_1</i>	41.64	0.51	53.56	0.28	2.26	1.12	97.91
<i>cf195_bcp_x_96_ap_1</i>	40.56	1.09	52.98	0.28	2.26	1.16	96.86
<i>cf195_bcp_x_96_ap_2</i>	40.55	0.71	53.08	0.52	2.34	1.09	96.77
<i>cf195_bcp_x_96_ap_3</i>	39.16	1.71	53.07	1.20	2.13	1.27	97.17
<i>cf195_ca_ap_1</i>	40.11	0.47	53.79	0.40	2.38	0.98	96.59
<i>cf195_cc_ap_1</i>	41.03	0.50	54.72	0.40	2.15	1.00	98.41
<i>cf195_cc_ap_2</i>	41.08	0.59	54.19	0.15	2.20	1.01	97.80
<i>cf195_cc_ap_4</i>	40.93	0.52	54.09	0.41	2.19	1.00	97.73
<i>cf195_cc_ap_5</i>	41.15	0.42	54.16	0.39	2.12	0.99	97.86
<i>cf195_cc_ap_6</i>	41.10	0.42	53.87	0.34	2.12	0.98	97.46
<i>cf195_cd_ap_1</i>	39.96	1.52	52.75	0.64	2.58	0.84	96.61

Table A5.1 | Major and trace element compositions of clinopyroxene-hosted apatite inclusions from Monte Nuovo. All elements were measured by EPMA. Analyses in italics were in contact with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. These are excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Monte Nuovo biotite-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>cf195_bi55_ap_1</i>	40.42	1.67	51.90	0.30	2.09	0.74	95.77
<i>CF195_bi13_ap_3</i>	39.11	0.51	53.36	0.30	2.15	0.95	94.99
<i>CF195_bi13_ap_1</i>	40.83	0.54	54.02	0.61	2.19	0.96	97.74
<i>cf195_bi64_ap_1</i>	39.80	1.06	53.11	0.78	2.23	0.97	96.51
<i>cf195_bi50_ap_1</i>	41.04	0.64	53.56	0.40	2.13	1.03	97.42
<i>cf195_bi51_ap_1</i>	41.61	0.59	53.64	0.33	2.16	1.01	97.95
<i>cf195_bi64_ap_4</i>	40.32	1.13	52.79	0.25	2.60	0.89	96.30
<i>cf195_bi37_ap_1</i>	39.04	0.49	53.06	0.41	2.17	0.99	94.76
<i>cf195_bi37_ap_3</i>	39.99	0.56	53.24	0.51	2.32	1.03	96.15
<i>cf195_bi37_ap_4</i>	40.76	0.48	53.50	0.47	1.95	1.03	96.93
<i>cf195_bi39_ap_2</i>	40.97	0.71	53.94	0.56	2.14	0.95	97.87
<i>cf195_bi40_ap_1</i>	40.83	0.80	53.12	0.32	2.06	1.00	96.80
<i>cf195_bi40_ap_2</i>	40.74	0.71	53.41	0.26	2.29	1.01	96.93
<i>cf195_bi42_ap_1</i>	39.96	0.84	53.68	0.77	2.11	1.07	97.07

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>cf195_bi43_ap_1</i>	41.60	0.54	54.12	0.41	2.01	1.01	98.38
<i>cf195_bi43_ap_3</i>	41.69	0.51	53.52	0.51	2.07	1.05	98.01
<i>cf195_bi43_ap_4</i>	41.28	0.45	53.12	0.43	2.09	1.06	97.09
<i>cf195_bi45_ap_1</i>	40.40	0.41	54.19	0.36	2.23	0.91	97.06
<i>cf195_bi45_ap_2</i>	39.32	0.45	53.96	0.42	2.27	0.91	95.86
<i>cf195_bi46_ap_1</i>	39.77	0.52	53.90	0.34	2.31	0.89	96.24
<i>cf195_bi46_ap_2</i>	39.81	0.51	54.18	0.47	2.31	0.92	96.71
<i>cf195_bi50_ap_2</i>	41.03	0.66	53.46	0.48	2.45	0.85	97.35
<i>cf195_bi51_ap_2</i>	41.44	0.58	53.39	0.37	2.01	1.04	97.52
<i>cf195_bi64_ap_2</i>	40.24	0.55	53.36	0.41	2.20	0.93	96.27
<i>cf195_bi64_ap_3</i>	41.62	0.54	53.72	0.36	2.16	0.91	97.91
<i>cf195_bi65_ap_2</i>	39.36	1.97	51.14	0.51	2.05	0.99	94.69
<i>cf195_bi65_ap_3</i>	41.13	0.69	53.22	0.59	2.11	1.04	97.41
<i>cf195_bi66_ap_1</i>	39.73	1.11	53.19	0.89	2.23	1.06	96.77
<i>CF195_bi10_ap_2</i>	41.02	0.53	54.05	0.44	2.24	1.04	97.88
<i>CF195_bi13_ap_5</i>	41.07	0.66	53.85	0.68	2.20	0.95	97.98
<i>CF195_bi17_ap_1</i>	41.36	0.58	53.79	0.58	2.24	0.95	98.04
<i>CF195_bi17_ap_2</i>	40.89	0.62	53.29	0.41	2.13	0.94	96.91
<i>CF195_bi21_ap_1</i>	40.94	0.67	53.54	0.56	1.96	1.06	97.46
<i>CF195_bi27_ap_1</i>	40.55	0.49	53.59	0.56	2.01	1.00	96.90
<i>CF195_bi30_ap_2</i>	40.69	0.97	53.16	0.49	1.96	1.04	97.05
<i>CF195_bi30_ap_3</i>	41.44	0.58	54.01	0.44	2.18	1.00	98.23
<i>CF195_bi31_ap_1</i>	40.62	0.73	53.29	0.63	1.99	1.06	97.03
<i>CF195_bi34_ap_1</i>	39.94	1.81	52.53	0.17	2.17	0.97	96.18
<i>CF195_bi34_ap_2</i>	40.72	0.60	53.09	0.24	2.21	0.92	96.35
<i>CF195_bi34_ap_3</i>	40.80	0.62	54.10	0.31	2.17	0.91	97.51

Table A5.2 | Major and trace element compositions of biotite-hosted apatite inclusions from Monte Nuovo. All elements were measured by EPMA. Analyses in italics were in contact with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. These are excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Astroni 1 clinopyroxene-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF69_cpx160_ap_1	40.31	1.00	53.91	0.77	2.06	0.99	97.72
CF69_cpx11_ap_2	41.33	0.63	54.45	0.35	2.12	1.15	98.67
CF69_cpx192_ap_2	41.06	0.80	54.14	0.46	2.24	1.12	98.38
CF69_cpx145_ap_1	41.59	0.55	54.35	0.49	2.24	1.14	98.91
CF69_cpx202_ap_4	41.39	0.74	53.67	0.32	2.32	1.09	98.03
CF69_cpx157_ap_1	40.63	1.60	53.61	0.38	2.51	0.97	98.07

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF69_cpx31_ap_2	41.80	0.49	54.10	0.45	2.42	1.03	98.73
CF69_cpx76_ap_1	40.59	0.85	54.09	0.72	2.34	1.11	98.19
CF69_cpx40_ap_1	41.23	0.44	54.11	0.35	2.37	1.09	98.05
CF69_cpx55_ap_2	41.25	0.55	54.52	0.49	2.45	1.03	98.70
CF69_cpx132_ap_1	41.13	0.61	53.37	0.38	2.37	1.09	97.42
CF69_cpx155_ap_1	41.42	0.59	54.39	0.36	2.45	1.04	98.66
CF69_cpx202_ap_3	41.39	0.58	54.36	0.27	2.38	1.11	98.55
CF69_cpx35_ap_1	41.68	0.66	54.34	0.29	2.43	1.06	98.90
CF69_cpx122_ap_2	41.58	0.62	54.47	0.56	2.47	1.04	99.14
CF69_cpx110_ap_2	41.43	0.46	54.53	0.47	2.45	1.05	98.81
CF69_cpx200_ap_1	40.84	0.85	53.92	0.18	2.30	1.19	97.79
CF69_cpx32_ap_1	41.30	0.77	54.36	0.30	2.42	1.10	98.68
CF69_cpx42_ap_1	41.02	0.77	54.32	0.48	2.47	1.06	98.52
CF69_cpx110_ap_1	41.28	0.64	53.31	0.12	2.38	1.14	97.34
CF69_cpx62_ap_1	41.16	0.90	53.91	0.24	2.49	1.05	98.14
CF69_cpx73_ap_4	41.64	0.65	54.33	0.37	2.40	1.13	98.96
CF69_cpx182_ap_1	40.84	0.67	53.68	0.37	2.31	1.20	97.58
CF69_cpx69_ap_1	41.24	0.68	54.09	0.15	2.50	1.05	98.10
CF69_cpx159_ap_1	40.90	0.56	54.26	0.55	2.48	1.07	98.21
CF69_cpx198_ap_1	41.38	0.67	53.72	0.11	2.52	1.04	97.81
CF69_cpx175_ap_4	41.20	0.57	54.06	0.37	2.51	1.06	98.14
CF69_cpx106_ap_1	40.39	1.70	53.01	0.13	2.49	1.07	97.18
CF69_cpx139_ap_2	41.33	0.57	54.14	0.18	2.59	1.00	98.14
CF69_cpx21_ap_1	41.10	0.66	53.94	0.24	2.57	1.02	97.86
CF69_cpx60_ap_1	41.20	0.62	54.24	0.61	2.40	1.17	98.69
CF69_cpx88_ap_1	41.45	0.66	53.97	0.28	2.51	1.08	98.32
CF69_cpx44_ap_6	40.94	0.56	53.97	0.46	2.57	1.03	97.87
CF69_cpx104_ap_1	40.50	0.78	53.95	0.29	2.51	1.10	97.50
CF69_cpx76_ap_2	38.81	1.88	52.55	0.76	2.42	1.17	96.03
CF69_cpx40_ap_2	41.11	0.56	53.90	0.58	2.56	1.06	98.12
CF69_cpx73_ap_2	41.07	0.82	53.78	0.24	2.59	1.04	97.87
CF69_cpx175_ap_3	39.66	1.39	53.06	0.33	2.48	1.14	96.46
CF69_cpx180_ap_1	41.18	0.46	54.19	0.39	2.61	1.07	98.21
CF69_cpx202_ap_2	40.97	0.57	54.17	0.41	2.61	1.08	98.13
CF69_cpx78_ap_1	40.93	0.97	53.81	0.40	2.67	1.10	98.15
CF69_cpx2_ap_1	40.42	0.87	53.79	0.79	2.53	1.12	97.89
CF69_cpx6_ap_1	40.64	0.88	53.78	0.18	2.59	1.05	97.45
CF69_cpx7_ap_1	40.78	0.59	53.91	0.46	2.56	1.09	97.73
CF69_cpx8_ap_1	40.56	0.89	53.65	0.36	2.51	1.08	97.41
CF69_cpx10_ap_1	41.24	0.66	53.92	0.15	2.37	1.02	97.83
CF69_cpx10_ap_2	41.31	0.68	54.05	0.09	2.51	1.03	98.05
CF69_cpx10_ap_4	41.43	0.53	53.92	0.42	2.44	1.06	98.23
CF69_cpx11_ap_1	40.99	0.76	53.92	0.32	2.31	1.17	97.97

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF69_cpx12_ap_1	41.63	0.45	54.67	0.45	2.41	1.07	99.12
CF69_cpx12_ap_2	40.41	0.88	53.70	0.24	2.48	1.08	97.18
CF69_cpx13_ap_1	41.11	0.75	54.07	0.11	2.45	1.09	97.99
CF69_cpx13_ap_2	41.66	0.53	54.08	0.23	2.50	1.06	98.45
CF69_cpx16_ap_1	40.88	0.68	53.99	0.30	2.46	1.06	97.77
CF69_cpx16_ap_2	40.64	1.47	53.48	0.26	2.39	1.03	97.73
CF69_cpx21_ap_2	41.36	0.55	54.03	0.25	2.48	1.16	98.24
CF69_cpx24_ap_1	40.90	0.91	53.73	0.14	2.49	1.10	97.66
CF69_cpx24_ap_2	40.83	0.85	53.38	0.12	2.45	1.06	97.11
CF69_cpx31_ap_1	41.22	0.62	54.11	0.50	2.41	1.04	98.34
CF69_cpx35_ap_2	40.94	0.77	53.83	0.44	2.49	1.08	97.94
CF69_cpx44_ap_1	41.04	0.67	53.83	0.31	2.57	1.08	97.83
CF69_cpx44_ap_2	41.43	0.65	54.33	0.31	2.50	1.04	98.64
CF69_cpx44_ap_3	40.56	0.90	53.75	0.21	2.43	1.08	97.37
CF69_cpx44_ap_4	41.39	0.67	53.97	0.36	2.55	1.05	98.34
CF69_cpx44_ap_5	41.25	0.63	53.72	0.25	2.57	1.06	97.82
CF69_cpx47_ap_1	41.45	0.49	53.74	0.40	2.40	1.09	98.02
CF69_cpx53_ap_1	40.97	1.84	52.88	0.22	2.46	1.05	97.82
CF69_cpx55_ap_1	41.80	0.54	54.09	0.38	2.45	1.04	98.72
CF69_cpx62_ap_2	41.22	0.51	54.00	0.51	2.52	1.06	98.20
CF69_cpx63_ap_1	41.43	0.45	54.44	0.36	2.48	1.03	98.58
CF69_cpx64_ap_1	41.70	0.50	54.62	0.31	2.52	1.02	99.04
CF69_cpx65_ap_1	40.28	1.20	54.28	0.80	2.40	1.13	98.53
CF69_cpx65_ap_2	41.33	0.72	54.62	0.17	2.54	1.05	98.80
CF69_cpx65_ap_3	39.53	1.32	53.33	1.01	2.44	1.12	97.18
CF69_cpx65_ap_4	38.52	1.98	52.99	1.19	2.35	1.16	96.67
CF69_cpx73_ap_1	40.34	1.03	53.43	0.20	2.41	1.03	96.89
CF69_cpx73_ap_3	41.20	0.58	54.55	0.39	2.45	1.05	98.64
CF69_cpx75_ap_1	41.06	0.66	53.86	0.24	2.50	1.03	97.73
CF69_cpx76_ap_3	40.82	0.65	54.03	0.35	2.57	0.96	97.72
CF69_cpx77_ap_1	41.36	0.64	54.40	0.23	2.64	1.03	98.58
CF69_cpx78_ap_2	40.39	1.53	53.22	0.26	2.44	1.07	97.32
CF69_cpx79_ap_1	40.51	0.94	54.45	0.80	2.13	0.67	98.13
CF69_cpx81_ap_1	40.87	1.12	54.01	0.21	2.41	1.04	98.10
CF69_cpx95_ap_1	41.11	0.74	53.59	0.23	2.46	1.06	97.60
CF69_cpx95_ap_2	40.95	0.67	53.81	0.24	2.43	1.03	97.55
CF69_cpx95_ap_3	40.83	0.74	54.00	0.55	2.44	1.10	98.09
CF69_cpx95_ap_4	41.76	0.56	54.10	0.44	2.51	1.09	98.84
CF69_cpx95_ap_5	41.54	0.50	54.32	0.45	2.40	1.02	98.68
CF69_cpx95_ap_6	41.16	0.98	53.84	0.38	2.44	1.05	98.27
CF69_cpx95_ap_7	41.29	0.57	54.40	0.47	2.45	1.07	98.66
CF69_cpx97_ap_1	41.49	0.57	54.23	0.23	2.52	1.04	98.46
CF69_cpx105_ap_1	40.36	1.15	54.75	0.90	1.89	0.51	98.34

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF69_cpx108_ap_1	41.30	0.78	54.02	0.31	2.38	1.10	98.35
CF69_cpx110_ap_3	41.31	0.66	54.44	0.62	2.39	1.08	98.95
CF69_cpx112_ap_1	41.39	0.50	54.33	0.47	2.43	1.03	98.58
CF69_cpx114_ap_1	40.82	0.57	54.11	0.74	2.28	0.94	97.97
CF69_cpx117_ap_1	41.20	0.81	54.18	0.16	2.57	1.05	98.30
CF69_cpx119_ap_1	41.10	0.67	53.77	0.54	2.54	1.11	98.09
CF69_cpx119_ap_2	41.56	0.53	54.07	0.42	2.49	1.08	98.54
CF69_cpx119_ap_3	41.33	0.63	54.23	0.54	2.35	1.08	98.64
CF69_cpx120_ap_1	40.74	0.67	53.51	0.50	2.49	1.10	97.41
CF69_cpx135_ap_1	41.51	0.50	54.21	0.46	2.48	1.07	98.62
CF69_cpx135_ap_2	41.38	0.68	53.57	0.12	2.38	1.11	97.70
CF69_cpx137_ap_1	41.24	0.61	53.72	0.32	2.45	1.07	97.82
CF69_cpx139_ap_1	41.26	0.68	53.80	0.35	2.42	1.12	98.05
CF69_cpx146_ap_1	40.08	1.01	53.31	0.13	2.47	1.06	96.46
CF69_cpx150_ap_1	41.16	0.58	53.86	0.52	2.39	1.04	98.01
CF69_cpx151_ap_1	40.57	0.94	53.52	0.15	2.56	1.08	97.16
CF69_cpx151_ap_2	41.42	0.59	53.80	0.36	2.58	1.08	98.15
CF69_cpx152_ap_1	41.67	0.57	54.21	0.38	2.49	1.07	98.77
CF69_cpx153_ap_1	41.63	0.53	54.18	0.18	2.31	1.09	98.42
CF69_cpx153_ap_2	41.18	0.59	53.71	0.33	2.26	1.14	97.74
CF69_cpx158_ap_1	40.46	0.82	53.60	0.26	2.55	1.07	97.12
CF69_cpx160_ap_2	40.75	0.86	54.55	0.69	2.30	0.97	98.64
CF69_cpx163_ap_1	41.25	0.41	54.86	0.37	2.49	1.03	98.80
CF69_cpx163_ap_3	40.98	0.81	54.07	0.22	2.52	1.05	98.02
CF69_cpx167_ap_1	41.50	0.44	54.38	0.33	2.41	1.06	98.56
CF69_cpx167_ap_2	41.05	0.58	53.97	0.46	2.54	1.16	98.12
CF69_cpx167_ap_3	40.95	1.92	52.94	0.45	2.49	1.07	98.22
CF69_cpx168_ap_1	40.56	1.01	53.57	0.14	2.22	1.21	97.28
CF69_cpx169_ap_1	40.97	0.55	54.23	0.71	2.51	1.13	98.47
CF69_cpx172_ap_1	41.39	0.64	54.01	0.28	2.45	1.10	98.28
CF69_cpx175_ap_1	41.35	0.57	54.41	0.38	2.40	1.09	98.65
CF69_cpx175_ap_2	41.68	0.49	54.14	0.35	2.46	1.06	98.60
CF69_cpx176_ap_1	41.17	0.52	54.08	0.31	2.39	1.08	98.01
CF69_cpx176_ap_2	41.58	0.47	54.76	0.37	2.51	1.08	99.15
CF69_cpx178_ap_1	41.75	0.32	54.62	0.30	2.49	1.05	98.92
CF69_cpx179_ap_1	39.98	0.81	52.82	0.67	2.33	1.01	96.12
CF69_cpx180_ap_2	41.51	0.59	54.41	0.29	2.41	1.06	98.70
CF69_cpx182_ap_2	40.94	0.71	53.96	0.24	2.24	1.21	97.84
CF69_cpx186_ap_1	41.87	0.40	54.09	0.40	2.44	1.05	98.68
CF69_cpx187_ap_1	40.97	1.51	53.24	0.36	2.44	1.07	98.00
CF69_cpx192_ap_1	41.71	0.44	54.52	0.44	2.19	1.15	99.04
CF69_cpx192_ap_3	41.71	0.42	54.39	0.43	2.22	1.12	98.86
CF69_cpx193_ap_1	41.06	0.75	53.37	0.17	2.73	0.94	97.25

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>CF69_cpx197_ap_1</i>	40.99	0.87	54.16	0.28	2.45	1.05	98.21
<i>CF69_cpx202_ap_1</i>	41.80	0.48	54.32	0.36	2.46	1.06	98.89
<i>CF69_cpx202_ap_5</i>	40.63	0.74	53.64	0.18	2.51	1.16	97.23
<i>CF69_cpx202_ap_7</i>	41.37	0.71	54.33	0.29	2.36	1.12	98.66

Table A5.3 | Major and trace element compositions of clinopyroxene-hosted apatite inclusions from Astroni 1. All elements were measured by EPMA. Analyses in italics were in contact with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. These are excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Astroni 1 biotite-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF69_bi113_ap_2	40.89	0.96	55.24	0.78	1.81	0.96	99.47
CF69_bi142_ap_1	40.32	0.76	54.78	0.81	2.18	1.11	98.55
CF69_bi142_ap_2	40.82	0.56	54.13	0.56	2.24	1.10	97.95
CF69_bi138_ap_1	41.53	0.55	54.56	0.43	2.39	1.00	98.92
CF69_bi24_ap_1	41.42	0.54	53.88	0.52	2.34	1.05	98.24
CF69_bi7_ap_4	41.24	0.66	53.92	0.36	2.32	1.07	98.07
CF69_bi146_ap_4	41.06	0.61	54.04	0.36	2.36	1.05	97.96
CF69_bi23_ap_3	41.18	0.59	54.18	0.38	2.36	1.05	98.22
CF69_bi48_ap_1	41.14	0.59	54.14	0.31	2.37	1.04	98.06
CF69_bi79_ap_1	40.78	0.80	53.97	0.48	2.34	1.07	97.92
CF69_bi23_ap_2	41.60	0.56	53.97	0.34	2.36	1.07	98.39
CF69_bi140_ap_1	40.93	0.59	53.78	0.33	2.42	1.02	97.50
CF69_bi138_ap_3	40.97	0.50	54.40	0.34	2.42	1.03	98.11
CF69_bi117_ap_1	41.55	0.53	54.51	0.38	2.43	1.03	98.86
CF69_bi88_ap_3	40.59	0.49	54.30	0.32	2.43	1.03	97.59
CF69_bi164_ap_5	40.95	0.60	54.35	0.27	2.44	1.03	98.06
CF69_bi15_ap_1	41.61	0.53	53.92	0.31	2.30	1.13	98.31
CF69_bi133_ap_1	39.91	0.69	54.27	0.65	2.37	1.09	97.44
CF69_bi125_ap_1	40.12	0.70	53.79	0.43	2.34	1.12	96.98
CF69_bi98_ap_1	40.98	0.58	53.87	0.54	2.46	1.02	97.86
CF69_bi7_ap_2	41.70	0.62	53.90	0.36	2.43	1.05	98.48
CF69_bi27_ap_1	41.78	0.50	53.99	0.29	2.44	1.04	98.47
CF69_bi98_ap_2	40.42	1.09	53.27	0.38	2.41	1.08	97.09
CF69_bi38_ap_2	40.82	0.73	53.71	0.36	2.45	1.05	97.54
CF69_bi100_ap_2	41.12	0.81	53.53	0.24	2.46	1.06	97.63
CF69_bi110_ap_1	40.34	0.64	54.01	0.29	2.47	1.05	97.20
CF69_bi140_ap_2	40.93	0.64	54.28	0.29	2.56	0.99	98.03
CF69_bi38_ap_3	41.09	0.69	53.86	0.58	2.48	1.06	98.15

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF69_bi144_ap_1	40.41	0.56	53.71	0.32	2.48	1.06	96.93
CF69_bi38_ap_4	41.35	0.56	53.61	0.37	2.49	1.06	97.83
CF69_bi97_ap_3	41.66	0.55	53.82	0.32	2.52	1.06	98.29
CF69_bi125_ap_2	40.45	0.58	54.05	0.38	2.40	1.17	97.47
CF69_bi146_ap_1	40.21	0.74	54.29	0.38	2.51	1.07	97.58
CF69_bi75_ap_2	40.56	0.68	53.63	0.36	2.55	1.07	97.21
CF69_bi3_ap_1	40.98	0.74	53.66	0.37	2.53	1.07	97.71
CF69_bi7_ap_1	41.17	0.66	53.63	0.33	2.28	1.04	97.63
CF69_bi7_ap_5	41.01	1.03	52.93	0.32	2.40	1.04	97.18
CF69_bi10_ap_1	40.94	0.83	53.50	0.20	2.38	1.08	97.39
CF69_bi20_ap_1	40.91	0.68	53.69	0.76	1.93	1.09	97.81
CF69_bi27_ap_2	40.01	1.41	52.71	0.16	2.37	1.10	96.22
CF69_bi35_ap_1	41.64	0.47	54.06	0.42	2.50	1.07	98.55
CF69_bi35_ap_2	41.52	0.42	54.24	0.37	2.31	1.07	98.43
CF69_bi35_ap_3	41.13	0.54	54.00	0.50	2.38	1.08	98.09
CF69_bi38_ap_1	40.81	0.72	53.66	0.36	2.45	1.02	97.45
CF69_bi75_ap_1	40.93	0.59	53.88	0.26	2.39	1.04	97.55
CF69_bi79_ap_2	40.80	0.79	54.19	0.43	2.37	1.06	98.10
CF69_bi88_ap_1	40.89	0.61	54.02	0.46	2.38	1.02	97.85
CF69_bi97_ap_1	41.32	0.60	54.30	0.56	2.41	1.07	98.71
CF69_bi100_ap_3	39.86	1.15	53.45	0.27	2.54	1.07	96.69
CF69_bi112_ap_1	41.49	0.47	53.99	0.44	2.53	1.03	98.33
CF69_bi121_ap_1	41.16	0.51	53.64	0.44	2.29	1.05	97.61
CF69_bi131_ap_2	39.85	1.39	53.14	0.15	2.46	1.09	96.49
CF69_bi132_ap_1	40.60	0.59	54.02	0.41	2.36	1.04	97.49
CF69_bi133_ap_2	39.97	0.66	54.11	0.58	2.53	1.05	97.27
CF69_bi146_ap_2	40.67	0.64	54.52	0.22	2.46	1.05	97.97
CF69_bi147_ap_1	40.47	0.53	54.21	0.50	2.50	1.04	97.63
CF69_bi147_ap_2	40.96	0.58	54.20	0.38	2.60	1.07	98.11
CF69_bi147_ap_3	40.88	0.52	54.30	0.46	2.42	1.04	98.05
CF69_bi149_ap_1	40.49	0.74	54.37	0.27	2.39	1.06	97.78
CF69_bi149_ap_2	40.55	0.67	54.35	0.28	2.47	1.02	97.73
CF69_bi149_ap_3	40.78	0.63	54.31	0.29	2.41	1.03	97.90
CF69_bi150_ap_1	41.16	0.46	54.07	0.41	2.49	1.02	98.00
CF69_bi156_ap_1	40.85	0.51	54.49	0.40	2.35	1.04	98.12
CF69_bi158_ap_1	41.75	0.45	54.59	0.44	2.49	1.06	99.16
CF69_bi158_ap_2	41.07	0.41	54.29	0.42	2.42	1.06	98.11
CF69_bi164_ap_1	41.25	0.65	54.54	0.28	2.52	1.06	98.67
CF69_bi164_ap_2	40.27	0.62	54.03	0.29	2.35	1.00	97.03
CF69_bi167_ap_1	40.13	0.59	53.81	0.35	2.56	1.06	96.84
CF69_bi170_ap_1	40.97	0.40	54.01	0.40	2.46	1.04	97.68
CF69_bi170_ap_2	40.90	0.42	54.53	0.42	2.49	1.07	98.22
CF69_bi184_ap_1	40.53	0.54	53.88	0.37	2.54	1.04	97.24

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>CF69_bi185_ap_1</i>	<i>40.30</i>	<i>0.68</i>	<i>53.06</i>	<i>0.25</i>	<i>2.39</i>	<i>1.01</i>	<i>96.16</i>
<i>CF69_bi185_ap_2</i>	<i>40.23</i>	<i>0.61</i>	<i>54.23</i>	<i>0.29</i>	<i>2.58</i>	<i>1.00</i>	<i>97.26</i>
<i>CF69_bi185_ap_3</i>	<i>40.63</i>	<i>0.54</i>	<i>54.24</i>	<i>0.24</i>	<i>2.29</i>	<i>1.02</i>	<i>97.47</i>
<i>CF69_bi188_ap_1</i>	<i>39.43</i>	<i>0.61</i>	<i>53.12</i>	<i>0.54</i>	<i>2.41</i>	<i>1.07</i>	<i>95.63</i>

Table A5.4 | Major and trace element compositions of biotite-hosted apatite inclusions from Astroni 1. All elements were measured by EPMA. Analyses in italics were in contact with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. These are excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Fondi di Baia clinopyroxene-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF88_cpx85_ap_1	40.02	1.25	53.55	0.56	2.28	0.72	96.90
CF88_cpx116_ap_1	39.79	1.28	52.78	0.00	2.88	0.48	95.34
CF88_cpx72_ap_1	39.87	1.49	53.05	0.00	2.92	0.46	95.91
CF88_cpx136_ap_1	40.49	1.33	52.90	0.00	2.90	0.48	96.22
<i>CF88_cpx118_ap_1</i>	<i>39.71</i>	<i>1.50</i>	<i>52.48</i>	<i>0.00</i>	<i>2.90</i>	<i>0.50</i>	<i>95.21</i>
<i>CF88_cpx136_ap_2</i>	<i>40.11</i>	<i>1.41</i>	<i>52.93</i>	<i>0.02</i>	<i>2.84</i>	<i>0.49</i>	<i>95.96</i>

Table A5.5 | Major and trace element compositions of clinopyroxene-hosted apatite inclusions from Fondi di Baia. All elements were measured by EPMA. Analyses in italics were in contact with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. These are excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Fondi di Baia biotite-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF88_bi36_ap_1	40.38	1.08	53.70	0.53	2.48	0.60	97.17
CF88_bi36_ap_2	39.88	1.03	53.74	0.55	2.76	0.63	96.80

Table A5.6 | Major and trace element compositions of biotite-hosted apatite inclusions from Fondi di Baia. All elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Pisani 1 clinopyroxene-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
cf25_cpx_127_ap_1	40.24	0.58	54.60	0.45	2.15	1.01	97.64
cf25_cpx_181_ap_1	39.77	2.49	52.70	0.33	2.25	0.96	97.05
cf25_cpx_1_ap_1	40.83	0.42	54.57	0.37	2.13	1.11	98.06
cf25_cpx_171_ap_2	39.25	1.26	52.89	0.55	2.10	1.21	95.89
cf25_cpx_171_ap_1	40.08	0.72	54.29	0.50	2.19	1.16	97.52
cf25_cpx_100_ap_3	39.90	1.08	53.49	0.23	2.11	1.23	96.67
cf25_cpx_139_ap_2	40.51	0.64	54.02	0.50	2.22	1.19	97.64
cf25_cpx_142_ap_4	40.64	0.56	54.84	0.40	2.26	1.17	98.40
cf25_cpx_142_ap_1	40.13	0.56	54.48	0.46	2.27	1.18	97.62
cf25_cpx_115_ap_1	40.55	0.56	54.20	0.49	2.30	1.18	97.79
cf25_cpx_18_ap_2	41.28	0.49	54.23	0.43	2.33	1.17	98.43
cf25_cpx_173_ap_1	41.05	0.47	54.97	0.44	2.28	1.22	98.95
cf25_cpx_142_ap_3	40.13	0.79	54.38	0.45	2.30	1.21	97.77
cf25_cpx_100_ap_2	40.77	0.94	54.46	0.24	2.26	1.26	98.46
cf25_cpx_54_ap_3	40.62	0.53	54.26	0.46	2.36	1.18	97.87
cf25_cpx_100_ap_1	39.58	1.90	52.76	0.14	2.25	1.27	96.44
cf25_cpx_54_ap_2	40.62	0.77	55.01	0.49	2.35	1.19	98.91
cf25_cpx_139_ap_1	40.41	0.64	55.03	0.57	2.34	1.19	98.67
cf25_cpx_100_ap_4	40.21	0.92	54.32	0.31	2.29	1.24	97.81
cf25_cpx_86_ap_1	39.48	1.51	52.95	0.22	2.31	1.26	96.23
cf25_cpx_153_ap_1	40.82	0.62	54.35	0.54	2.38	1.19	98.36
cf25_cpx_115_ap_2	40.72	0.50	54.91	0.47	2.19	1.16	98.52
cf25_cpx_118_ap_1	40.54	0.47	54.35	0.44	2.33	1.18	97.80
cf25_cpx_118_ap_4	40.72	1.00	54.03	0.55	2.29	1.19	98.30
cf25_cpx_121_ap_1	40.04	0.54	53.77	0.63	2.23	1.24	97.00
cf25_cpx_122_ap_1	40.88	0.40	54.52	0.46	2.23	1.09	98.14
cf25_cpx_136_ap_1	40.77	0.45	54.58	0.40	2.17	1.20	98.17
cf25_cpx_136_ap_2	41.04	0.51	53.99	0.41	2.20	1.18	97.91
cf25_cpx_137_ap_1	40.55	0.49	54.45	0.46	2.31	1.14	97.91
cf25_cpx_142_ap_2	40.68	0.42	54.45	0.37	2.34	1.17	97.91
cf25_cpx_18_ap_1	40.78	0.47	53.90	0.44	2.25	1.18	97.56
cf25_cpx_28_ap_1	40.56	0.60	54.29	0.45	2.31	1.19	97.91
cf25_cpx_28_ap_2	41.25	0.70	54.34	0.41	2.18	1.18	98.66
cf25_cpx_41_ap_1	40.95	0.51	54.68	0.51	2.34	1.23	98.71
cf25_cpx_43_ap_1	40.97	0.54	54.22	0.45	2.22	1.18	98.14
cf25_cpx_43_ap_2	40.67	0.69	54.06	0.56	2.26	1.21	97.98
cf25_cpx_54_ap_1	40.68	0.49	54.55	0.43	2.34	1.19	98.15
cf25_cpx_71_ap_1	41.00	0.51	54.56	0.46	2.22	1.16	98.48
cf25_cpx_74_ap_1	40.96	0.48	54.30	0.46	2.30	1.16	98.17
cf25_cpx_86_ap_2	39.95	1.07	54.04	0.16	2.32	1.26	97.29
cf25_cpx_98_ap_1	40.68	0.45	54.38	0.35	2.23	1.00	97.64
cf25_cpx_98_ap_2	40.79	0.40	54.44	0.25	2.16	0.98	97.62

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>cf25_cpx_98_ap_3</i>	39.41	1.14	53.73	0.49	2.07	1.20	96.70
<i>cf25_cpx_98_ap_5</i>	40.22	0.78	54.04	0.58	2.20	1.07	97.47
<i>cf25_cpx_98_ap_6</i>	40.73	0.72	54.57	0.41	2.11	1.01	98.19
<i>cf25_cpx_98_ap_7</i>	40.57	0.62	54.14	0.47	2.18	1.09	97.65

Table A5.7 | Major and trace element compositions of clinopyroxene-hosted apatite inclusions from Pisani 1. All elements were measured by EPMA. Analyses in italics were in contact with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. These are excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Pisani 1 biotite-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>cf25_bi73_ap_3</i>	41.51	0.47	54.47	0.40	2.02	0.89	98.46
<i>cf25_bi35_ap_1</i>	40.71	0.58	54.54	0.48	2.09	0.89	97.93
<i>cf25_bi73_ap_2</i>	41.50	0.43	54.94	0.40	2.10	0.90	98.91
<i>cf25_bi73_ap_1</i>	41.63	0.45	55.09	0.38	2.18	0.89	99.21
<i>cf25_bi98_ap_1</i>	41.27	0.49	54.81	0.46	2.22	0.92	98.73
<i>cf25_bi73_ap_4</i>	41.35	0.59	55.02	0.51	2.25	0.92	99.19
<i>cf25_bi69_ap_1</i>	41.08	0.58	54.46	0.54	2.05	1.08	98.46
<i>cf25_bi37_ap_1</i>	40.78	0.54	54.44	0.56	2.10	1.07	98.13
<i>cf25_bi126_ap_1</i>	41.05	0.63	53.96	0.34	2.13	1.05	97.78
<i>cf25_bi20_ap_2</i>	39.93	0.60	54.45	0.68	2.05	1.12	97.50
<i>cf25_bi25_ap_2</i>	40.65	1.44	52.31	0.46	2.13	1.10	96.71
<i>cf25_bi47_ap_1</i>	41.44	0.47	54.28	0.41	2.12	1.12	98.46
<i>cf25_bi112_ap_1</i>	39.20	0.50	54.46	0.36	2.28	1.05	96.38
<i>cf25_bi55_ap_1</i>	41.66	0.35	54.60	0.31	2.23	1.12	98.83
<i>cf25_bi8_ap_1</i>	41.58	0.51	54.20	0.52	2.19	1.17	98.74
<i>cf25_bi25_ap_1</i>	41.06	0.55	54.48	0.52	2.31	1.14	98.55
<i>cf25_bi19_ap_2</i>	40.71	0.56	54.33	0.50	2.12	1.14	97.99
<i>cf25_bi20_ap_1</i>	40.84	0.42	55.19	0.36	2.08	1.06	98.60
<i>cf25_bi20_ap_3</i>	40.08	0.64	54.11	0.46	2.16	1.06	97.11
<i>cf25_bi20_ap_4</i>	40.92	0.49	54.26	0.46	2.04	1.05	97.89
<i>cf25_bi20_ap_5</i>	40.83	0.55	54.22	0.40	2.13	1.08	97.82
<i>cf25_bi28_ap_1</i>	41.35	0.51	55.27	0.50	2.07	1.08	99.45
<i>cf25_bi34_ap_1</i>	41.20	0.58	54.30	0.48	2.19	1.09	98.42
<i>cf25_bi37_ap_3</i>	41.15	0.59	53.92	0.47	2.12	1.08	97.96
<i>cf25_bi38_ap_1</i>	40.71	0.40	54.89	0.42	2.11	1.06	98.23
<i>cf25_bi38_ap_2</i>	41.28	0.38	54.64	0.34	2.14	1.09	98.48
<i>cf25_bi40_ap_1</i>	41.56	0.37	54.81	0.37	2.07	1.10	98.93
<i>cf25_bi40_ap_2</i>	40.97	0.48	54.67	0.32	2.12	1.07	98.25

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>cf25_bi41_ap_1</i>	41.50	0.59	54.22	0.44	1.95	0.88	98.32
<i>cf25_bi43_ap_1</i>	41.55	0.46	54.75	0.36	1.99	0.87	98.70
<i>cf25_bi53_ap_1</i>	41.03	0.52	54.70	0.52	2.03	0.94	98.43
<i>cf25_bi66_ap_1</i>	40.58	0.68	54.37	0.69	2.16	1.12	98.20
<i>cf25_bi67_ap_1</i>	41.47	0.38	55.19	0.45	2.05	0.90	99.11
<i>cf25_bi67_ap_2</i>	40.36	0.39	54.55	0.42	2.00	0.90	97.33
<i>cf25_bi68_ap_1</i>	40.33	0.52	54.49	0.55	2.11	1.09	97.72
<i>cf25_bi68_ap_2</i>	41.14	0.44	54.83	0.41	2.13	1.05	98.62
<i>cf25_bi68_ap_4</i>	41.17	0.46	54.31	0.34	2.20	1.06	98.12
<i>cf25_bi68_ap_5</i>	40.97	0.42	54.27	0.41	2.07	1.07	97.87
<i>cf25_bi68_ap_6</i>	41.14	0.51	54.45	0.49	2.13	1.10	98.45
<i>cf25_bi69_ap_2</i>	40.76	0.60	54.54	0.58	2.15	1.11	98.36
<i>cf25_bi69_ap_3</i>	40.79	0.46	54.18	0.52	2.06	1.09	97.77
<i>cf25_bi73_ap_5</i>	41.66	0.38	54.90	0.36	2.05	0.89	98.91
<i>cf25_bi82_ap_1</i>	41.64	0.40	54.87	0.39	2.18	1.11	99.17
<i>cf25_bi82_ap_2</i>	41.42	0.38	54.45	0.39	2.16	1.10	98.50
<i>cf25_bi90_ap_1</i>	41.09	0.48	54.71	0.45	2.09	1.08	98.56
<i>cf25_bi91_ap_1</i>	41.18	0.71	53.82	0.39	2.08	1.06	97.89
<i>cf25_bi93_ap_1</i>	40.01	0.45	54.56	0.46	2.10	1.11	97.33
<i>cf25_bi103_ap_2</i>	40.59	0.84	53.87	0.53	2.04	1.07	97.62
<i>cf25_bi104_ap_1</i>	40.64	0.59	54.94	0.54	2.20	1.05	98.54
<i>cf25_bi110_ap_1</i>	41.47	0.37	54.13	0.31	2.02	1.05	98.05
<i>cf25_bi111_ap_1</i>	40.92	0.70	53.94	0.67	1.96	0.90	97.82
<i>cf25_bi115_ap_1</i>	40.45	0.72	54.16	0.61	1.89	0.94	97.56
<i>CF25_bi3_ap_1</i>	41.02	0.41	54.80	0.41	2.07	0.95	98.32

Table A5.8 | Major and trace element compositions of biotite-hosted apatite inclusions from Pisani 1. All elements were measured by EPMA. Analyses in italics were in contact with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. These are excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Pomici Principali clinopyroxene-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>cf6_cpx_138_ap_2</i>	40.99	0.50	53.23	0.13	2.19	0.99	96.61
<i>cf6_cpx_138_ap_1</i>	40.41	0.96	53.94	0.64	2.07	1.07	97.75
<i>cf6_cpx_135_ap_1</i>	40.18	0.85	53.61	0.41	2.23	0.96	96.81
<i>cf6_cpx_177_ap_1</i>	39.89	0.92	53.71	0.66	2.16	1.07	97.01
<i>cf6_cpx_146_ap_1</i>	40.50	0.54	54.50	0.60	2.22	1.03	97.95
<i>cf6_cpx_159_ap_2</i>	40.21	0.80	53.33	0.55	2.25	1.02	96.71
<i>cf6_cpx_173_ap_1</i>	40.08	0.81	53.77	0.65	2.23	1.05	97.14

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
cf6_cpx_159_ap_1	39.60	0.93	53.31	0.64	2.29	1.10	96.38
cf6_cpx_203_ap_2	40.18	0.81	53.56	0.62	2.33	1.09	97.09
cf6_cpx_179_ap_1	40.33	0.79	53.64	0.56	2.41	1.05	97.22
<i>cf6_cpx_100_ap1</i>	<i>40.56</i>	<i>0.76</i>	<i>53.47</i>	<i>0.63</i>	<i>2.25</i>	<i>1.02</i>	97.23
<i>cf6_cpx_146_ap_2</i>	<i>40.12</i>	<i>0.78</i>	<i>53.97</i>	<i>0.74</i>	<i>2.12</i>	<i>1.00</i>	97.36
<i>cf6_cpx_166_ap_1</i>	<i>40.97</i>	<i>0.66</i>	<i>54.31</i>	<i>0.54</i>	<i>2.44</i>	<i>1.06</i>	98.40
<i>cf6_cpx_172_ap_1</i>	<i>41.18</i>	<i>0.78</i>	<i>54.12</i>	<i>0.62</i>	<i>2.17</i>	<i>1.02</i>	98.48
<i>cf6_cpx_187_ap_1</i>	<i>40.74</i>	<i>0.94</i>	<i>54.26</i>	<i>0.56</i>	<i>2.40</i>	<i>1.04</i>	98.39
<i>cf6_cpx_19_ap_1</i>	<i>41.35</i>	<i>0.43</i>	<i>54.66</i>	<i>0.27</i>	<i>2.31</i>	<i>1.00</i>	98.52
<i>cf6_cpx_2_ap_1</i>	<i>40.30</i>	<i>0.86</i>	<i>53.96</i>	<i>0.63</i>	<i>2.31</i>	<i>1.07</i>	97.64
<i>cf6_cpx_203_ap_1</i>	<i>39.83</i>	<i>0.84</i>	<i>53.51</i>	<i>0.67</i>	<i>2.23</i>	<i>1.04</i>	96.69
<i>cf6_cpx_203_ap_3</i>	<i>40.27</i>	<i>0.90</i>	<i>53.41</i>	<i>0.55</i>	<i>2.17</i>	<i>1.02</i>	96.92
<i>cf6_cpx_205_ap_1</i>	<i>40.53</i>	<i>0.79</i>	<i>54.01</i>	<i>0.78</i>	<i>2.30</i>	<i>1.08</i>	98.01
<i>cf6_cpx_37_ap_1</i>	<i>40.34</i>	<i>0.69</i>	<i>53.51</i>	<i>0.54</i>	<i>2.39</i>	<i>1.02</i>	96.94
<i>cf6_cpx_64_ap_1</i>	<i>40.50</i>	<i>0.68</i>	<i>53.97</i>	<i>0.52</i>	<i>2.13</i>	<i>0.99</i>	97.40
<i>cf6_cpx_64_ap_2</i>	<i>40.53</i>	<i>0.68</i>	<i>53.58</i>	<i>0.55</i>	<i>2.12</i>	<i>1.06</i>	97.15
<i>cf6_cpx_73_ap1</i>	<i>40.60</i>	<i>0.72</i>	<i>54.13</i>	<i>0.80</i>	<i>2.15</i>	<i>1.01</i>	98.02
<i>cf6_cpx_91_ap1</i>	<i>40.67</i>	<i>0.83</i>	<i>53.60</i>	<i>0.69</i>	<i>2.26</i>	<i>1.05</i>	97.64
<i>cf6_cpx_96_ap1</i>	<i>40.30</i>	<i>0.70</i>	<i>53.58</i>	<i>0.51</i>	<i>2.47</i>	<i>1.04</i>	96.99
<i>cf6_cpx_98_ap1</i>	<i>39.50</i>	<i>0.94</i>	<i>53.37</i>	<i>0.63</i>	<i>2.30</i>	<i>1.08</i>	96.32

Table A5.9 | Major and trace element compositions of clinopyroxene-hosted apatite inclusions from Pomici Principali. All elements were measured by EPMA. Analyses in italics were in contact with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. These are excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Pomici Principali biotite-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF6_bi42_ap_1	40.49	0.95	53.89	0.53	1.92	0.92	97.45
CF6_bi83_ap_1	40.80	0.70	54.18	0.55	2.09	0.94	97.92
CF6_bi31_ap_3	40.83	0.89	53.67	0.58	2.08	0.97	97.67
CF6_bi76_ap_1	40.52	0.73	53.60	0.67	2.13	0.94	97.22
CF6_bi3_ap_1	39.78	0.76	53.20	0.49	2.12	0.96	95.95
CF6_bi31_ap_2	40.85	0.70	53.68	0.57	2.13	0.96	97.51
CF6_bi34_ap_1	40.59	0.73	53.60	0.61	2.08	1.00	97.26
CF6_bi26_ap_1	40.75	0.76	54.04	0.55	2.14	0.97	97.84
CF6_bi94_ap_1	40.31	0.93	53.39	0.60	2.16	0.97	96.95
CF6_bi3_ap_2	41.03	0.67	53.51	0.47	2.01	0.94	97.33
CF6_bi14_ap_1	41.02	0.59	53.92	0.44	2.18	0.96	97.68
CF6_bi26_ap_2	39.55	1.38	53.19	0.50	2.07	0.92	96.27

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF6_bi26_ap_3	40.68	0.73	53.63	0.48	2.08	0.99	97.24
CF6_bi31_ap_1	40.86	0.69	53.68	0.48	2.03	0.96	97.38
CF6_bi57_ap_1	40.43	0.77	53.43	0.59	2.12	0.95	96.91
CF6_bi75_ap_1	40.01	0.94	53.31	0.73	2.13	1.00	96.74
CF6_bi80_ap_1	40.86	0.63	54.16	0.49	2.13	0.96	97.85
CF6_bi80_ap_2	40.22	0.80	53.43	0.54	2.12	0.93	96.66
CF6_bi91_ap_1	40.68	0.81	54.01	0.52	2.18	0.94	97.73
CF6_bi91_ap_2	40.31	0.91	53.72	0.64	2.10	0.94	97.27
CF6_bi112_ap_1	40.72	0.68	54.16	0.51	2.12	0.96	97.77
CF6_bi115_ap_2	40.47	0.91	52.96	0.55	2.04	0.93	96.54

Table A5.10 | Major and trace element compositions of biotite-hosted apatite inclusions from Pomici Principali. All elements were measured by EPMA. Analyses in *italics* were in contact with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. These are excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Minopoli 1 clinopyroxene-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF13_cpx9_ap_1	41.73	0.56	54.37	0.60	1.92	0.84	98.78
CF13_cpx71_ap_1	41.91	0.49	53.86	0.48	1.97	0.83	98.26
CF13_cpx125_ap_2	40.68	1.24	53.26	0.58	1.96	0.84	97.30
CF13_cpx43_ap_1	41.64	0.47	54.23	0.39	1.97	0.85	98.27
CF13_cpx16_ap_1	41.02	0.79	53.98	0.50	1.89	0.90	97.85
CF13_cpx13_ap_1	40.44	0.55	54.26	0.52	1.99	0.86	97.33
CF13_cpx208_ap_1	41.25	0.48	54.41	0.47	1.93	0.89	98.18
CF13_cpx142_ap_2	41.47	0.41	54.17	0.45	2.00	0.87	98.07
CF13_cpx28_ap_1	41.61	0.41	54.32	0.45	2.03	0.87	98.39
CF13_cpx28_ap_2	41.11	0.69	54.55	0.54	2.06	0.87	98.48
cf13_cpx_195_ap_1	39.83	0.55	54.06	0.55	1.96	0.92	96.60
cf13_cpx_213_ap_1	41.07	0.52	54.52	0.53	2.04	0.96	98.32
CF13_cpx3_ap_1	39.50	1.64	53.04	0.30	1.87	1.14	96.28
<i>cf13_cpx_143_ap_1</i>	<i>41.47</i>	<i>0.52</i>	<i>53.94</i>	<i>0.49</i>	<i>2.10</i>	<i>0.92</i>	<i>98.08</i>
<i>cf13_cpx_169_ap_1</i>	<i>41.91</i>	<i>0.42</i>	<i>54.40</i>	<i>0.41</i>	<i>2.04</i>	<i>0.96</i>	<i>98.82</i>
<i>cf13_cpx_173_ap_2</i>	<i>40.59</i>	<i>0.89</i>	<i>54.60</i>	<i>0.71</i>	<i>1.91</i>	<i>0.55</i>	<i>98.01</i>
<i>cf13_cpx_179_ap_1</i>	<i>41.49</i>	<i>1.37</i>	<i>53.47</i>	<i>0.39</i>	<i>2.05</i>	<i>0.82</i>	<i>98.27</i>
<i>CF13_cpx16_ap_2</i>	<i>40.65</i>	<i>0.57</i>	<i>54.37</i>	<i>0.49</i>	<i>1.94</i>	<i>0.84</i>	<i>97.62</i>
<i>CF13_cpx88_ap_1</i>	<i>40.67</i>	<i>0.58</i>	<i>53.54</i>	<i>0.38</i>	<i>2.05</i>	<i>0.84</i>	<i>96.74</i>
<i>CF13_cpx125_ap_1</i>	<i>41.51</i>	<i>0.46</i>	<i>54.07</i>	<i>0.51</i>	<i>1.93</i>	<i>0.86</i>	<i>98.09</i>
<i>CF13_cpx142_ap_1</i>	<i>41.57</i>	<i>0.50</i>	<i>54.94</i>	<i>0.54</i>	<i>1.96</i>	<i>0.86</i>	<i>99.10</i>
<i>CF13_cpx142_ap_3</i>	<i>40.00</i>	<i>1.76</i>	<i>52.97</i>	<i>0.69</i>	<i>1.81</i>	<i>0.89</i>	<i>96.95</i>

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>CF13_cpx142_ap_4</i>	<i>41.03</i>	<i>0.54</i>	<i>54.43</i>	<i>0.47</i>	<i>2.00</i>	<i>0.88</i>	<i>98.06</i>
<i>CF13_cpx151_ap_3</i>	<i>41.47</i>	<i>0.50</i>	<i>54.17</i>	<i>0.43</i>	<i>2.30</i>	<i>0.50</i>	<i>97.88</i>
<i>CF13_cpx188_ap_1</i>	<i>41.74</i>	<i>0.45</i>	<i>54.72</i>	<i>0.42</i>	<i>2.42</i>	<i>0.51</i>	<i>98.71</i>

Table A5.11 | Major and trace element compositions of clinopyroxene-hosted apatite inclusions from Minopoli 1. All elements were measured by EPMA. Analyses in italics were in contact with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. These are excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Minopoli 1 biotite-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>CF13_bi128_ap_1</i>	<i>41.42</i>	<i>0.46</i>	<i>54.19</i>	<i>0.36</i>	<i>1.82</i>	<i>0.80</i>	<i>97.87</i>
<i>CF13_bi14_ap_1</i>	<i>41.56</i>	<i>0.47</i>	<i>53.59</i>	<i>0.45</i>	<i>1.86</i>	<i>0.84</i>	<i>97.58</i>
<i>CF13_bi57_ap_1</i>	<i>41.10</i>	<i>0.78</i>	<i>54.09</i>	<i>0.43</i>	<i>1.94</i>	<i>0.77</i>	<i>97.86</i>
<i>CF13_bi70_ap_1</i>	<i>41.24</i>	<i>0.69</i>	<i>54.51</i>	<i>0.69</i>	<i>1.95</i>	<i>0.87</i>	<i>98.69</i>
<i>CF13_bi14_ap_2</i>	<i>41.43</i>	<i>0.49</i>	<i>54.05</i>	<i>0.48</i>	<i>1.93</i>	<i>0.82</i>	<i>97.96</i>
<i>CF13_bi20_ap_1</i>	<i>40.91</i>	<i>0.43</i>	<i>54.47</i>	<i>0.44</i>	<i>1.97</i>	<i>1.12</i>	<i>98.06</i>
<i>CF13_bi30_ap_2</i>	<i>41.46</i>	<i>0.47</i>	<i>54.03</i>	<i>0.49</i>	<i>1.85</i>	<i>0.83</i>	<i>97.93</i>
<i>CF13_bi44_ap_1</i>	<i>41.80</i>	<i>0.39</i>	<i>54.09</i>	<i>0.54</i>	<i>1.82</i>	<i>0.90</i>	<i>98.36</i>
<i>CF13_bi59_ap_1</i>	<i>40.63</i>	<i>0.48</i>	<i>54.10</i>	<i>0.46</i>	<i>1.87</i>	<i>0.85</i>	<i>97.18</i>
<i>CF13_bi95_ap_1</i>	<i>41.59</i>	<i>0.61</i>	<i>54.16</i>	<i>0.64</i>	<i>1.91</i>	<i>0.88</i>	<i>98.56</i>
<i>CF13_bi99_ap_1</i>	<i>41.31</i>	<i>0.56</i>	<i>54.30</i>	<i>0.57</i>	<i>1.97</i>	<i>0.90</i>	<i>98.34</i>
<i>CF13_bi114_ap_1</i>	<i>41.47</i>	<i>0.55</i>	<i>54.15</i>	<i>0.55</i>	<i>1.88</i>	<i>0.89</i>	<i>98.27</i>
<i>CF13_bi130_ap_1</i>	<i>41.35</i>	<i>0.54</i>	<i>54.29</i>	<i>0.51</i>	<i>1.84</i>	<i>0.85</i>	<i>98.19</i>

Table A5.12 | Major and trace element compositions of biotite-hosted apatite inclusions from Minopoli 1. All elements were measured by EPMA. Analyses in italics were in contact with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. These are excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Accademia clinopyroxene-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>CF163_2_cpx1_ap_2</i>	39.97	0.85	54.22	0.72	2.84	1.19	97.96
<i>CF163_2_cpx2_ap_1</i>	40.90	0.59	54.60	0.34	3.44	0.49	98.14
<i>CF163_2_cpx4_ap_1</i>	39.78	0.81	53.32	0.47	3.30	0.85	96.38
<i>CF163_2_cpx5_ap_3</i>	38.76	1.75	52.76	0.10	3.47	0.77	95.37
<i>CF163_2_cpx11_ap_1</i>	41.21	0.74	53.65	0.40	2.91	1.04	98.07

Table A5.13 | Major and trace element compositions of clinopyroxene-hosted apatite inclusions from Accademia. All elements were measured by EPMA. All of the analysed crystals were in contact the with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. They are therefore excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Accademia biotite-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
<i>CF163_2_bi5_ap_1</i>	38.81	1.20	52.50	0.84	3.29	0.55	95.07
<i>CF163_2_bi7_ap_1</i>	40.37	0.58	54.11	0.60	3.19	0.89	97.69
<i>CF163_2_bi7_ap_2</i>	40.78	0.63	53.83	0.27	2.74	0.98	97.46
<i>CF163_2_bi7_ap_3</i>	40.82	0.70	54.37	0.38	3.49	0.42	97.91

Table A5.14 | Major and trace element compositions of biotite-hosted apatite inclusions from Accademia. All elements were measured by EPMA. All of the analysed crystals were in contact the with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. They are therefore excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Mt Olibano clinopyroxene-hosted apatite inclusions							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF200_B_cpx1_ap_1	41.45	0.68	54.12	0.15	2.36	1.11	98.34
CF200_B_cpx1_ap_3	40.68	0.66	53.88	0.47	3.06	0.72	97.50
CF200_B_cpx3_ap_1	40.72	0.76	54.19	0.24	2.98	0.87	97.83
CF200_B_cpx4_ap_1	39.04	0.53	54.30	0.45	2.75	0.89	96.18
CF200_B_cpx9_ap_1	40.57	0.64	53.84	0.51	2.76	1.17	97.70
CF200_B_cpx9_ap_3	40.76	0.82	53.73	0.19	2.63	1.16	97.59
CF200_B_cpx10_ap_1	40.86	0.70	53.75	0.42	2.52	1.16	97.79
CF200_B_cpx11_ap_1	40.54	0.66	53.59	0.29	2.48	1.20	97.15
CF200_B_cpx12_ap_1	40.93	0.56	53.58	0.38	2.47	1.31	97.62
CF200_B_cpx12_ap_2	41.53	0.45	53.69	0.35	2.55	1.12	98.04
CF200_B_cpx13_ap_1	40.87	0.63	54.30	0.45	1.98	1.23	98.18
CF200_B_cpx16_ap_1	41.14	0.60	53.92	0.12	2.11	1.20	97.74
CF200_B_cpx16_ap_2	40.93	0.70	53.29	0.14	2.20	1.36	97.19
CF200_B_cpx17_ap_1	41.02	0.72	53.81	0.47	2.68	1.07	98.04
CF200_B_cpx17_ap_2	40.90	0.55	54.31	0.52	3.33	0.50	97.97
CF200_B_cpx18_ap_1	40.97	0.63	53.82	0.43	3.38	0.69	97.73
CF200_B_cpx20_ap_1	40.77	0.67	53.97	0.63	2.01	1.15	97.91
CF200_B_cpx20_ap_3	40.99	0.66	54.24	0.28	3.19	0.70	98.01
CF200_B_cpx21_ap_1	40.80	0.78	53.43	0.51	2.40	1.23	97.60
CF200_B_cpx22_ap_1	41.19	0.60	53.79	0.27	3.48	0.47	97.54
CF200_B_cpx23_ap_1	40.80	0.73	54.14	0.14	3.13	0.80	97.72
CF200_B_cpx23_ap_2	40.84	0.61	54.20	0.54	2.58	1.03	98.12
CF200_B_cpx23_ap_3	41.37	0.50	54.18	0.40	2.52	1.29	98.64
CF200_B_cpx23_ap_4	41.28	0.56	54.44	0.39	2.63	1.14	98.73
CF200_B_cpx24_ap_1	40.49	0.54	54.06	0.44	3.21	0.96	97.64
CF200_B_cpx25_ap_1	41.25	0.52	53.86	0.38	1.97	1.26	97.96
CF200_B_cpx26_ap_1	39.94	1.19	53.11	0.16	2.12	1.35	96.50
CF200_B_cpx26_ap_3	41.42	0.60	53.92	0.16	2.27	1.18	98.07
CF200_B_cpx26_ap_5	40.55	0.96	54.03	0.42	2.32	1.18	97.97

Table A5.15 | Major and trace element compositions of clinopyroxene-hosted apatite inclusions from Mt Olibano. All elements were measured by EPMA. All of the analysed crystals were in contact the with matrix glass, melt inclusions or cracks in the host phenocryst, which may have provided pathways for post-entrapment volatile exchange with melts/fluids. They are therefore excluded from Figure A5.1. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Appendix 5.2. Apatite microphenocryst EPMA data

Monte Nuovo apatite microphenocrysts							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap2_CF195_19	38.91	1.60	53.97	1.34	2.18	0.07	97.13
CFmap2_CF195_98	41.36	0.63	54.67	0.16	3.74	0.14	99.09
CFmap2_CF195_81	39.95	0.74	53.65	0.52	3.20	0.46	97.06
CFmap2_CF195_74	40.36	0.90	53.78	0.13	2.82	0.64	97.30
CFmap2_CF195_34	41.22	0.32	53.57	0.36	2.04	0.93	97.37
CFmap2_CF195_49	41.63	0.66	53.42	0.14	2.81	0.93	98.21
CFmap2_CF195_57	41.42	0.57	54.36	0.56	2.70	0.93	99.20
CFmap2_CF195_79	40.83	0.54	54.21	0.40	2.19	0.93	97.97
CFmap2_CF195_42	41.84	0.43	54.61	0.40	1.97	0.94	99.14
CFmap2_CF195_22	40.93	0.69	53.28	0.44	2.53	0.94	97.54
CFmap2_CF195_30	41.34	0.58	54.32	0.19	2.73	0.95	98.75
CFmap2_CF195_44	41.09	0.47	53.64	0.54	2.01	0.95	97.64
CFmap2_CF195_35	41.37	0.44	53.49	0.42	2.05	0.97	97.64
CFmap2_CF195_9	41.58	0.41	53.70	0.47	1.96	0.97	98.04
CFmap2_CF195_15	41.51	0.46	53.78	0.45	2.05	0.97	98.13
CFmap2_CF195_8	41.38	0.42	54.00	0.41	2.03	0.97	98.14
CFmap2_CF195_11	42.07	0.40	54.18	0.35	2.14	0.97	99.00
CFmap2_CF195_46	41.39	0.41	53.37	0.27	2.52	0.98	97.65
CFmap2_CF195_28	40.41	0.75	53.62	0.67	1.91	0.99	97.32
CFmap2_CF195_55	40.25	0.88	53.79	0.59	2.47	0.99	97.70
CFmap2_CF195_14	41.43	0.54	53.62	0.38	1.93	0.99	97.85
CFmap2_CF195_16	41.20	0.58	54.09	0.70	2.01	0.99	98.50
CFmap2_CF195_27	41.50	0.43	53.54	0.19	2.53	1.00	97.90
CFmap2_CF195_48	41.00	0.58	53.56	0.62	2.12	1.00	97.75
CFmap2_CF195_71	41.50	0.43	54.51	0.50	2.10	1.00	98.94
CFmap2_CF195_3	41.06	0.77	53.85	0.17	2.01	1.00	97.80
CFmap2_CF195_95	41.47	0.38	54.68	0.36	2.02	1.01	98.83
CFmap2_CF195_84	41.69	0.38	54.57	0.40	2.47	1.01	99.24
CFmap2_CF195_99	41.53	0.43	54.98	0.29	2.06	1.01	99.21
CFmap2_CF195_4	40.90	0.81	53.61	0.67	2.01	1.02	97.94
CFmap2_CF195_66	41.52	0.34	54.58	0.39	2.09	1.02	98.83
CFmap2_CF195_62	41.50	0.40	55.36	0.39	2.15	1.02	99.68
CFmap2_CF195_65	41.31	0.44	54.27	0.37	2.09	1.03	98.39
CFmap2_CF195_91	40.88	0.55	54.00	0.55	2.43	1.03	98.19
CFmap2_CF195_69	41.34	0.49	54.30	0.42	2.05	1.03	98.54
CFmap2_CF195_36	41.27	0.65	53.58	0.42	2.49	1.04	98.17
CFmap2_CF195_93	41.31	0.39	54.61	0.43	2.05	1.04	98.73
CFmap2_CF195_31	40.47	1.32	52.93	0.17	1.98	1.05	96.85
CFmap2_CF195_70	40.71	0.67	53.83	0.12	2.54	1.05	97.61
CFmap2_CF195_72	41.42	0.57	54.66	0.33	2.08	1.06	99.00

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap2_CF195_85	41.03	0.63	54.14	0.33	2.57	1.07	98.44
CFmap2_CF195_38	40.09	0.85	52.59	0.63	2.02	1.07	96.15
CFmap2_CF195_75	40.66	0.61	53.84	0.56	1.96	1.08	97.65
CFmap2_CF195_17	41.37	0.40	54.28	0.42	1.99	1.08	98.47
CFmap2_CF195_90	40.46	0.92	53.25	0.12	2.68	1.09	97.14
CFmap2_CF195_45	40.97	0.68	53.20	0.25	2.17	1.09	97.20
CFmap2_CF195_7	41.37	0.36	53.47	0.23	2.32	1.10	97.62
CFmap2_CF195_12	41.32	0.61	53.68	0.56	2.38	1.11	98.41
CFmap2_CF195_25	41.17	0.75	53.50	0.14	2.33	1.13	97.78
CFmap2_CF195_56	41.44	0.54	54.71	0.55	2.36	1.13	99.47
CFmap2_CF195_67	41.41	0.61	54.36	0.38	2.70	1.13	99.19
CFmap2_CF195_18	41.35	0.62	54.03	0.16	2.33	1.14	98.40
CFmap2_CF195_58	40.30	0.67	53.96	0.74	1.96	1.15	97.69
CFmap2_CF195_40	41.62	0.60	53.43	0.13	2.40	1.15	98.06
CFmap2_CF195_24	40.92	0.55	53.79	0.56	2.35	1.15	98.07
CFmap2_CF195_83	41.48	0.62	54.18	0.14	2.51	1.15	98.76
CFmap2_CF195_5	41.79	0.53	54.25	0.34	2.39	1.16	99.18
CFmap2_CF195_82	41.10	0.53	54.16	0.40	2.43	1.16	98.48
CFmap2_CF195_92	40.57	0.62	53.99	0.22	2.31	1.17	97.63
CFmap2_CF195_64	41.06	0.43	54.19	0.42	2.06	1.17	98.19
CFmap2_CF195_61	41.69	0.57	54.54	0.57	2.56	1.17	99.75
CFmap2_CF195_97	40.99	0.54	54.32	0.23	2.34	1.19	98.36
CFmap2_CF195_68	40.40	0.87	53.25	0.19	2.31	1.19	96.97
CFmap2_CF195_100	41.27	0.53	54.26	0.25	2.46	1.20	98.66
CFmap2_CF195_96	40.73	0.82	53.80	0.17	2.40	1.21	97.84
CFmap2_CF195_80	40.47	0.55	53.72	0.54	2.39	1.21	97.59
CFmap2_CF195_78	41.21	0.59	54.32	0.12	2.48	1.22	98.63
CFmap2_CF195_53	40.31	0.73	53.64	0.24	2.34	1.22	97.22
CFmap2_CF195_94	41.37	0.46	54.48	0.49	2.11	1.31	99.04

Table A5.16 | Major and trace element compositions of apatite microphenocrysts from Monte Nuovo. All elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Astroni 1 apatite microphenocrysts							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap2_CF69_47	41.50	0.64	54.55	0.39	3.20	0.62	99.41
CFmap2_CF69_74	41.01	0.64	54.30	0.22	2.30	0.62	97.99
CFmap2_CF69_92	40.42	1.05	53.66	0.07	2.45	0.87	97.29
CFmap2_CF69_9	40.28	1.32	53.40	0.35	2.42	0.88	97.43
CFmap2_CF69_10	41.65	0.61	53.38	0.45	2.47	0.98	98.28
CFmap2_CF69_17	40.93	0.56	53.74	0.31	2.48	0.99	97.74

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap2_CF69_24	40.90	0.75	53.46	0.57	2.58	1.00	97.94
CFmap2_CF69_29	42.62	0.06	53.77	0.15	2.42	1.00	98.77
CFmap2_CF69_63	40.99	0.56	53.88	0.14	2.90	1.01	98.03
CFmap2_CF69_78	40.95	0.63	54.48	0.57	2.52	1.03	98.89
CFmap2_CF69_89	40.69	1.08	53.03	0.03	2.53	1.03	97.10
CFmap2_CF69_27	41.55	0.57	54.24	0.63	2.54	1.03	99.26
CFmap2_CF69_62	40.78	0.45	54.64	0.38	2.21	1.03	98.32
CFmap2_CF69_12	40.85	0.58	53.21	0.62	2.67	1.03	97.61
CFmap2_CF69_58	41.16	0.45	54.61	0.36	2.11	1.03	98.60
CFmap2_CF69_40	41.75	0.40	54.29	0.39	2.47	1.04	99.07
CFmap2_CF69_51	41.14	0.44	54.65	0.50	2.04	1.04	98.72
CFmap2_CF69_22	42.17	0.61	53.78	0.16	2.48	1.04	98.95
CFmap2_CF69_6	41.40	0.56	53.84	0.63	2.45	1.04	98.66
CFmap2_CF69_42	41.29	0.63	53.76	0.18	2.52	1.04	98.12
CFmap2_CF69_43	41.30	0.60	53.40	0.15	2.52	1.04	97.71
CFmap2_CF69_14	41.42	0.62	53.68	0.26	2.63	1.04	98.31
CFmap2_CF69_2	41.64	0.61	54.23	0.29	2.40	1.04	98.95
CFmap2_CF69_48	41.40	0.53	53.91	0.55	2.42	1.04	98.60
CFmap2_CF69_36	41.04	0.92	53.01	0.09	2.46	1.04	97.28
CFmap2_CF69_37	41.00	0.77	53.02	0.09	2.62	1.04	97.20
CFmap2_CF69_16	41.80	0.46	54.53	0.44	2.57	1.04	99.53
CFmap2_CF69_4	41.78	0.53	54.12	0.51	2.56	1.04	99.22
CFmap2_CF69_26	41.26	0.76	53.59	0.22	2.39	1.04	98.01
CFmap2_CF69_64	40.87	0.63	53.51	0.18	2.18	1.04	97.26
CFmap2_CF69_20	41.16	0.66	53.77	0.45	2.44	1.05	98.26
CFmap2_CF69_49	40.05	1.10	53.01	0.18	2.46	1.05	96.58
CFmap2_CF69_44	41.24	0.73	53.19	0.19	2.59	1.05	97.65
CFmap2_CF69_67	41.56	0.48	55.00	0.36	2.10	1.05	99.42
CFmap2_CF69_33	41.89	0.62	53.99	0.26	2.42	1.05	98.97
CFmap2_CF69_94	40.90	0.51	53.62	0.57	2.12	1.05	97.62
CFmap2_CF69_21	41.78	0.62	53.98	0.28	2.50	1.05	98.92
CFmap2_CF69_30	40.84	0.67	53.46	0.49	2.45	1.05	97.69
CFmap2_CF69_31	41.08	0.79	53.33	0.18	2.41	1.05	97.60
CFmap2_CF69_28	41.76	0.69	53.58	0.61	2.41	1.06	98.85
CFmap2_CF69_15	41.92	0.49	54.11	0.60	2.58	1.06	99.43
CFmap2_CF69_11	41.27	0.55	53.71	0.55	2.36	1.06	98.27
CFmap2_CF69_19	41.16	0.67	53.39	0.14	2.49	1.06	97.61
CFmap2_CF69_13	41.20	0.60	53.70	0.59	2.54	1.06	98.37
CFmap2_CF69_41	41.23	0.54	53.99	0.57	2.53	1.06	98.62
CFmap2_CF69_3	41.62	0.67	53.54	0.11	2.27	1.06	98.08
CFmap2_CF69_39	41.25	0.56	54.07	0.65	2.45	1.06	98.76
CFmap2_CF69_80	41.06	0.73	53.35	0.07	2.45	1.06	97.46
CFmap2_CF69_81	41.01	0.59	53.49	0.23	2.52	1.06	97.60

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap2_CF69_90	41.02	0.66	53.93	0.34	2.42	1.07	98.19
CFmap2_CF69_45	40.67	0.82	53.97	0.50	2.57	1.07	98.28
CFmap2_CF69_5	41.87	0.58	54.14	0.66	2.44	1.07	99.49
CFmap2_CF69_70	41.31	0.56	53.93	0.35	2.54	1.07	98.45
CFmap2_CF69_50	41.34	0.63	54.17	0.37	2.52	1.07	98.79
CFmap2_CF69_87	41.00	0.75	54.11	0.20	2.56	1.07	98.37
CFmap2_CF69_18	41.04	0.57	53.67	0.40	2.50	1.07	97.96
CFmap2_CF69_53	40.74	0.66	53.84	0.24	2.46	1.07	97.73
CFmap2_CF69_77	41.28	0.61	54.16	0.12	2.39	1.08	98.39
CFmap2_CF69_54	40.77	0.60	54.28	0.39	2.46	1.08	98.30
CFmap2_CF69_96	40.12	1.25	53.09	0.19	1.92	1.08	96.60
CFmap2_CF69_60	40.98	0.71	54.56	0.06	2.57	1.08	98.64
CFmap2_CF69_86	41.37	0.56	53.95	0.12	2.55	1.08	98.32
CFmap2_CF69_88	41.25	0.55	54.42	0.27	2.48	1.09	98.77
CFmap2_CF69_69	41.17	0.44	54.34	0.38	2.55	1.09	98.66
CFmap2_CF69_1	40.78	0.72	53.95	0.94	2.42	1.10	98.63
CFmap2_CF69_98	41.25	0.64	54.47	0.37	2.59	1.10	99.08
CFmap2_CF69_97	40.67	0.63	54.32	0.38	2.64	1.10	98.38
CFmap2_CF69_46	41.46	0.68	53.35	0.17	2.52	1.10	97.97
CFmap2_CF69_57	40.30	0.64	54.35	0.57	2.41	1.11	98.11
CFmap2_CF69_85	40.64	0.65	53.86	0.69	2.53	1.11	98.16
CFmap2_CF69_59	41.15	0.59	54.50	0.16	2.41	1.11	98.65
CFmap2_CF69_76	40.99	0.58	54.20	0.11	2.51	1.12	98.20
CFmap2_CF69_79	41.40	0.46	54.51	0.47	2.51	1.12	99.16
CFmap2_CF69_32	40.85	0.80	52.57	0.10	2.61	1.12	96.70
CFmap2_CF69_23	41.16	0.57	53.66	0.35	2.26	1.12	97.92
CFmap2_CF69_8	41.83	0.58	53.38	0.18	2.22	1.12	98.12
CFmap2_CF69_7	41.15	0.53	53.65	0.49	2.34	1.12	98.04
CFmap2_CF69_65	40.69	0.53	54.66	0.51	2.59	1.12	98.77
CFmap2_CF69_25	41.73	0.70	53.82	0.12	2.36	1.13	98.61
CFmap2_CF69_71	40.90	0.64	54.01	0.26	2.48	1.14	98.12
CFmap2_CF69_35	40.88	0.74	53.13	0.17	2.32	1.14	97.14
CFmap2_CF69_75	40.18	0.91	53.59	0.12	2.44	1.14	97.09
CFmap2_CF69_99	41.23	0.59	54.31	0.27	2.60	1.14	98.78
CFmap2_CF69_68	40.26	0.96	53.35	0.09	2.45	1.14	96.96
CFmap2_CF69_84	40.27	0.99	53.04	0.27	2.44	1.15	96.87
CFmap2_CF69_82	41.08	0.74	53.95	0.15	2.43	1.15	98.23
CFmap2_CF69_52	40.41	0.70	53.55	0.16	2.47	1.16	97.14
CFmap2_CF69_55	39.73	1.22	53.76	0.14	2.51	1.16	97.19
CFmap2_CF69_66	40.84	0.56	54.52	0.55	2.41	1.16	98.75
CFmap2_CF69_34	41.07	0.65	53.68	0.68	2.36	1.17	98.35
CFmap2_CF69_38	40.50	0.99	52.61	0.17	2.52	1.18	96.63
CFmap2_CF69_61	38.68	1.75	52.27	0.22	2.62	1.18	95.35

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap2_CF69_93	40.76	0.77	54.27	0.17	2.23	1.19	98.18
CFmap2_CF69_100	38.79	1.89	52.56	0.06	2.44	1.19	95.62
CFmap2_CF69_56	41.28	0.40	54.24	0.37	2.32	1.19	98.57
CFmap2_CF69_73	40.90	0.71	54.12	0.27	2.39	1.20	98.31
CFmap2_CF69_83	41.01	0.77	53.84	0.21	2.45	1.21	98.18
CFmap2_CF69_72	40.96	0.56	54.76	0.63	2.28	1.22	99.18
CFmap2_CF69_91	40.65	0.64	53.79	0.15	2.24	1.22	97.48
CFmap2_CF69_95	40.85	0.49	53.90	0.59	2.33	1.26	98.15

Table A5.17 | Major and trace element compositions of apatite microphenocrysts from Astroni 1. All elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Accademia apatite microphenocrysts							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap2_CF163_65	40.72	1.05	54.06	0.14	3.74	0.03	98.16
CFmap2_CF163_86	40.99	0.69	54.12	0.26	3.86	0.04	98.32
CFmap2_CF163_96	40.82	0.62	54.32	0.22	4.46	0.04	98.59
CFmap2_CF163_67	42.27	0.31	55.53	0.28	3.42	0.04	100.41
CFmap1_CF163_42	39.97	1.19	54.42	1.01	2.10	0.04	97.84
CFmap2_CF163_64	40.77	1.18	53.99	0.14	3.62	0.05	98.21
CFmap2_CF163_98	41.38	0.56	54.98	0.29	3.95	0.05	99.52
CFmap2_CF163_63	41.15	0.60	54.37	0.31	3.84	0.05	98.69
CFmap2_CF163_72	40.96	0.68	54.23	0.26	3.84	0.05	98.39
CFmap1_CF163_25	40.90	0.57	54.08	0.54	3.55	0.05	98.18
CFmap2_CF163_54	41.57	0.60	54.55	0.27	4.04	0.05	99.36
CFmap2_CF163_83	41.35	0.49	55.01	0.27	4.45	0.05	99.73
CFmap2_CF163_68	40.23	1.05	53.68	0.10	4.48	0.05	97.70
CFmap2_CF163_100	41.06	0.77	54.29	0.13	3.67	0.05	98.42
CFmap2_CF163_78	41.18	0.61	54.31	0.50	3.74	0.05	98.81
CFmap2_CF163_53	41.59	0.60	54.50	0.18	4.30	0.06	99.41
CFmap2_CF163_77	41.75	0.58	54.40	0.11	3.70	0.06	99.02
CFmap2_CF163_89	41.79	0.58	54.68	0.38	3.80	0.06	99.68
CFmap2_CF163_58	40.94	0.58	54.38	0.23	4.38	0.06	98.71
CFmap2_CF163_87	39.94	1.19	53.88	0.33	4.25	0.06	97.85
CFmap2_CF163_92	41.46	0.62	54.66	0.35	3.98	0.06	99.44
CFmap2_CF163_76	40.68	1.11	53.74	0.09	4.29	0.06	98.14
CFmap2_CF163_88	41.70	0.57	54.46	0.44	4.44	0.07	99.79
CFmap2_CF163_56	40.53	0.81	53.64	0.12	3.71	0.08	97.31
CFmap2_CF163_91	40.97	0.49	54.52	0.56	3.74	0.13	98.82
CFmap2_CF163_90	41.29	0.64	54.24	0.29	3.57	0.22	98.70
CFmap2_CF163_62	41.19	0.50	54.59	0.17	4.31	0.26	99.14

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap1_CF163_5	40.93	0.51	53.55	0.44	3.21	0.52	97.68
CFmap1_CF163_14	41.50	0.68	54.24	0.24	3.24	0.72	99.10
CFmap1_CF163_30	41.50	0.47	53.62	0.21	2.50	0.90	97.95
CFmap1_CF163_48	41.19	0.70	53.70	0.18	2.82	0.93	98.11
CFmap1_CF163_16	41.28	0.66	53.48	0.14	2.48	0.97	97.75
CFmap1_CF163_10	40.51	0.76	53.20	0.23	2.50	0.97	96.90
CFmap1_CF163_13	41.30	0.57	53.75	0.26	2.61	0.98	98.16
CFmap1_CF163_6	40.99	0.58	53.68	0.33	2.64	0.98	97.87
CFmap1_CF163_44	41.34	0.52	53.89	0.37	2.74	0.99	98.46
CFmap1_CF163_37	40.96	0.57	53.64	0.30	2.48	0.99	97.68
CFmap1_CF163_9	41.51	0.60	54.40	0.16	2.60	0.99	98.93
CFmap2_CF163_55	41.58	0.46	55.16	0.18	2.60	0.99	99.65
CFmap1_CF163_4	41.24	0.54	53.52	0.18	2.45	1.00	97.67
CFmap1_CF163_29	42.20	0.62	54.22	0.18	2.54	1.00	99.48
CFmap1_CF163_32	41.21	0.62	53.64	0.16	2.57	1.01	97.90
CFmap1_CF163_40	40.73	0.82	53.74	0.14	2.31	1.01	97.54
CFmap1_CF163_39	40.88	0.77	53.81	0.14	2.49	1.01	97.83
CFmap1_CF163_34	41.64	0.56	54.25	0.42	2.55	1.02	99.13
CFmap1_CF163_17	41.29	0.55	53.84	0.26	2.53	1.02	98.19
CFmap1_CF163_49	41.07	0.63	52.88	0.24	2.54	1.02	97.09
CFmap1_CF163_33	41.15	0.58	53.72	0.25	2.56	1.02	97.97
CFmap2_CF163_79	41.10	0.61	54.16	0.32	2.78	1.03	98.59
CFmap1_CF163_36	40.12	0.85	53.01	0.12	2.54	1.03	96.37
CFmap1_CF163_46	41.73	0.35	53.90	0.35	2.71	1.04	98.71
CFmap2_CF163_81	40.86	0.62	53.73	0.29	2.57	1.04	97.80
CFmap1_CF163_38	41.37	0.70	53.30	0.21	2.69	1.05	97.94
CFmap1_CF163_45	40.69	0.72	53.44	0.26	2.62	1.05	97.44
CFmap1_CF163_27	40.66	0.71	53.58	0.30	2.48	1.05	97.50
CFmap1_CF163_28	41.20	0.77	53.47	0.22	2.47	1.05	97.90
CFmap1_CF163_1	40.29	1.19	53.32	0.17	2.70	1.06	97.36
CFmap1_CF163_2	40.48	0.58	54.52	0.46	2.66	1.06	98.41
CFmap2_CF163_95	41.05	0.48	54.62	0.35	2.63	1.06	98.84
CFmap2_CF163_94	41.81	0.36	55.01	0.38	2.92	1.07	100.08
CFmap2_CF163_85	41.00	0.65	54.17	0.19	2.51	1.07	98.28
CFmap1_CF163_47	40.85	0.83	53.75	0.09	2.54	1.07	97.82
CFmap1_CF163_43	41.18	0.67	53.58	0.38	2.68	1.07	98.19
CFmap2_CF163_73	40.94	0.47	54.10	0.39	2.49	1.09	98.18
CFmap2_CF163_59	41.01	0.69	54.01	0.25	2.63	1.10	98.34
CFmap1_CF163_8	40.93	0.57	53.72	0.65	2.59	1.10	98.22
CFmap1_CF163_7	41.06	0.61	53.13	0.62	2.44	1.10	97.69
CFmap2_CF163_60	41.20	0.69	53.85	0.21	2.60	1.12	98.32
CFmap2_CF163_51	41.19	0.58	53.45	0.11	2.55	1.12	97.68
CFmap2_CF163_75	41.43	0.64	54.23	0.16	2.28	1.13	98.65

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap2_CF163_71	40.77	0.78	54.30	0.22	2.60	1.14	98.45
CFmap2_CF163_80	41.23	0.68	54.36	0.15	2.43	1.14	98.71
CFmap1_CF163_24	41.38	0.66	54.08	0.27	2.64	1.16	98.81
CFmap1_CF163_35	42.06	0.20	53.66	0.16	2.51	1.16	98.43
CFmap2_CF163_84	40.71	0.64	53.91	0.64	2.68	1.16	98.36
CFmap2_CF163_97	40.52	0.72	53.13	0.44	2.60	1.17	97.22
CFmap1_CF163_41	41.27	0.81	53.35	0.15	2.61	1.17	97.99
CFmap2_CF163_82	41.39	0.60	54.47	0.19	2.44	1.18	98.98
CFmap2_CF163_66	41.26	0.61	54.50	0.21	2.57	1.18	98.98
CFmap1_CF163_11	40.68	0.67	53.35	0.25	2.41	1.20	97.28
CFmap2_CF163_70	40.61	0.89	53.92	0.17	2.40	1.22	97.91
CFmap2_CF163_69	38.90	2.11	53.05	0.84	2.51	1.23	97.30
CFmap2_CF163_93	41.06	0.74	54.62	0.54	2.61	1.25	99.44
CFmap2_CF163_57	40.75	0.79	53.49	0.12	2.52	1.25	97.58
CFmap1_CF163_20	40.94	0.63	53.47	0.17	2.47	1.29	97.65
CFmap2_CF163_52	40.44	0.87	53.64	0.13	2.72	1.39	97.74
CFmap2_CF163_74	41.05	0.73	53.64	0.15	2.96	1.47	98.42

Table A5.18 | Major and trace element compositions of apatite microphenocrysts from Accademia. All elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Mt Olibano apatite microphenocrysts							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF200_B_ap_26	41.53	0.60	54.29	0.43	3.92	0.08	99.17
CF200_B_ap_32	41.32	0.45	54.92	0.43	4.35	0.09	99.70
CF200_B_ap_36	41.14	0.59	53.86	0.33	3.71	0.09	98.13
CF200_B_ap_11	40.39	1.02	53.37	0.18	4.34	0.09	97.54
CF200_B_ap_27	41.49	0.58	54.44	0.57	3.74	0.09	99.32
CF200_B_ap_15	41.68	0.45	55.09	0.26	4.37	0.09	100.08
CF200_B_ap_9	41.27	0.55	54.38	0.27	4.45	0.10	99.12
CF200_B_ap_14	41.65	0.47	54.66	0.29	4.05	0.12	99.51
CF200_B_ap_41	41.55	0.47	54.85	0.29	4.27	0.13	99.74
CF200_B_ap_51	40.81	0.52	53.91	0.25	3.92	0.16	97.87
CF200_B_ap_22	41.52	0.66	54.50	0.18	4.35	0.18	99.51
CF200_B_ap_18	41.42	0.59	54.30	0.26	4.11	0.19	99.09
CF200_B_ap_44	40.95	0.69	54.38	0.07	3.77	0.20	98.42
CF200_B_ap_28	41.30	0.45	54.79	0.32	3.93	0.20	99.28
CF200_B_ap_45	40.61	0.58	54.27	0.33	3.44	0.20	97.93
CF200_B_ap_24	41.52	0.44	54.57	0.40	4.29	0.24	99.60
CF200_B_ap_42	41.85	0.34	54.63	0.22	3.56	0.26	99.29
CF200_B_ap_37	40.98	0.60	53.99	0.54	3.49	0.30	98.35
CF200_B_ap_8	40.60	0.81	54.37	0.22	3.92	0.30	98.50

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CF200_B_ap_40	41.18	0.59	54.86	0.50	3.73	0.32	99.53
CF200_B_ap_54	40.60	0.82	53.95	0.65	4.02	0.33	98.61
CF200_B_ap_20	40.91	0.41	53.56	0.44	3.84	0.33	97.80
CF200_B_ap_34	41.33	0.73	54.46	0.19	3.50	0.39	99.05
CF200_B_ap_3	39.68	1.02	53.43	0.84	3.37	0.56	97.36
CF200_B_ap_39	41.37	0.54	54.47	0.35	3.33	0.63	99.14
CF200_B_ap_1	40.76	0.60	54.06	0.15	3.32	0.64	97.99
CF200_B_ap_53	40.62	0.60	53.92	0.50	3.22	0.64	98.01
CF200_B_ap_29	40.71	0.61	53.94	0.37	3.34	0.68	98.08
CF200_B_ap_13	40.32	0.87	53.83	0.64	3.20	0.72	98.08
CF200_B_ap_25	41.12	0.37	54.21	0.36	3.34	0.73	98.55
CF200_B_ap_21	41.08	0.60	54.51	0.36	3.16	0.73	98.95
CF200_B_ap_46	40.65	0.66	54.06	0.46	3.18	0.75	98.25
CF200_B_ap_30	40.77	0.54	53.34	0.45	3.04	0.77	97.46
CF200_B_ap_10	40.40	0.69	53.39	0.59	2.72	0.78	97.25
CF200_B_ap_17	41.08	0.70	54.00	0.12	2.78	0.85	98.16
CF200_B_ap_23	40.91	0.48	54.02	0.47	2.90	0.88	98.24
CF200_B_ap_43	41.05	0.54	54.52	0.36	2.86	0.91	98.84
CF200_B_ap_5	40.61	0.51	54.04	0.43	2.81	0.92	97.93
CF200_B_ap_4	40.37	0.78	53.99	0.40	2.95	0.93	97.97
CF200_B_ap_38	41.62	0.43	54.34	0.40	2.80	0.95	99.15
CF200_B_ap_19	41.43	0.62	54.13	0.14	2.77	0.97	98.67
CF200_B_ap_33	41.60	0.46	54.01	0.37	2.68	0.98	98.75
CF200_B_ap_31	40.41	0.64	53.53	0.36	3.13	1.01	97.52
CF200_B_ap_6	40.75	0.57	53.69	0.34	2.45	1.20	97.70
CF200_B_ap_35	39.27	1.53	52.93	0.24	2.55	1.23	96.40

Table A5.19 | Major and trace element compositions of apatite microphenocrysts from Mt Olibano. All elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Fondi di Baia apatite microphenocrysts							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap1_CF88_3	41.61	0.00	55.46	0.00	2.74	0.02	98.67
CFmap1_CF88_31	38.69	1.40	54.42	1.38	2.49	0.05	97.37
CFmap1_CF88_44	40.04	0.80	54.28	0.77	2.25	0.05	97.23
CFmap1_CF88_8	40.04	0.79	54.43	0.89	2.75	0.10	97.82
CFmap1_CF88_50	39.79	0.86	53.96	0.85	2.89	0.10	97.21
CFmap1_CF88_9	39.09	0.92	53.61	1.13	2.66	0.11	96.37
CFmap1_CF88_47	39.70	1.14	52.96	0.06	2.94	0.42	95.88
CFmap1_CF88_45	40.03	1.00	53.65	0.05	2.98	0.48	96.83
CFmap1_CF88_17	39.93	1.20	52.64	0.03	2.72	0.60	95.85
CFmap1_CF88_23	39.21	0.96	53.12	0.73	2.32	0.62	95.84

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap1_CF88_4	40.92	0.34	53.86	0.06	3.29	0.63	97.57
CFmap1_CF88_1	40.15	0.72	54.23	0.72	2.51	0.67	97.79
CFmap1_CF88_27	40.14	0.89	53.52	0.64	2.68	0.68	97.26
CFmap1_CF88_28	40.56	0.54	53.96	0.33	2.58	0.68	97.41
CFmap1_CF88_12	40.03	0.97	53.86	0.52	2.63	0.68	97.43
CFmap1_CF88_22	39.84	1.15	53.36	0.48	2.63	0.69	96.87
CFmap1_CF88_2	40.01	0.79	53.97	0.76	2.59	0.69	97.57
CFmap1_CF88_10	39.43	1.02	53.80	0.90	2.18	0.78	97.03
CFmap1_CF88_37	41.47	0.39	54.02	0.43	2.40	0.81	98.32
CFmap1_CF88_38	41.24	0.42	53.89	0.45	2.36	0.83	98.00
CFmap1_CF88_32	40.83	0.52	53.92	0.58	2.10	0.89	97.75
CFmap1_CF88_34	41.23	0.42	53.98	0.43	2.15	0.90	98.01
CFmap1_CF88_11	40.42	0.54	54.05	0.39	2.25	0.90	97.42
CFmap1_CF88_48	41.21	0.42	54.63	0.52	2.21	0.92	98.76
CFmap1_CF88_26	40.78	0.52	54.01	0.28	2.22	0.92	97.59
CFmap1_CF88_43	40.29	0.79	53.19	0.13	2.21	0.92	96.39
CFmap1_CF88_16	40.52	0.61	54.01	0.20	2.09	0.93	97.27
CFmap1_CF88_20	41.41	0.54	53.76	0.34	2.34	0.93	98.13
CFmap1_CF88_15	39.90	0.70	53.41	0.70	2.25	0.93	96.74
CFmap1_CF88_40	40.69	0.38	54.25	0.34	2.18	0.95	97.65
CFmap1_CF88_46	41.07	0.33	54.09	0.20	2.16	0.95	97.67
CFmap1_CF88_18	41.07	0.60	53.64	0.16	2.00	0.95	97.36
CFmap1_CF88_49	40.97	0.50	54.14	0.34	1.99	0.96	97.84
CFmap1_CF88_5	40.06	0.77	53.58	0.09	2.08	0.96	96.45
CFmap1_CF88_42	39.99	0.49	53.95	0.39	2.15	0.97	96.82
CFmap1_CF88_6	39.91	0.74	53.77	0.15	2.15	0.97	96.57
CFmap1_CF88_36	40.88	0.73	53.77	0.18	2.12	0.97	97.54
CFmap1_CF88_7	40.73	0.45	54.03	0.41	2.13	0.98	97.62
CFmap1_CF88_24	41.34	0.34	54.26	0.45	1.94	0.99	98.29
CFmap1_CF88_35	41.31	0.68	53.80	0.23	2.13	0.99	98.02
CFmap1_CF88_30	41.05	0.40	54.35	0.40	2.14	0.99	98.22
CFmap1_CF88_33	39.95	0.94	52.89	0.56	1.92	1.00	96.23
CFmap1_CF88_39	39.71	1.33	53.03	0.21	1.95	1.02	96.20
CFmap1_CF88_25	40.40	0.71	54.33	0.22	2.07	1.02	97.65
CFmap1_CF88_29	40.76	0.51	54.19	0.61	2.14	1.04	98.11
CFmap1_CF88_21	40.93	0.46	54.12	0.50	2.25	1.08	98.15
CFmap1_CF88_19	40.69	0.65	54.11	0.57	2.18	1.10	98.12
CFmap1_CF88_13	40.85	0.62	54.05	0.47	2.49	1.11	98.29

Table A5.20 | Major and trace element compositions of apatite microphenocrysts from Fondi di Baia. All elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Pisani 1 apatite microphenocrysts							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap1_CF25_1	42.41	0.00	54.89	0.02	2.83	0.02	98.97
CFmap1_CF25_27	42.09	0.25	54.21	0.09	3.16	0.06	98.53
CFmap1_CF25_5	39.38	1.16	54.16	1.21	2.18	0.06	97.21
CFmap1_CF25_30	38.17	1.59	53.33	1.24	3.25	0.08	96.27
CFmap1_CF25_22	38.27	1.46	52.97	1.18	3.25	0.13	95.86
CFmap1_CF25_16	42.02	0.24	53.88	0.05	3.07	0.54	98.39
CFmap1_CF25_39	41.62	0.29	54.11	0.08	3.03	0.57	98.30
CFmap1_CF25_26	41.72	0.29	53.68	0.05	2.94	0.60	97.91
CFmap1_CF25_13	41.53	0.30	53.91	0.04	3.10	0.60	98.03
CFmap1_CF25_49	41.94	0.24	54.03	0.03	2.82	0.63	98.37
CFmap1_CF25_37	42.14	0.24	54.00	0.03	2.99	0.64	98.64
CFmap1_CF25_18	40.64	0.75	53.70	0.63	2.00	0.65	97.38
CFmap1_CF25_2	41.82	0.29	54.10	0.06	2.97	0.66	98.50
CFmap1_CF25_9	39.66	1.10	53.41	0.38	2.52	0.80	96.62
CFmap1_CF25_38	41.24	0.42	53.64	0.41	2.03	0.95	97.62
CFmap1_CF25_34	41.50	0.46	53.94	0.41	2.09	0.95	98.26
CFmap1_CF25_23	41.61	0.43	54.89	0.39	2.14	0.96	99.29
CFmap1_CF25_17	41.48	0.39	54.23	0.47	1.96	0.96	98.44
CFmap1_CF25_50	41.11	0.68	53.91	0.13	2.08	0.96	97.78
CFmap1_CF25_8	40.96	0.47	54.03	0.50	1.97	0.96	97.85
CFmap1_CF25_44	42.19	0.34	53.91	0.34	2.11	0.97	98.74
CFmap1_CF25_10	41.13	0.42	54.03	0.36	2.00	0.97	97.86
CFmap1_CF25_40	40.99	0.47	53.71	0.55	1.99	0.97	97.62
CFmap1_CF25_20	40.89	0.54	53.67	0.46	2.01	0.97	97.48
CFmap1_CF25_12	41.24	0.50	54.17	0.40	2.03	0.98	98.25
CFmap1_CF25_29	41.63	0.42	54.27	0.37	2.08	0.99	98.66
CFmap1_CF25_42	40.54	0.66	53.93	0.51	2.34	0.99	97.76
CFmap1_CF25_45	40.87	0.72	53.63	0.31	1.91	1.00	97.42
CFmap1_CF25_31	40.42	0.82	53.30	0.58	2.16	1.01	97.15
CFmap1_CF25_35	41.02	0.75	53.41	0.21	2.01	1.02	97.34
CFmap1_CF25_15	40.75	0.59	53.72	0.70	2.17	1.02	97.81
CFmap1_CF25_33	39.77	1.26	52.64	0.61	2.08	1.03	96.28
CFmap1_CF25_4	40.77	0.57	53.83	0.72	2.02	1.10	97.90
CFmap1_CF25_19	40.39	0.66	53.43	0.68	1.94	1.11	97.15
CFmap1_CF25_46	41.45	0.29	53.52	0.09	2.22	1.12	97.50
CFmap1_CF25_3	40.88	0.67	54.32	0.67	2.00	1.13	98.57
CFmap1_CF25_14	40.62	0.60	53.66	0.66	1.99	1.13	97.57
CFmap1_CF25_28	41.08	0.64	53.88	0.67	2.01	1.14	98.32
CFmap1_CF25_7	41.14	0.59	53.65	0.69	2.01	1.15	98.12
CFmap1_CF25_24	41.06	0.53	53.27	0.48	2.18	1.15	97.49
CFmap1_CF25_6	42.24	0.24	53.96	0.27	2.24	1.15	98.90
CFmap1_CF25_47	41.63	0.37	53.45	0.40	2.06	1.16	97.94

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap1_CF25_21	40.34	0.78	53.11	0.82	2.07	1.18	97.17
CFmap1_CF25_36	41.59	0.49	53.69	0.49	2.18	1.23	98.48
CFmap1_CF25_25	41.49	0.33	53.84	0.34	2.05	1.23	98.13
CFmap1_CF25_48	40.51	0.69	52.77	0.41	2.20	1.24	96.61
CFmap1_CF25_41	40.55	0.77	53.02	0.36	2.16	1.25	96.91
CFmap1_CF25_11	39.29	0.91	53.46	1.28	1.99	1.26	97.07

Table A5.21 | Major and trace element compositions of apatite microphenocrysts from Pisani 1. All elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Pomici Principali apatite microphenocrysts							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap2_CF6_33	40.86	0.77	53.59	0.79	3.58	0.02	98.09
CFmap2_CF6_37	38.06	1.86	52.96	1.48	2.58	0.06	95.90
CFmap2_CF6_62	40.05	1.11	54.96	1.09	2.09	0.09	98.50
CFmap2_CF6_39	41.25	0.66	54.30	0.66	1.67	0.59	98.29
CFmap2_CF6_47	41.61	0.49	54.18	0.38	1.88	0.69	98.29
CFmap2_CF6_25	41.66	0.52	54.00	0.39	2.49	0.70	98.55
CFmap2_CF6_95	41.87	0.36	54.37	0.24	2.18	0.77	98.69
CFmap2_CF6_90	41.75	0.50	54.79	0.38	2.33	0.78	99.38
CFmap2_CF6_30	42.03	0.35	54.16	0.48	2.06	0.79	98.83
CFmap2_CF6_28	41.89	0.43	54.20	0.32	2.15	0.82	98.72
CFmap2_CF6_24	41.79	0.48	54.34	0.44	2.35	0.83	99.06
CFmap2_CF6_26	41.45	0.48	53.87	0.44	2.98	0.86	98.63
CFmap2_CF6_48	41.74	0.45	53.93	0.43	2.95	0.88	98.94
CFmap2_CF6_12	40.51	0.73	53.16	0.71	2.29	0.89	97.12
CFmap2_CF6_79	41.29	0.36	54.18	0.36	2.81	0.92	98.53
CFmap2_CF6_91	40.97	0.51	54.75	0.50	2.37	0.92	98.82
CFmap2_CF6_43	42.28	0.36	52.83	0.37	2.07	0.94	97.77
CFmap2_CF6_21	42.04	0.42	53.64	0.34	2.07	0.95	98.37
CFmap2_CF6_5	42.06	0.39	54.16	0.43	2.18	0.95	99.04
CFmap2_CF6_29	42.29	0.40	54.28	0.42	2.07	0.95	99.32
CFmap2_CF6_35	41.60	0.66	53.63	0.24	2.07	0.96	98.08
CFmap2_CF6_10	41.71	0.52	53.74	0.34	2.08	0.96	98.25
CFmap2_CF6_11	41.58	0.55	53.83	0.29	2.13	0.97	98.22
CFmap2_CF6_27	41.21	0.74	53.75	0.25	2.10	0.97	97.92
CFmap2_CF6_73	40.72	0.92	53.84	0.43	2.35	0.97	98.02
CFmap2_CF6_7	41.78	0.41	53.74	0.37	2.05	0.97	98.24
CFmap2_CF6_16	40.46	0.70	53.33	0.23	2.21	0.97	96.75
CFmap2_CF6_68	40.34	0.92	53.88	0.58	2.57	0.97	97.95
CFmap2_CF6_9	41.06	0.69	53.43	0.22	2.08	0.97	97.35

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap2_CF6_1	41.29	0.60	53.02	0.64	2.00	0.99	97.47
CFmap2_CF6_38	40.94	1.25	53.34	0.40	1.91	0.99	97.80
CFmap2_CF6_99	41.35	0.38	54.22	0.42	2.08	0.99	98.35
CFmap2_CF6_40	42.10	0.46	54.26	0.45	1.99	1.00	99.19
CFmap2_CF6_42	41.34	0.60	53.38	0.54	2.21	1.00	97.92
CFmap2_CF6_19	41.75	0.43	54.25	0.41	2.44	1.01	99.03
CFmap2_CF6_78	41.45	0.45	54.10	0.48	2.17	1.01	98.52
CFmap2_CF6_6	42.00	0.60	54.04	0.22	2.14	1.01	98.89
CFmap2_CF6_53	40.92	0.42	54.56	0.37	2.01	1.01	98.22
CFmap2_CF6_96	41.86	0.53	53.97	0.35	1.96	1.01	98.64
CFmap2_CF6_8	40.36	0.89	53.95	0.91	2.22	1.02	98.18
CFmap2_CF6_51	41.47	0.46	54.69	0.47	2.05	1.02	99.06
CFmap2_CF6_49	40.27	1.00	52.89	0.13	2.30	1.02	96.41
CFmap2_CF6_64	41.13	0.53	54.18	0.16	2.77	1.02	98.40
CFmap2_CF6_97	41.60	0.45	54.69	0.42	1.99	1.03	99.11
CFmap2_CF6_80	41.47	0.31	54.00	0.22	2.82	1.03	98.44
CFmap2_CF6_89	36.67	7.74	47.17	0.14	2.05	1.04	93.72
CFmap2_CF6_72	41.90	0.42	54.70	0.37	2.12	1.04	99.42
CFmap2_CF6_75	41.45	0.50	54.23	0.28	2.02	1.04	98.43
CFmap2_CF6_32	40.00	1.29	52.40	0.18	2.26	1.04	95.98
CFmap2_CF6_74	41.14	0.53	54.04	0.49	2.01	1.04	98.16
CFmap2_CF6_54	41.12	0.61	53.94	0.24	2.17	1.04	97.97
CFmap2_CF6_61	41.27	0.56	54.74	0.44	2.00	1.04	98.98
CFmap2_CF6_3	41.77	0.49	54.51	0.48	2.32	1.05	99.40
CFmap2_CF6_52	41.25	0.47	54.65	0.54	2.04	1.05	98.91
CFmap2_CF6_81	41.34	0.62	53.95	0.70	1.97	1.05	98.56
CFmap2_CF6_92	40.23	1.10	53.31	0.19	2.37	1.05	97.01
CFmap2_CF6_34	41.37	0.52	54.38	0.64	2.13	1.06	98.97
CFmap2_CF6_23	40.71	0.62	53.83	0.68	1.92	1.07	97.78
CFmap2_CF6_76	41.66	0.54	54.52	0.41	2.03	1.07	99.13
CFmap2_CF6_17	40.97	0.64	53.61	0.56	2.13	1.08	97.85
CFmap2_CF6_15	41.04	0.53	53.97	0.75	2.18	1.08	98.38
CFmap2_CF6_71	41.78	0.48	54.76	0.38	2.08	1.08	99.44
CFmap2_CF6_20	40.71	1.01	53.48	0.21	2.24	1.08	97.54
CFmap2_CF6_57	40.28	1.07	53.15	0.09	2.24	1.08	96.72
CFmap2_CF6_66	41.62	0.49	54.75	0.45	2.42	1.08	99.55
CFmap2_CF6_86	40.54	0.89	53.54	0.12	2.39	1.09	97.33
CFmap2_CF6_58	40.41	0.69	54.00	0.62	2.20	1.09	97.83
CFmap2_CF6_59	40.61	0.65	54.32	0.73	1.95	1.09	98.29
CFmap2_CF6_93	40.10	1.37	53.40	0.16	2.02	1.09	97.04
CFmap2_CF6_41	40.01	1.32	52.60	0.18	2.24	1.09	96.26
CFmap2_CF6_13	41.03	0.60	53.92	0.75	2.06	1.10	98.34
CFmap2_CF6_83	41.43	0.63	54.45	0.50	2.32	1.10	99.21

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap2_CF6_85	41.84	0.50	54.25	0.56	2.26	1.10	99.32
CFmap2_CF6_100	39.99	1.17	52.68	0.07	2.30	1.10	96.10
CFmap2_CF6_18	40.75	0.57	53.41	0.79	2.12	1.11	97.61
CFmap2_CF6_77	40.63	0.96	53.59	0.16	2.16	1.11	97.45
CFmap2_CF6_63	39.74	1.25	53.01	0.17	2.25	1.12	96.33
CFmap2_CF6_67	39.38	1.90	53.32	0.58	2.06	1.12	97.24
CFmap2_CF6_88	40.99	0.52	54.09	0.61	2.29	1.12	98.41
CFmap2_CF6_84	40.99	0.60	53.85	0.55	2.16	1.13	98.12
CFmap2_CF6_87	41.04	0.61	54.45	0.63	2.31	1.13	98.94
CFmap2_CF6_70	40.98	0.54	54.16	0.44	2.05	1.13	98.19
CFmap2_CF6_44	41.73	0.48	54.28	0.56	2.17	1.18	99.23
CFmap2_CF6_46	41.36	0.67	53.89	0.77	2.21	1.18	98.89
CFmap2_CF6_4	41.28	0.64	54.26	0.56	2.23	1.19	98.95
CFmap2_CF6_98	40.93	0.65	54.01	0.72	2.13	1.20	98.46
CFmap2_CF6_56	41.55	0.71	54.24	0.21	2.20	1.25	98.96
CFmap2_CF6_94	35.92	2.55	52.23	2.06	2.09	1.33	94.99

Table A5.22 | Major and trace element compositions of apatite microphenocrysts from Pomici Principali. All elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Minopoli 1 apatite microphenocrysts							
	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap1_CF13_43	40.24	0.60	54.82	0.44	3.23	0.02	98.00
CFmap1_CF13_50	40.66	0.48	54.54	0.18	3.26	0.02	97.76
CFmap1_CF13_4	39.50	0.84	54.03	0.74	2.24	0.03	96.44
CFmap1_CF13_38	38.59	1.65	53.61	1.49	2.61	0.06	96.89
CFmap1_CF13_30	38.93	1.34	54.05	1.36	2.38	0.06	97.11
CFmap1_CF13_1	40.87	0.44	54.93	0.30	3.11	0.09	98.42
CFmap1_CF13_25	40.24	0.81	54.54	1.02	2.46	0.09	98.11
CFmap1_CF13_48	41.06	0.40	54.69	0.09	2.17	0.09	97.58
CFmap1_CF13_37	39.78	0.88	54.19	1.05	2.70	0.11	97.55
CFmap1_CF13_44	39.10	1.40	53.31	1.08	3.10	0.12	96.78
CFmap1_CF13_8	42.39	0.06	54.64	0.00	2.93	0.12	98.88
CFmap1_CF13_35	39.61	0.84	53.84	0.89	2.97	0.14	97.00
CFmap1_CF13_19	41.39	0.50	54.92	0.47	1.83	0.47	98.71
CFmap1_CF13_41	39.39	1.20	54.10	0.97	1.81	0.59	97.16
CFmap1_CF13_39	40.93	0.60	54.34	0.63	2.14	0.60	98.21
CFmap1_CF13_33	39.70	1.12	54.59	0.98	1.78	0.64	97.91
CFmap1_CF13_28	40.59	0.58	53.61	0.74	2.33	0.65	97.36
CFmap1_CF13_17	40.08	0.54	53.89	0.71	1.95	0.67	96.87
CFmap1_CF13_16	39.82	0.75	53.63	0.81	1.97	0.68	96.68

	P ₂ O ₅	SiO ₂	CaO	SO ₂	F	Cl	Total
CFmap1_CF13_15	40.58	0.89	53.57	0.81	1.99	0.69	97.53
CFmap1_CF13_49	41.19	0.39	53.81	0.11	2.11	0.80	97.33
CFmap1_CF13_46	41.55	0.38	54.50	0.30	2.22	0.83	98.66
CFmap1_CF13_45	41.09	0.47	54.57	0.48	2.15	0.90	98.56
CFmap1_CF13_36	41.26	0.40	54.16	0.35	2.02	0.94	98.06
CFmap1_CF13_7	40.81	0.51	53.92	0.59	1.97	0.95	97.71
CFmap1_CF13_21	41.13	0.49	53.71	0.37	1.97	0.96	97.58
CFmap1_CF13_10	40.70	0.45	53.86	0.31	2.08	0.96	97.27
CFmap1_CF13_42	41.37	0.41	53.81	0.42	2.12	0.97	97.99
CFmap1_CF13_12	41.02	0.49	53.93	0.41	2.01	0.97	97.76
CFmap1_CF13_40	40.85	0.50	53.42	0.43	1.98	0.98	97.10
CFmap1_CF13_29	40.69	0.50	53.96	0.57	2.04	0.98	97.66
CFmap1_CF13_34	41.25	0.39	53.68	0.42	2.13	0.99	97.74
CFmap1_CF13_26	41.26	0.36	54.43	0.44	2.17	0.99	98.52
CFmap1_CF13_9	40.35	0.65	53.50	0.23	2.08	0.99	96.70
CFmap1_CF13_24	41.01	0.41	54.06	0.44	2.21	0.99	97.97
CFmap1_CF13_18	41.05	0.48	53.54	0.48	2.07	0.99	97.51
CFmap1_CF13_31	41.03	0.42	54.06	0.44	1.98	1.00	97.87
CFmap1_CF13_6	41.02	0.69	53.70	0.25	1.95	1.00	97.56
CFmap1_CF13_2	40.13	1.00	52.90	0.19	2.00	1.00	96.16
CFmap1_CF13_11	39.80	0.82	53.14	0.36	2.19	1.01	96.16
CFmap1_CF13_32	41.08	0.53	54.51	0.44	2.06	1.01	98.53
CFmap1_CF13_14	40.33	0.92	53.36	0.18	2.21	1.02	96.86
CFmap1_CF13_5	39.61	1.39	53.01	0.16	1.94	1.03	96.10
CFmap1_CF13_22	40.04	1.20	53.26	0.17	2.04	1.04	96.66
CFmap1_CF13_27	40.78	0.63	53.77	0.33	2.79	1.04	97.92
CFmap1_CF13_47	41.14	0.46	53.58	0.39	2.19	1.05	97.65
CFmap1_CF13_20	41.13	0.58	54.15	0.41	1.99	1.07	98.25
CFmap1_CF13_3	40.85	0.37	54.34	0.36	2.15	1.24	98.12

Table A5.23 | Major and trace element compositions of apatite microphenocrysts from Minopoli 1. All elements were measured by EPMA. Totals were corrected for O $\equiv$ F, Cl. Concentrations are in wt%.

Appendix 5.3. Apatite inclusion SIMS data

Monte Nuovo clinopyroxene-hosted apatite inclusions			
	F	Cl	OH
CF195_cpx63_ap1	2.16	0.97	0.47
CF195_cpx80_ap4	2.39	0.90	0.35
CF195_cpx83_ap3	2.27	0.92	0.37
CF195_cpx80_ap1	2.40	0.90	0.35
CF195_cpx128_ap1	2.34	0.99	0.41
CF195_cpx128_ap4	2.41	0.78	0.40
CF195_cpx133_ap1	2.11	0.96	0.50
CF195_cpx137_ap1	2.56	0.90	0.36
CF195_cpx173_ap1	2.09	0.90	0.60
CF195_cpx121_ap1	2.57	0.91	0.36
CF195_cpx188_ap1	2.58	0.77	0.31
CF195_cpx208_ap1	2.03	0.89	0.54
CF195_cpx250_ap4	2.43	0.91	0.34

Table A5.24 | Volatile element compositions of clinopyroxene-hosted apatite inclusions from Monte Nuovo. All elements were measured by SIMS. Concentrations are in wt%.

Monte Nuovo biotite-hosted apatite inclusions			
	F	Cl	OH
CF195_bi40_ap1	2.41	1.05	0.52
CF195_bi46_ap1	2.46	0.88	0.45
CF195_bi64_ap3	2.53	0.93	0.40

Table A5.25 | Volatile element compositions of biotite-hosted apatite inclusions from Monte Nuovo. All elements were measured by SIMS. Concentrations are in wt%.

Astroni 1 clinopyroxene-hosted apatite inclusions			
	F	Cl	OH
CF69_cpx10_ap2	2.39	0.92	0.32
CF69_cpx11_ap1	2.20	1.01	0.44
CF69_cpx32_ap1	2.29	0.94	0.44
CF69_cpx35_ap1	2.47	0.93	0.38
CF69_cpx69_ap1	2.43	0.93	0.40
CF69_cpx73_ap2	2.38	0.90	0.39
CF69_cpx95_ap2	2.41	0.91	0.37
CF69_cpx104_ap1	2.42	0.90	0.36

	F	Cl	OH
CF69_cpx110_ap1	2.32	0.98	0.38
CF69_cpx132_ap1	1.92	0.89	0.35
CF69_cpx137_ap1	2.40	0.90	0.43
CF69_cpx139_ap2	2.52	0.88	0.39
CF69_cpx153_ap2	2.27	1.01	0.50
CF69_cpx151_ap1	2.36	0.93	0.42
CF69_cpx112_ap1	2.41	0.92	0.42
CF69_cpx65_ap2	2.51	0.91	0.43
CF69_cpx21_ap2	2.35	0.95	0.34
CF69_cpx44_ap6	2.34	0.85	0.41
CF69_cpx73_ap2	2.38	0.92	0.43

Table A5.26 | Volatile element compositions of clinopyroxene-hosted apatite inclusions from Astroni 1. All elements were measured by SIMS. Concentrations are in wt%.

Astroni 1 biotite-hosted apatite inclusions			
	F	Cl	OH
CF69_bi23_ap2	2.45	0.92	0.46
CF69_bi23_ap3	2.55	0.95	0.49
CF69_bi38_ap3	2.57	0.95	0.43
CF69_bi48_ap1	2.48	0.91	0.50
CF69_bi97_ap1	2.45	0.93	0.45
CF69_bi117_ap1	2.60	0.98	0.50
CF69_bi156_ap1	2.42	0.92	0.45
CF69_bi167_ap1	2.45	0.90	0.45
CF69_bi35_ap1	2.48	0.90	0.45
CF69_bi27_ap1	2.43	0.91	0.42
CF69_bi149_ap1	2.48	0.92	0.49
CF69_bi98_ap1	2.51	0.92	0.41
CF69_bi164_ap5	2.56	0.91	0.50
CF69_bi164_ap1	2.62	0.93	0.49
CF69_bi158_ap1	2.48	0.93	0.41
CF69_bi170_ap1	2.49	0.92	0.41

Table A5.27 | Volatile element compositions of biotite-hosted apatite inclusions from Astroni 1. All elements were measured by SIMS. Concentrations are in wt%.

Fondi di Baia clinopyroxene-hosted apatite inclusions			
	F	Cl	OH
CF88_cpx118_ap1	2.85	0.43	0.72
CF88_cpx136_ap1	2.94	0.44	0.74
CF88_cpx85_ap1	2.53	0.65	0.92
CF88_cpx116_ap1	2.89	0.43	0.70

Table A5.28 | Volatile element compositions of clinopyroxene-hosted apatite inclusions from Fondi di Baia. All elements were measured by SIMS. Concentrations are in wt%.

Fondi di Baia biotite-hosted apatite inclusion			
	F	Cl	OH
CF88_bi36_ap1	2.77	0.55	0.62

Table A5.29 | Volatile element composition of a biotite-hosted apatite inclusion from Fondi di Baia. All elements were measured by SIMS. Concentrations are in wt%.

Pisani 1 clinopyroxene-hosted apatite inclusions			
	F	Cl	OH
CF25_cpx98_ap2	1.97	0.84	0.71
CF25_cpx98_ap5	1.97	0.93	0.71
CF25_cpx121_ap1	2.08	1.04	0.73
CF25_cpx122_ap1	1.94	0.90	0.76
CF25_cpx142_ap2	2.01	1.02	0.60

Table A5.30 | Volatile element compositions of clinopyroxene-hosted apatite inclusions from Pisani 1. All elements were measured by SIMS. Concentrations are in wt%.

Pisani 1 biotite-hosted apatite inclusions			
	F	Cl	OH
CF25_bi40_ap1	2.12	1.02	0.63
CF25_bi67_ap2	1.98	0.85	0.78
CF25_bi98_ap1	1.98	0.86	0.66
CF25_bi112_ap1	2.08	1.00	0.70
CF25_bi110_ap1	2.07	1.02	0.62

Table A5.31 | Volatile element compositions of biotite-hosted apatite inclusions from Pisani 1. All elements were measured by SIMS. Concentrations are in wt%.

Pomici Principali clinopyroxene-hosted apatite inclusions			
	F	Cl	OH
CF6_cpx19_ap1	2.13	0.86	0.67
CF6_cpx64_ap1	2.05	0.99	0.88
CF6_cpx96_ap1	2.19	0.95	0.60
CF6_cpx138_ap1	1.99	0.92	0.74

Table A5.32 | Volatile element compositions of clinopyroxene-hosted apatite inclusions from Pomici Principali. All elements were measured by SIMS. Concentrations are in wt%.

Pomici Principali biotite-hosted apatite inclusions			
	F	Cl	OH
CF6_bi94_ap1	2.31	0.96	0.75
CF6_bi112_ap1	2.27	0.98	0.77
CF6_bi26_ap1	2.32	0.98	0.78

Table A5.33 | Volatile element compositions of biotite-hosted apatite inclusions from Pomici Principali. All elements were measured by SIMS. Concentrations are in wt%.

Minopoli 1 clinopyroxene-hosted apatite inclusion			
	F	Cl	OH
CF13_cpx169_ap1	1.97	0.75	0.63

Table A5.34 | Volatile element composition of a clinopyroxene-hosted apatite inclusion from Minopoli 1. All elements were measured by SIMS. Concentrations are in wt%.

Minopoli 1 biotite-hosted apatite inclusion			
	F	Cl	OH
CF13_bi114_ap1	1.98	0.85	0.74

Table A5.35 | Volatile element composition of a biotite-hosted apatite inclusion from Minopoli 1. All elements were measured by SIMS. Concentrations are in wt%.

Appendix 5.4. Apatite microphenocryst SIMS data

Monte Nuovo apatite microphenocrysts			
	F	Cl	OH
CFmap2_CF195_19	2.38	0.09	0.99
CFmap2_CF195_16	2.11	0.93	0.75
CFmap2_CF195_17	2.10	0.91	0.75
CFmap2_CF195_8	2.20	0.93	0.81
CFmap2_CF195_49	2.93	0.89	0.44
CFmap2_CF195_38	2.16	1.02	0.80
CFmap2_CF195_35	2.16	0.92	0.77
CFmap2_CF195_30	2.67	0.87	0.44
CFmap2_CF195_24	2.37	1.05	0.56
CFmap2_CF195_22	2.65	0.89	0.50
CFmap2_CF195_45	2.36	1.06	0.71
CFmap2_cf195_31	2.04	0.94	0.81
CFmap2_cf195_12	2.50	0.98	0.36
CFmap2_cf195_97	2.38	1.04	0.50
CFmap2_cf195_46	2.53	0.89	0.40
CFmap2_cf195_64	2.11	1.04	0.65
CFmap2_cf195_74	2.96	0.54	0.36
CFmap2_cf195_98	3.32	0.12	0.11

Table A5.36 | Volatile element compositions of apatite microphenocrysts from Monte Nuovo. All elements were measured by SIMS. Concentrations are in wt%.

Astroni 1 apatite microphenocrysts			
	F	Cl	OH
CFmap2_CF69_47	3.27	0.54	0.23
CFmap2_CF69_32	2.67	1.07	0.52
CFmap2_CF69_29	2.68	0.95	0.54
CFmap2_CF69_10	2.78	0.93	0.53
CFmap2_CF69_26	2.64	0.97	0.56
CFmap2_CF69_6	2.58	0.97	0.55
CFmap2_CF69_19	2.58	0.97	0.56
CFmap2_CF69_22	2.59	0.93	0.57
CFmap2_CF69_20	2.50	0.95	0.56
CFmap2_CF69_21	2.52	0.94	0.57
CFmap2_CF69_49	2.70	1.01	0.58
CFmap2_CF69_46	2.41	1.00	0.59
CFmap2_cf69_91	2.03	1.07	0.56
CFmap2_cf69_85	2.58	0.99	0.42
CFmap2_cf69_2	2.53	0.98	0.45

	F	Cl	OH
CFmap2_cf69_82	2.50	1.02	0.47
CFmap2_cf69_18	2.60	1.01	0.44
CFmap2_cf69_74	2.32	0.56	0.81

Table A5.37 | Volatile element compositions of apatite microphenocrysts from Astroni 1. All elements were measured by SIMS. Concentrations are in wt%.

Accademia apatite microphenocrysts			
	F	Cl	OH
CFmap2_CF163_14	3.03	0.67	0.18
CFmap2_CF163_5	3.34	0.49	0.04
CFmap2_CF163_42	2.28	0.07	1.01
CFmap2_CF163_25	3.71	0.07	0.00
CFmap2_CF163_24	2.60	1.05	0.39
CFmap2_CF163_28	2.56	0.98	0.45
CFmap2_CF163_20	2.68	1.18	0.30
CFmap2_CF163_46	2.59	0.90	0.34
CFmap2_CF163_39	2.69	0.96	0.43
CFmap2_CF163_32	2.59	0.97	0.44
CFmap2_CF163_8	2.38	0.90	0.47
CFmap2_CF163_6	2.70	0.90	0.37
CFmap2_CF163_11	2.70	1.18	0.41
CFmap2_CF163_10	2.90	0.93	0.38
CF163_mpc_ap10	3.35	0.10	0.00
CF163_mpc_ap9	3.75	0.07	0.00
CF163_mpc_ap8	3.85	0.11	0.00
CFmap2_cf163_100	4.02	0.05	0.00
CFmap2_cf163_63	4.01	0.05	0.00
CFmap2_cf163_12	3.83	0.08	0.00

Table A5.38 | Volatile element compositions of apatite microphenocrysts from Accademia. All elements were measured by SIMS. Concentrations are in wt%.

Mt Olibano apatite microphenocrysts			
	F	Cl	OH
CF200_map30	3.02	0.70	0.15
CF200_map29	3.76	0.24	0.00
CF200_map35	2.83	1.06	0.27
CF200_map36	3.79	0.09	0.00

Table A5.39 | Volatile element compositions of apatite microphenocrysts from Mt Olibano. All elements were measured by SIMS. Concentrations are in wt%.

Fondi di Baia apatite microphenocrysts			
	F	Cl	OH
CFmap1_CF88_7	2.08	0.90	0.67
CFmap1_CF88_42	2.13	0.87	0.64
CFmap1_CF88_49	2.14	0.91	0.70
CFmap1_CF88_34	2.37	0.89	0.67
CFmap1_CF88_16	2.16	0.88	0.68
CFmap1_cf88_11	2.31	0.80	0.61
CFmap1_cf88_10	2.32	0.74	0.65
CFmap1_cf88_18	2.11	0.89	0.61
CFmap1_cf88_33	2.11	0.88	0.62
CFmap1_cf88_43	2.46	0.93	0.67
CFmap1_cf88_30	2.12	0.91	0.65
CFmap1_cf88_3	2.65	0.03	0.67
CFmap1_cf88_8	2.94	0.10	0.68
CFmap1_cf88_50	2.97	0.10	0.60
CFmap1_cf88_44	2.49	0.06	0.80
CFmap1_cf88_31	2.73	0.04	0.70
CFmap1_cf88_45	3.21	0.43	0.38
CFmap1_cf88_22	2.86	0.63	0.49
CFmap1_cf88_17	2.94	0.57	0.53
CFmap1_cf88_12	2.72	0.62	0.47
CFmap1_cf88_1	2.85	0.63	0.52

Table A5.40 | Volatile element compositions of apatite microphenocrysts from Fondi di Baia. All elements were measured by SIMS. Concentrations are in wt%.

Pisani 1 apatite microphenocrysts			
	F	Cl	OH
CFmap1_CF25_41	2.25	1.16	0.59
CFmap1_CF25_29	2.21	0.96	0.71
CFmap1_CF25_19	2.21	1.11	0.74
CFmap1_CF25_7	2.03	1.06	0.67
CFmap1_CF25_44	2.18	0.93	0.69
CFmap1_cf25_5	2.20	0.06	0.92
CFmap1_cf25_2	3.01	0.56	0.29
CFmap1_cf25_22	3.83	0.13	0.27
CFmap1_cf25_30	3.55	0.10	0.33
CFmap1_cf25_18	2.10	0.59	0.83
CFmap1_cf25_46	2.20	1.02	0.58
CFmap1_cf25_37	3.04	0.57	0.27
CFmap1_cf25_50	2.07	0.91	0.70
CFmap1_cf25_11	2.15	1.12	0.66

	F	Cl	OH
CFmap1_cf25_9	2.74	0.76	0.53
CFmap1_cf25_3	2.08	1.02	0.68
CFmap1_cf25_1	2.75	0.02	0.71
CFmap1_cf25_16	3.21	0.47	0.24
CFmap1_cf25_27	3.11	0.07	0.36
CFmap1_cf25_49	2.97	0.53	0.39

Table A5.41 | Volatile element compositions of apatite microphenocrysts from Pisani 1. All elements were measured by SIMS. Concentrations are in wt%.

Pomici Principali apatite microphenocrysts			
	F	Cl	OH
CFmap2_CF6_33	3.92	0.05	0.19
CFmap2_CF6_37	3.04	0.08	0.81
CFmap2_CF6_39	1.96	0.59	1.16
CFmap2_CF6_47	1.97	0.64	0.95
CFmap2_CF6_25	2.75	0.66	0.65
CFmap2_CF6_24	2.52	0.77	0.71
CFmap2_CF6_30	2.21	0.76	0.86
CFmap2_CF6_32	2.49	1.03	0.78
CFmap2_CF6_16	2.18	0.89	0.75
CFmap2_CF6_10	2.14	0.89	0.76
CFmap2_CF6_13	2.14	1.01	0.77
CFmap2_CF6_6	2.14	0.92	0.78
CFmap2_CF6_5	2.15	0.91	0.77
CFmap2_CF6_46	2.29	1.11	0.67
CFmap2_CF6_21	2.12	0.91	0.72
CFmap2_cf6_100	2.41	1.05	0.59
CFmap2_cf6_15	2.15	1.04	0.61
CFmap2_cf6_26	2.86	0.75	0.13
CFmap2_cf6_98	2.08	1.01	0.62
CFmap2_cf6_92	2.00	0.95	0.68
CFmap2_cf6_62	2.23	0.06	0.84

Table A5.42 | Volatile element compositions of apatite microphenocrysts from Pomici Principali. All elements were measured by SIMS. Concentrations are in wt%.

Minopoli 1 apatite microphenocrysts			
	F	Cl	OH
CFmap1_CF13_39	2.22	0.56	0.75
CFmap1_CF13_50	3.19	0.05	0.33
CFmap1_CF13_15_1	2.33	0.75	0.96
CFmap1_CF13_15_2	2.00	0.64	0.90
CFmap1_CF13_3	2.09	1.09	0.59
CFmap1_CF13_4	2.30	0.06	0.89
CFmap1_CF13_7	2.14	0.86	0.72
CFmap1_CF13_22	1.99	0.91	0.76
CFmap1_CF13_31	1.88	0.82	0.70
CFmap1_CF13_27	2.94	0.94	0.19
CFmap1_CF13_2	2.15	0.95	0.71
CFmap1_CF13_10	2.07	0.89	0.68
CFmap1_CF13_42	2.02	0.88	0.62
CFmap1_cf13_19	1.82	0.42	0.87
CFmap1_cf13_8	3.02	0.13	0.41
CFmap1_cf13_30	2.60	0.06	0.88
CFmap1_cf13_43	3.44	0.03	0.37
CFmap1_cf13_28	2.46	0.58	0.70
CFmap1_cf13_41	1.92	0.49	0.91
CFmap1_cf13_49	2.15	0.71	0.60
CFmap1_cf13_32	2.25	0.90	0.72

Table A5.43 | Volatile element compositions of apatite microphenocrysts from Minopoli 1. All elements were measured by SIMS. Concentrations are in wt%.