

**Determining the depths and timescales
of pre-eruptive processes before the
historical 1538 Monte Nuovo eruption
(Campi Flegrei caldera, Italy)**

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Abstract

Campi Flegrei, Italy is one of the most populated caldera volcanoes on Earth and a detailed understanding of its sub-volcanic magma system and pre-eruptive processes are essential for effective hazard mitigation. Of particular interest are the depths of magma storage and timescales of magma recharge, as this information can inform the interpretation of volcano monitoring data that is critical to civil protection. This study places new constraints on these important aspects of the Campi Flegrei magmatic system through detailed petrological analysis of clinopyroxene crystals produced in the most recent, AD 1538 Monte Nuovo eruption, which was preceded by important precursory activity at the Earth's surface, recorded in historic chronicles.

Through backscattered electron imaging (BSE) of >200 erupted crystals, I identified four texturally distinct clinopyroxene populations in Monte Nuovo eruption deposits, characterised by their zoning patterns. Using BSE images as a guide, we characterised the full compositional diversity of these clinopyroxenes by electron microprobe analysis (EPMA). This data was input into the Python tool Thermobar (Wieser, 2022) to find equilibrium matches with published Monte Nuovo whole-rock, melt inclusion and glass data, to determine clinopyroxene crystallisation pressures and temperatures using a geothermobarometer calibrated for alkali systems (Masotta et al., 2013).

Compositional zoning preserved in the Monte Nuovo clinopyroxenes is consistent with an open magmatic system where mafic and silicic magma often mix. Our barometric modelling suggests that all the erupted clinopyroxene crystals formed at temperatures and pressures of $\sim 986^\circ\text{C}$ and $\sim 1.4\text{--}2.4$ kbar. These pressures equate to a magma storage depth of $\sim 6\text{--}11$ km, in agreement with a deep melt zone identified beneath Campi Flegrei by seismic tomography (Zollo et al., 2008). The crystals do not display evidence of crystallisation at shallow depths, suggesting that the erupted magmas did not undergo prolonged storage at the depth of recent bradyseismic activity (Armienti et al., 1983). Hence, our data agree with previous studies (Stock et al., 2018b) which have suggested that recent Campi Flegrei eruptions are fed by magmas ascending directly from the mid-lower crust and undergo minimal interaction with magmas that have stalled at shallow depths.

After constraining the structure of the Monte Nuovo magma system, we extracted compositional profiles across the outermost zones of clinopyroxene crystals; these rim zones are interpreted as recording the transfer of crystals from one magmatic environment to another, shortly before eruption. We used Fe-Mg diffusion modelling to constrain the timing of these pre-eruptive processes. Our results show a correlation with a period of uplift which began in the Pozzuoli region 36 years prior to the Monte Nuovo eruption. This new insight gives a robust temporal constraint which can inform the interpretation of current monitoring data at Campi Flegrei and provide important information for future eruptive scenarios.

Dedication

To Dad,
You're my hero x

Acknowledgements

This research project would not have been possible without the help and support of many people. Firstly, words cannot adequately express my gratitude to my supervisors Mike Stock, Vicki Smith, and Euan Mutch. Mike has not only provided direction and expert knowledge on the project but has also been a true mentor, helping me to develop my skills within this project as well as guiding future career aspirations. Vicki has generously provided me with important scientific feedback throughout, and analysis in her lab, both of which were invaluable to the project. The time Euan spent helping me with understanding and carrying out the diffusion modelling, particularly in the final months of the project is something I am incredibly grateful for.

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Statements and Declarations

Due to travel restrictions and lab restrictions during the Covid-19 pandemic, EPMA data was collected on my behalf by Dr V. Smith at the University of Oxford.

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and it is entirely my own work.

I agree to deposit this thesis in the University's open access institutional repository or allow the Library to do so on my behalf, subject to Irish Copyright Legislation and Trinity College Library conditions of use and Acknowledgement.

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Signed: 

Lydia Jane Whittaker

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1. Introduction

This thesis aims to investigate the depths and timescales of magma storage at Campi Flegrei caldera before the 1538 eruption of Monte Nuovo. Current experimental constraints on the volcanic products produced at Campi Flegrei have yet to provide reliable timescales that correlate with geophysical observations at the surface. Therefore, the focus of this study is to place constraints on the depths of magma storage and timescales of magma recharge that can be used as a proxy to forecast future eruptive activity.

Background

Campi Flegrei (Naples, Italy) is one of the most populated caldera volcanoes on Earth and a detailed understanding of its sub-volcanic magma system and pre-eruption processes are essential for effective hazard mitigation. Of particular interest are the depths and timescales

of magma storage, this information can inform the interpretation of monitoring data and is critical for civil protection.

Underlain by unique magmatic systems, the processes operating beneath volcanoes controls the timing, style, and eruptive products. Understanding the rates of change within these systems can be used for eruption forecasting (Blundy and Cashman, 2008). Mineral compositions capture a snapshot of the conditions of the magma reservoir as they formed, from their initial nucleation to final quenching upon eruption (Saunders et al., 2012). Chemical zoning in crystals therefore preserves evidence of changes in intensive variables including; composition, pressure, temperature, oxygen fugacity, and volatile contents (Kahl et al., 2011). Consequently, mineral compositions can provide information on pre-eruptive processes including magma ascent, recharge, and mingling eg. (Costa and Chakraborty, 2004, Turner and Costa, 2007, Ubide and Kamber, 2018). This is particularly important for volcanoes such as Campi Flegrei which have not erupted in recent history and have little to no real-time data for previous eruptions. Therefore, petrological analysis gives unique insights into the evolution of magma dynamics and gives us the best record of past events.

Campi Flegrei resides within the Phlegraean Volcanic District and has densely populated surroundings of over 3 million people, alongside its eruptive potential making Campi Flegrei one of the most dangerous volcanoes on Earth. It is important to study Campi Flegrei because recent activity (Section 1.1.c) suggests that the volcano is becoming increasingly active (Berrino et al., 1984, Branno et al., 1984, Dvorak and Gasparini, 1991, D'Auria et al., 2015). There are currently few studies of Campi Flegrei which discern timescales of magmatic processes, of the studies that do exist it is unclear as to whether the timescales produced are useful when it comes to predicting eruptions from current monitoring data.

Monte Nuovo is the most recent eruption of Campi Flegrei and is the only eruption within the caldera documented in human history. There are eyewitness accounts detailed in historic chronicles outlining the volcanoes' observable behaviour providing insight into the local events before, during, and after eruption Falconi (1538), Marchesino (1538), Toledo (1539), Del Nero (1538), Porzio (1551) translated to English in Hamilton and Fabris (1776) and Lobley (1889). This makes Monte Nuovo an ideal candidate to combine geophysical observations with geochemical data and effectively predict past eruptive activity so we may

use it to predict future eruptions at Campi Flegrei.

1.1 Geological background

1.1.a Regional tectonic setting

Campi Flegrei is situated within the Phlegraean Volcanic District Italy. Geochemical processes of magma generation within this region are complex. Cretaceous to present convergence of the Eurasian and African plates and subsequent subduction is responsible for the formation of the Apennine volcanic chain (Carminati et al., 2012, Doglioni et al., 1999, Mantovani et al., 2002). The Tyrrhenian sea has played host to a broad range of magmatic activity from the Eocene to present (Peccerillo and Frezzotti, 2015).

The Plio-Quaternary volcanism of the Tyrrhenian Sea hosts a comprehensive magmatic compositional range. Opening of the Tyrrhenian Sea, differential collision of the Adriatic-Ionian foreland, and counter-clockwise rotation of the Italian peninsula resulted in longitudinal stretching of the Apennines. Transverse tectonic lines segment the Apennine arc into several arc sectors (Figure 1.1). This induces decompression along the arc allowing asthenospheric mantle material to rise to shallower levels where it partially melts (Serri, 1990, Bruno et al., 2000, Rosenbaum et al., 2008, Turtù et al., 2013, Peccerillo and Frezzotti, 2015). The outcome is magma production of varying compositions along the Apennine arc. Such magmas include low-k tholeiitic, calc-alkaline, shoshonitic, and ultrapotassic types. These magmas have unique isotopic and trace element fingerprints which are interpreted to reflect the enrichment of their source regions by subduction-related fluids. Current active volcanism directly relating to subduction processes is located in two regions; the central–eastern Aeolian Arc and the Neapolitan area (Peccerillo and Frezzotti, 2015).

The Phlegraean volcanic district is situated within the Neapolitan area, it comprises Campi Flegrei, Procida, Ischia and Submarine vents found in the Gulf of Naples (Orsi et al., 1996). Campi Flegrei is unequivocally the largest volcano in the area, the nested caldera system exhibiting a diameter of ~13 km (Barberi et al., 1991). The caldera system encompasses Pozzuoli town and neighbours the much larger city of Naples along the eastern border.

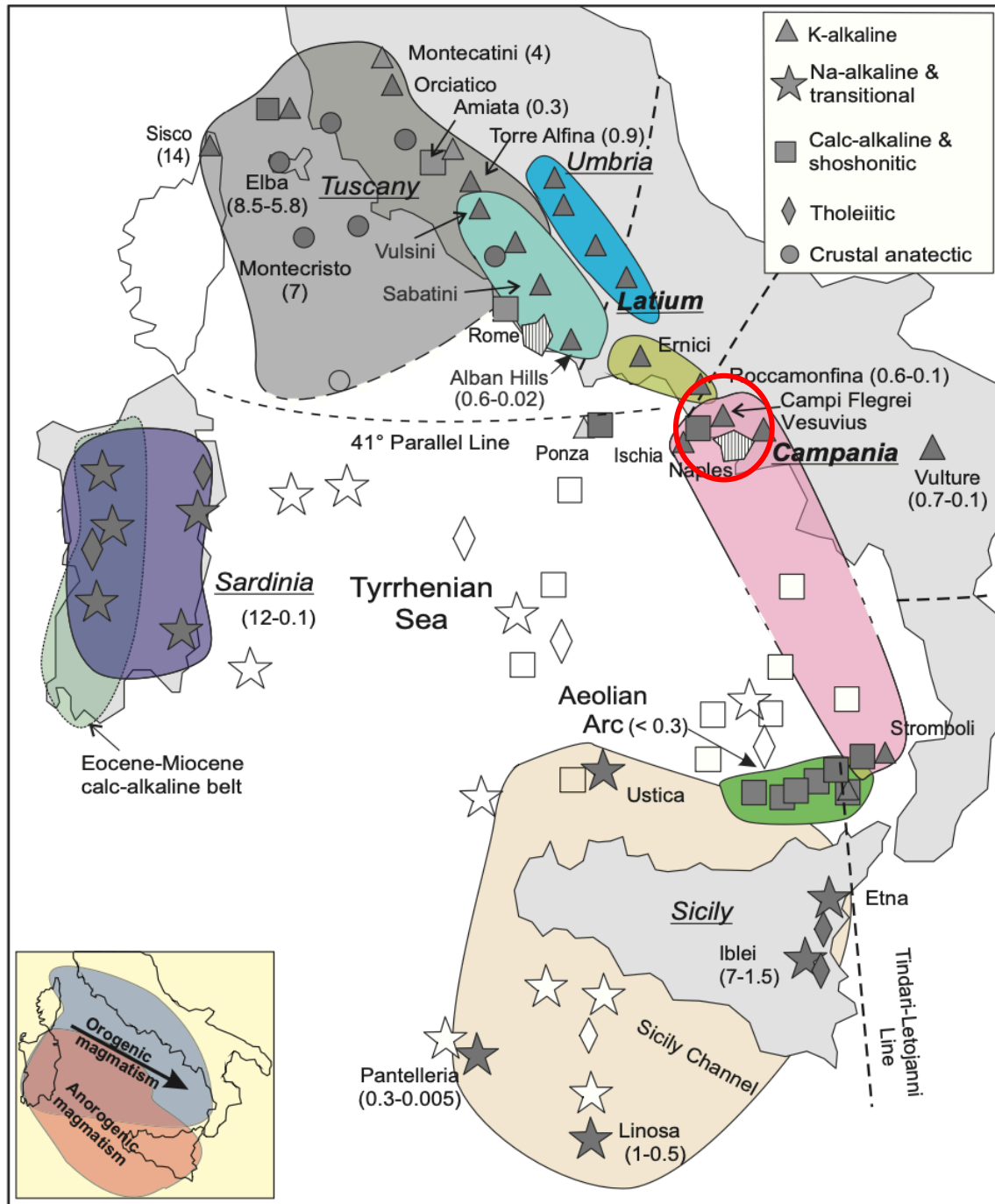


Figure 1.1. Distribution of Plio-Quaternary volcanism in the Tyrrhenian Sea. Distribution of Plio-Quaternary volcanism in the Tyrrhenian Sea, (ages are Ma) taken from (Peccerillo and Frezzotti, 2015) Open symbols indicate submarine volcanoes. Dashed lines indicate main traverse tectonic lines. Tectonic provinces include Tuscany, Umbria, Latium, Campania, Sicily, Aeolian Arc, and Sardinia. Campi Flegrei caldera is highlighted by the red circle.

1.1.b Eruptive history of Campi Flegrei

Campi Flegrei is a nested caldera system (figure 1.2) which results from multiple caldera collapse events in the past 40 ka (Orsi et al., 1996). It is widely accepted that the largest caldera-forming eruption was the Campanian Ignimbrite, classified as Volcanic Explosivity Index (VEI) 7 (Barberi et al., 1984, Mastrolorenzo et al., 2017). The eruption occurred 40 ka determined by $^{40}\text{Ar}/^{39}\text{Ar}$ dating (Giaccio et al., 2017). Consequent ignimbrite deposits cover 30,000 km² around the vent, including the Campanian Plain and Apennine Mountains (Barberi et al., 1984).

The Tufi Biancastri succession includes all deposits between the two largest caldera forming eruptions at Campi Flegrei, the Campanian Ignimbrite and Neapolitan Yellow Tuff (NYT). The Y3 Tephra, a smaller caldera-forming eruption was dated at 30 ka by $^{40}\text{Ar}/^{39}\text{Ar}$ dating placing it within this succession (Albert et al., 2015). The aerial distribution and volume of material erupted implies an eruption greater than VEI 6, suggesting that there was a third caldera-forming eruption between the Campanian Ignimbrite and NYT (Albert et al., 2019). The NYT eruption likely destroyed further evidence of this.

The NYT was the most recent Caldera forming eruption at Campi Flegrei, occurring 14.9 ka determined by $^{40}\text{Ar}/^{39}\text{Ar}$ dating. The eruption deposits covered an area >1000 km² (Deino et al., 2004). Outcrops of volcanic deposits extend from the Neapolitan Phlegrean area where the inferred vent is located up to 35 km away at the foot of the Apennines (Orsi et al., 1992). Tephrostratigraphy has been used to create a detailed timeline of eruption events at Campi Flegrei over the past 40 ka. Distal deposits can be geochemically paired to their proximal associates to give a comprehensive understanding of the eruptive history (Smith et al., 2011b).

Caldera resurgence began shortly after the caldera collapse of the NYT, in the last 15 ka. There is evidence of >60 eruptions of varying magnitude at Campi Flegrei in the last 12 ka, making it one of the most active volcanoes in Europe (Di Vito et al., 1999). Disjointed blocks orientated NE-SW and NW-SE from the caldera floor. Three epochs of eruptive activity at Campi Flegrei can be seen between these blocks. Epochs are divided by quiescent periods defined by widespread paleosols (Di Vito et al., 1999).

Epoch I occurred 15-10.6 ka, it produced 34 explosive eruptions at intervals of ~70 years. Vents during this epoch appeared along the marginal faults of the NYT caldera (Di Vito et al., 1999, Smith et al., 2011a). Epoch II took place 9.6-9.1 ka, 6 explosive eruptions at ~65-year intervals in the NE sector of the margin (Di Vito et al., 1999, Smith et al., 2011a). Epoch III occurred 5.5-3.5 ka with 27 small explosive eruptions and 4 effusive lava dome eruptions occurring at ~27-year intervals (Di Vito et al., 1999, Smith et al., 2011a). The last eruption at the caldera was at Monte Nuovo and took place in 1538 CE (Di Vito et al., 1987) following a >3ka dormant period (Smith et al., 2011b). This was not part of an Epoch but a stand-alone event which potentially signifies the beginning of a new eruptive cycle.

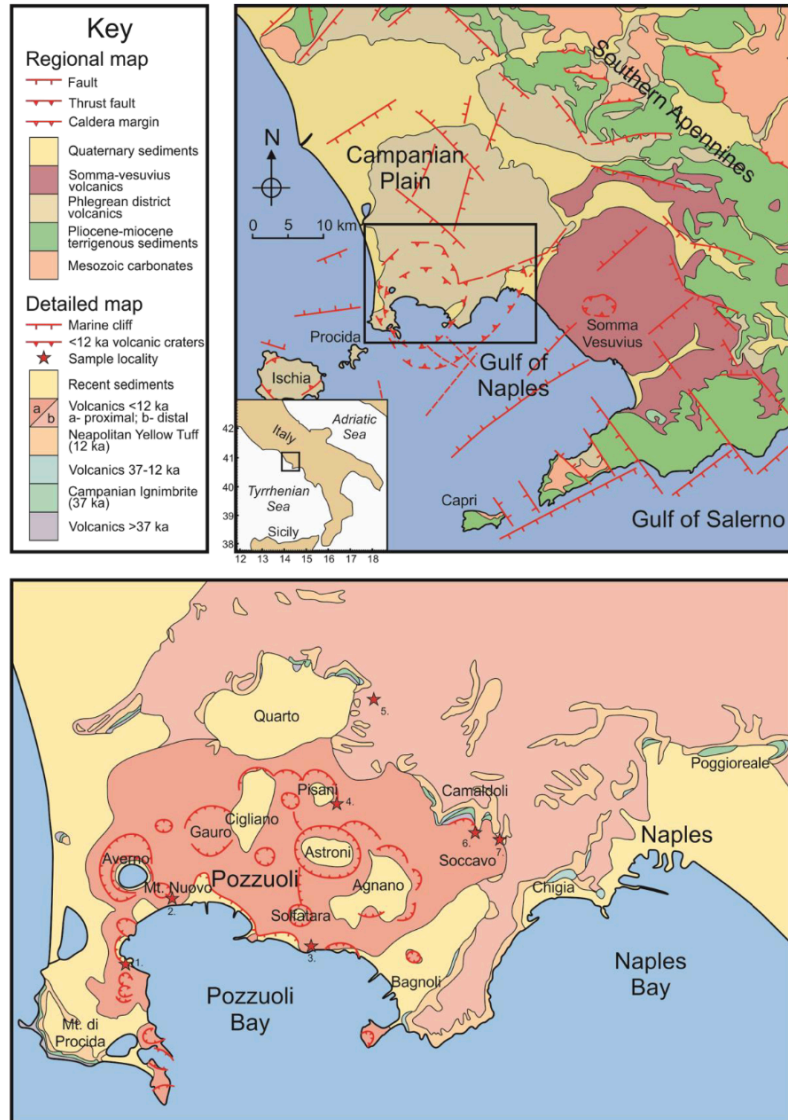


Figure 1.2. Geological Maps of the Phlegrean Volcanic District Geological Maps of the Phlegrean Volcanic District adapted by Stock (2016) from Orsi et al. (1996). Top: regional map of the Phlegrean volcanic district and surrounding area, showing regional-scale geology, major tectonic structure, and the position of the CI and NYT calderas. Position in reference to Italian coastline seen in Inset. Bottom: Detailed geological map of the CF Caldera.

1.1.c Current unrest at Campi Flegrei

Campi Flegrei has exhibited localised uplift and subsidence throughout its entire history (Figure 1.3). A new episode of uplift began in 1982 and continued until December 1984 with a maximum uplift of 1.78 m, centred at Pozzuoli (Berrino et al., 1984). During this event, intense shallow seismic swarms have been documented with the largest earthquake at a magnitude 4.2 (Branno et al., 1984). This resulted in structural damage to buildings within Pozzuoli town and an evacuation order for 40,000 people was executed (Barberi et al., 1984). This activity was concentrated within a 2 km wide zone north of Pozzuoli and a less intense area of activity 2 km beneath Pozzuoli Bay (Aster and Meyer, 1988). Following this extended period of unrest, between 1984-1991 the area once again experienced subsidence at an average of 150 mm/year (Dvorak and Gasparini, 1991).

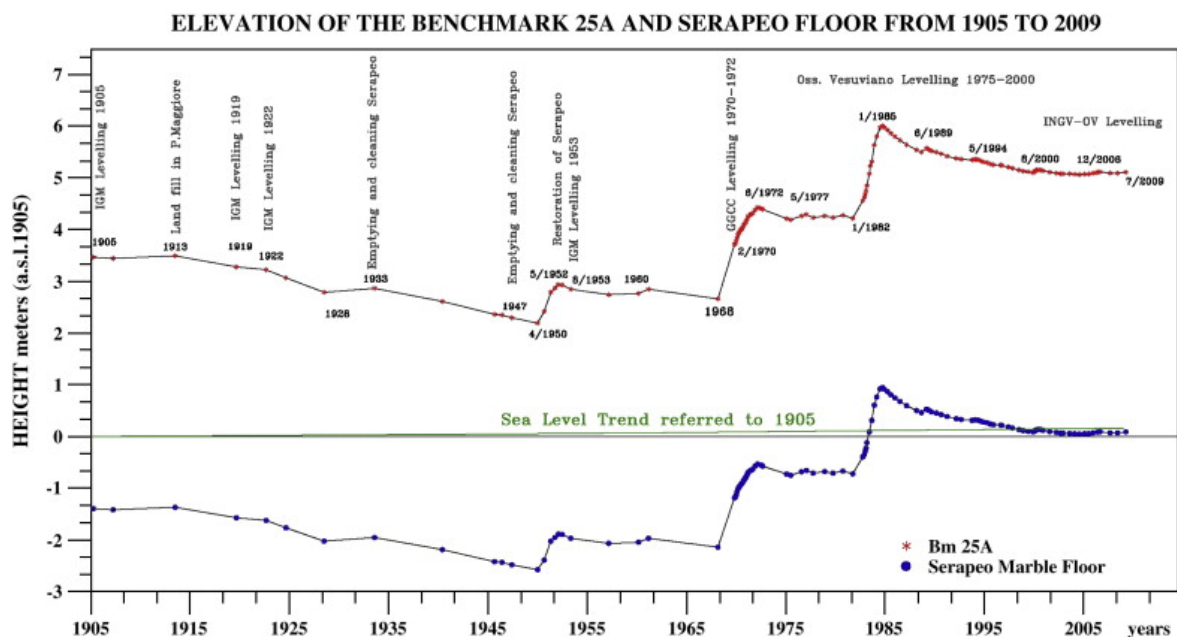


Figure 1.3. Localised sea level change at Campi Flegrei Localised Sea level change at Campi Flegrei 1905-2009. Benchmark 25A refers to a landmark used in a study by (Del Gaudio et al., 2010, Stock, 2016). Serapeo refers to the monument Serapis used for monitoring uplift since 1750. Both reference points show a clear correlation in the change of sea level throughout recent history. Figure taken from (Del Gaudio et al., 2010) where more details of this study can be found.

The bradyseismic behaviour of the crust at Campi Flegrei has been the subject of much debate. Armienti et al. (1983) concluded that the change in petrology observed in eruptions within the caldera was the result of new magma injections increasing pressure within the underlying magma chamber potentially resulting in uplift and bradyseismic activity at the caldera. However, (Martini, 1986) was unable to relate changes in gas emissions at the caldera during these bradyseismic events to magmatic sources, and instead attributed

changes to hydrothermal activity.

The subsidence at Campi Flegrei can be explained by the migration of hydrothermal fluids. It is controlled by the constant lithostatic load which provides the necessary force to remove the fluids from the water-saturated rock layer beneath the caldera (Dvorak and Gasparini, 1991). Magma injection inducing expansion of the underlying magma chamber causes the rapid uplift observed (Dvorak and Gasparini, 1991). It is suggested that the most intense inflation occurs when magma from a deeper magma reservoir estimated between 8-12km deep injects material into 3km deep reservoir (Caliro et al., 2014). Consequently, surrounding rocks are fractured, increasing groundwater percolation and flow rates. This ensures the water within the aquifer overlying the chamber flows faster out of the aquifer and thus inducing the slow subsidence that follows uplift events (Dvorak and Gasparini, 1991).

There is a clear correlation between ground deformation and geochemical parameters at the caldera between 2005-2011 (Chiodini et al., 2015). This correlation stopped in 2012, following a seismic swarm event on 7th September, suggesting the mechanism for uplift changed. During this seismic swarm event >200 earthquakes, reaching a maximum of 1.8 magnitude, occurred beneath the village of Pozzuoli over 1.5 hours. An intrusion of magma $0.0042 \pm 0.0002 \text{ km}^3$ detected at 3km depth correlates with the timing of this swarm event (D'Auria et al., 2015).

A volcanic hazard assessment of the restless caldera system has determined that an eruption would result in both tephra fallout and pyroclastic flows (Orsi et al., 2004). Almost all recent (last 12 ka) eruptions have alternated between magmatic and phreatomagmatic explosions. The explosivity of the eruptions indicates that tephra fallout would most likely encompass the caldera and surrounding area (Orsi et al., 2004). Consequent pyroclastic flows could be both dilute and turbulent, the energetic turbulent currents would likely breach morphological barriers and exit the lowlands of the system towards the north. Due to the nature of the ash deposits, heavy rainfall could also induce lahars in the area (Orsi et al., 2004). It is essential to understand these modern signals of unrest to confidently and appropriately mitigate these hazards as recent studies in other areas such as the Galapagos Archipelago suggest deep recharge is a more likely pre-eruption mechanism (Stock et al., 2018a).

1.1.d Eruptive events of 1538- Monte Nuovo

The 1538 CE Monte Nuovo eruption at Campi Flegrei was the most recent eruption at the site with a Volcanic Explosivity Index (VEI) of 2 (Liedl et al., 2019)(Figure 1.4). The cone is situated in the southwest of the caldera crater along the coast, north of the Starza marine terraces. (Di Vito et al., 1987) collated information from Italian eyewitness accounts: (Falconi, 1538), (Marchesino, 1538), (Toledo, 1539), (Del Nero, 1538), (Porzio, 1551) translated to English in (Hamilton and Fabris, 1776) and (Lobley, 1889). These were interpreted alongside field data and synthesised with a detailed analysis of the deposits to ascertain the sequence of events of the Monte Nuovo eruption (D'Oriano et al., 2005). The stratigraphic sequence of erupted deposits has been divided by multiple studies into variable units correlations between these are shown in Figure 1.5. This study uses the units defined by (Smith et al., 2011b).

The first signs of an impending eruption were observed in 1502 when uplift began with the emergence of new land in the region of Pozzuoli (Di Vito et al., 1987). Thirty-six years later between 27-28 September 1538, a bulge appeared in the area of future vent opening (Dvorak and Gasparini, 1991), hours before the onset of the eruption the opening of



Figure 1.4. A wooden gravure, artists impression of the 1538 Monte Nuovo eruption A wooden gravure, artists impression of the 1538 Monte Nuovo eruption. First published by Toledo (1539) digitised and republished by Morhange et al. (2006), Stock et al. (2018b). The image suggests changes to the morphology of the land surrounding the eruption, as well as an indication of localised damages as a result of erupted material.

fractures in this bulge were observed (Del Nero, 1538). Figure 1.6 shows a timeline of the eruption. The eruption began at 8 pm on 29th September, near Tripergole village, ~3km from Pozzuoli (Del Nero, 1538). The eruption had an explosive hydromagmatic opening phase with no sustained eruption column, evident from the lack of fallout in the deposits (Di Vito et al., 1987). During which pyroclastic flows radiated out of the vent, building the main cone and emplacing the largest deposit produced in the eruption (Di Vito et al., 1987). As a result of this explosive event, a 40 cm thick pumice raft was present in the bay of Pozzuoli (Del Nero, 1538).

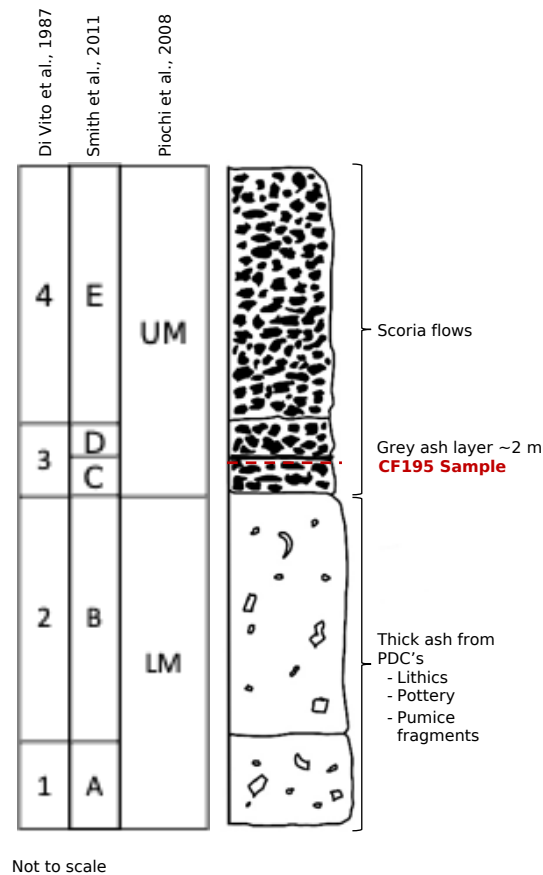


Figure 1.5. Stratigraphic sequence of the Monte Nuovo tuff cone
Stratigraphic sequence of the Monte Nuovo tuff cone, showing units as described in Piochi et al. (2008) Di Vito et al. (1987) and Smith et al. (2011b), (Perugini et al., 2015). The position of the CF195 sample used in this study’s stratigraphic position is highlighted in red.

From the 1-2 October, the mechanism of eruption changed to magmatic. The rate of water recharge was lower than the rate of consumption and thus exhausted resulting in a change to minor explosive activity. During this period of quiescence, (Toledo, 1539) climbed to the vent and observed a “boiling” inside which has been interpreted as mild Strombolian activity (Di Vito et al., 1987). On the 3 October, the volcano erupted explosively again at

a lower magnitude than the initial eruption (Toledo, 1539). This event is indicated in a grey ash layer within the scoria and was likely caused by a batch of less degassed surface magma (Di Vito et al., 1987). The increased pressure may have induced the opening of existing or new fractures within local lithologies, increasing the non-magmatic water flow to the conduit inducing a short phase of explosive activity. This activity continued until the water source was exhausted. Another period of quiescence followed from the 4-6 October with a phase of mild Strombolian activity. The final explosive phase occurred on the 6 October depositing ash from a radially distributed pyroclastic density current (D’Oriano et al., 2005). Prior to this, curious members of the public had begun to climb the cone, 24 of which were subsequently killed during this final phase of eruption (Falconi, 1538).

The total deposit from the eruption is a 800m wide 132m high monogenetic tuff cone with a large radial distribution of ash extending beyond the cone (D’Oriano et al., 2005) categorising the eruption as a VEI 2 with a DRE $<0.1 \text{ km}^3$ (Rosi and Sbrana, 1987). The body of the cone is formed by ash and pumice and then overlain with coarse lapilli deposits, an erosive surface separates the two. Deposits are poorly exposed as they are covered with thick vegetation visible from satellite imagery. Sedimentological and textural characteristics of the eruption are summarised by (Di Vito et al., 1999).

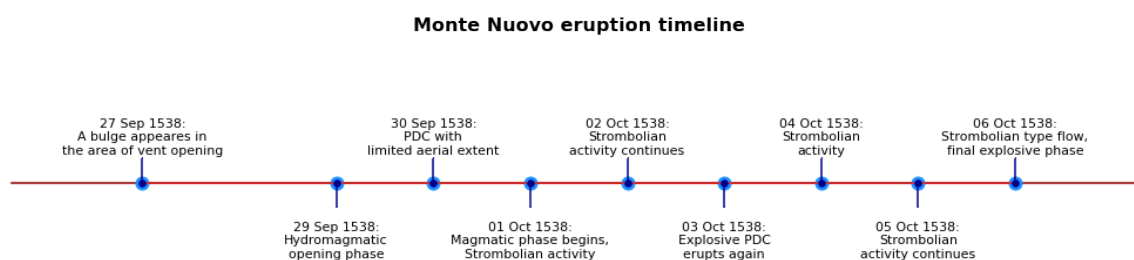


Figure 1.6. Timeline of main pre-cursory and eruptive events from the 1538 Monte Nuovo eruption. Timeline of main pre-cursory and eruptive events from the 1538 Monte Nuovo eruption. (Di Vito et al. (1987) Falconi (1538) , Marchesino (1538), (Stock et al., 2018b), Toledo (1539), Del Nero (1538), Porzio (1551) Hamilton and Fabris (1776) Lobley (1889), (Stock et al., 2016)).

1.2 Petrology of Campi Flegrei

1.2.a Magmatic Processes at Campi Flegrei

Deposits from the Campi Flegrei eruptions are pyroclastic rocks and subordinate lavas (Iovine et al., 2017). A compilation of the compositional variation of eruptive products from Campi Flegrei divided by Epochs (Figure 1.7). The volcano follows an alkaline differentiation trend from basaltic-trachyandesites to phonolites and trachytes (51.7-63.8 wt% SiO₂; e.g. (Smith et al., 2011a), the product of magmas modified by subducted fluids (Tonarini et al., 2004, D'Antonio et al., 2007, Mazzeo et al., 2014). Modelling shows that the compositional diversity of magmas erupted at Campi Flegrei can be achieved from the fractional crystallisation of a single shoshonitic parental magma (a K-rich basaltic trachyandesite Figure 1.7) (Civetta et al., 1991, Villemant, 1988).

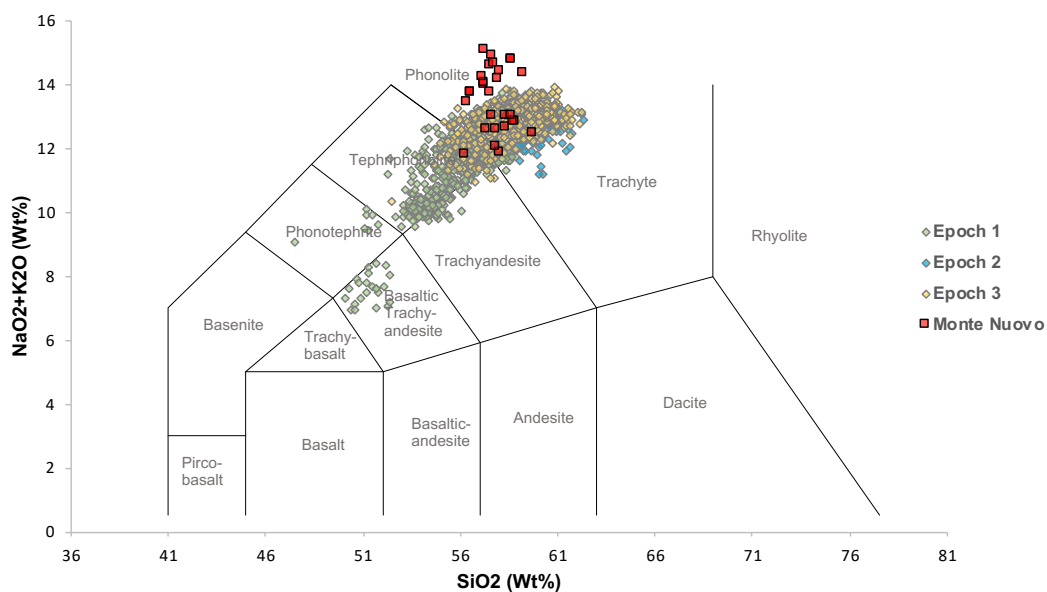


Figure 1.7. A compilation of Campi Flegrei major element compositional data. A compilation of Campi Flegrei major element compositional data plotted on a Total-Alkali Silica (TAS) diagram to show the compositional trend of eruptions through the epochs. Data adapted from Smith et al. (2011a).

Melt compositions prior to the NYT eruption are limited in their highly evolved compositional range (Pappalardo et al., 2002). There has been a larger compositional range of erupted melts in the past 15 kyr since the NYT eruption such as the more mafic Minopoli I eruption (Smith et al., 2011a). The most primitive melt compositions were erupted in Epoch I. Melt compositions from Epoch II and Epoch III are more evolved and only

distinguishable from each other by trace element analysis. Erupted melts from the Monte Nuovo eruption have an anomalously high Na₂O concentration (Smith et al., 2011b). The eruption at Monte Nuovo marked a critical change in the evolution of the volcanic system whereby crystallization enhanced signifying that the Campi Flegrei caldera is entering a new build up phase with a large volume eruption or caldera forming event likely at some currently undetermined point in the future (Forni et al., 2018).

It is understood that fractional crystallization occurs within the Campi Flegrei system (D'Antonio et al., 1999) combined with periodic recharge events (Pappalardo et al., 2002, Smith et al., 2011b). This is recorded in major and trace elements which show the evolutionary trend extending from mafic compositions to trachy-phonolites throughout time. Three distinct isotopic end-members at Campi Flegrei suggest that the magmas cannot have formed from fractional crystallization alone but also assimilation of country rock (Di Renzo et al., 2011, D'Antonio et al., 1999, Pappalardo et al., 2002). Geochemical analysis of erupted melt and geophysical data suggests that the Campi Flegrei caldera country rock consists of Meso-Cenozoic carbonate rocks above ~4 km and Syenite beneath within its basement (D'Antonio, 2011). Isotopic compositions are derived in the deep crust, before fractional crystallization can occur, these elements must be closely similar to evolve along the same liquid line of descent (Pappalardo et al., 1999). At Campi Flegrei the heterogeneity of Sr and Pb isotopes liquid line of descent is only compatible with minor crustal assimilation (D'Antonio et al., 2007, Fowler et al., 2007).

The three end-members have been defined by (Di Renzo et al., 2011) as the 'NYT component' ($^{87}\text{Sr}/^{86}\text{Sr}$ 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‰), the 'Minopoli 2 component' ($^{87}\text{Sr}/^{86}\text{Sr}$ ~0.70860, $^{143}\text{Nd}/^{144}\text{Nd}$ ~0.51236, $^{206}\text{Pb}/^{204}\text{Pb}$ ~18.90, $\delta^{11}\text{B}$ -7.32‰), and the 'Astroni 6 component' ($^{87}\text{Sr}/^{86}\text{Sr}$ ~0.70726, $^{143}\text{Nd}/^{144}\text{Nd}$ ~0.51250, $^{206}\text{Pb}/^{204}\text{Pb}$ ~19.08, $\delta^{11}\text{B}$ -9.8‰). The incidence of these isotopic components correlates to epoch activity. Epochs I and II have a prevalence of the NYT component and Minopoli 2 component mixing. Epoch III includes a mixture of the NYT and Minopoli 2 component and the Astroni 6 component. Monte Nuovo features an isotopic composition close to the Astroni 6 end-member. The higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and lower $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios signifies that the crustal assimilation that did occur was more dominant in Epoch I and Epoch II than in Epoch III and Monte Nuovo (D'Antonio et

al., 2007), (Di Renzo et al., 2011). Enrichment of $\delta^{11}\text{B}$ suggests a more metasomatized mantle source due to high fluid input from the subducting slab (D'Antonio et al., 2007) and/or lower inputs of subducted sediment from the mantle wedge (Tonarini et al., 2004) (Di Renzo et al., 2011). The Monte Nuovo eruption is the most recent eruption of Campi Flegrei and so is the best example of the volcano's current magmatic status, it has also been suggested the Monte Nuovo may signify the start of a new epoch (Bevilacqua et al., 2017).

Multiple data sets have been integrated and used to determine the depth of magma storage beneath Campi Flegrei using a consistent crustal density of 2.3 g cm^{-3} after (Rosi and Sbrana, 1987) shown in Figure 1.8. This demonstrates that crystallization and magma storage occur in two discrete zones (Stock et al., 2018b). There is shallow melt storage at around 2-5 km identified by melt inclusions (Fourmentaux et al., 2012, Vetere et al., 2011), ground deformation (Woo and Kilburn, 2010, Amoroso et al., 2014, D'Auria et al., 2015) and seismic tomography (Zollo et al., 2008, De Siena et al., 2010). There is also a deep melt storage region 4.7-13.3 km below the surface identified by melt inclusions (Arienzo et al., 2016, Arienzo et al., 2010), phase equilibria experiments (Bohrson et al., 2006, Fowler et al., 2007, Cannatelli, 2012) and seismic tomography (Zollo et al., 2008, De Siena et al., 2010).

All Campi Flegrei eruptions contain varying proportions of feldspar, clinopyroxene, biotite, oxides and apatite (Smith et al., 2011b). Pyroxenes have fast growth rates (10^{-7} - 10^{-8} cm/s (Ubide and Kamber, 2018)), and are highly sensitive to temperature and pressure changes, making the zoning of pyroxenes which have formed within volcanic systems to be used as a proxy for changes in magmatic conditions (Ubide and Kamber, 2018, Ubide et al., 2019). Clinopyroxene and plagioclase crystals erupted from Campi Flegrei have been petrologically analysed and thermobarometrically modelled to identify melt storage depths.

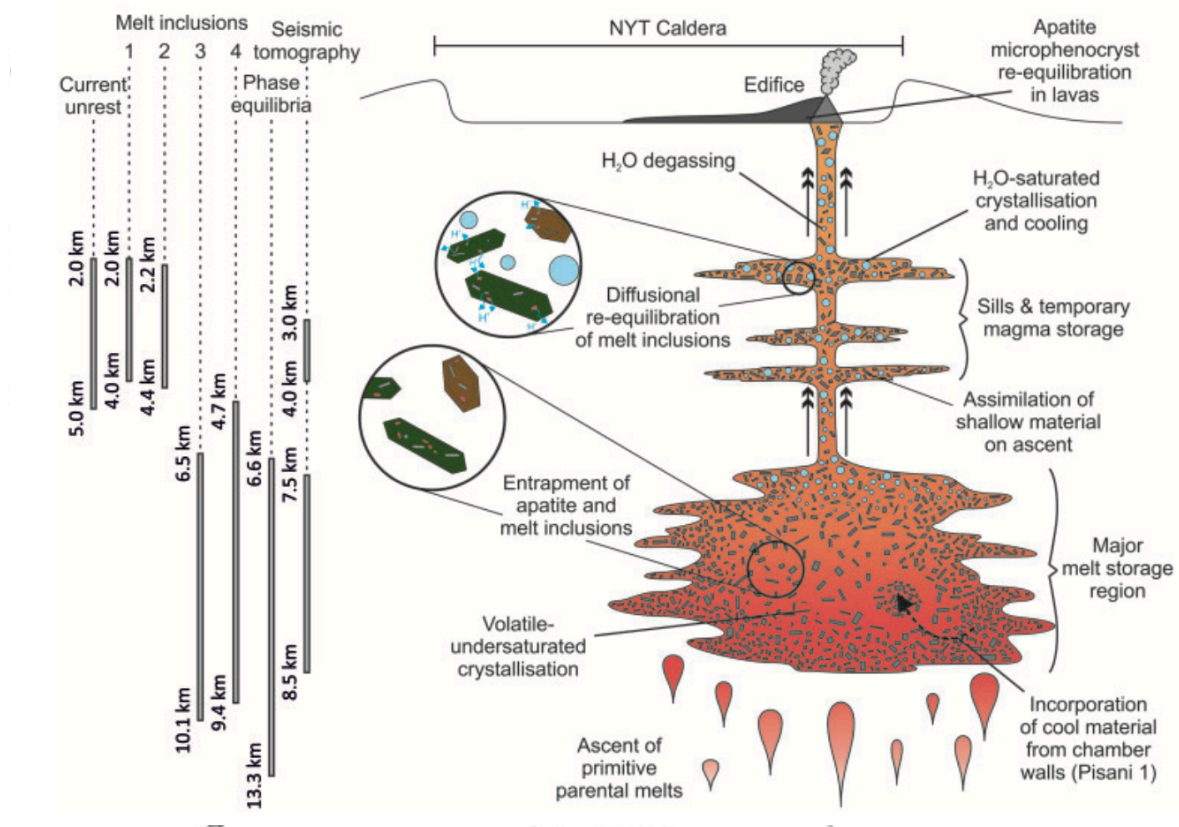


Figure 1.8. Schematic diagram from (Stock et al., 2018) summarising volatile systematics at Campi Flegrei. Schematic diagram summarizing volatile systematics in the Campi Flegrei sub-volcanic plumbing system, based on apatite and glass compositions. Grey bars (left) display relative estimates of CF magma storage depths. Stock et al. (2018) integrated multiple data sets and recalculated depths using a consistent crustal density of 2.3 kg cm⁻³ to determine pressure after Rosi and Sbrana (1987). Ground deformation data (Woo and Kilburn (2010), Amoroso et al. (2014), D’Auria et al. (2015) Arzilli et al. (2016)), fumarolic gas emissions, Carlini et al. (2015) Di Vito et al. (2016), heat flow measurements Di Maio et al. (2015), melt inclusion data for <15ka eruptions (Stock et al. (2018b), Vetere et al. (2011), Fourmentraux et al. (2012), Iovine et al. (2017), Arienzo et al. (2016) Arienzo et al. (2010), Astbury et al. (2018)) phase equilibria constraints Bohrsen et al. (2006), Pelullo et al. (2022), Fowler et al. (2007), Cannatelli (2012), seismic tomography (Zollo et al. (2008), De Siena et al. (2010)). Not to scale.

1.2.b Time constraints on magmatic processes

Various techniques have been used in an attempt to construe the timescales of magma processes at Campi Flegrei for multiple eruptions, with a particular emphasis on deducing the time elapsed between the final detectable magma recharge event and subsequent eruption (recharge-to-eruption timescale). Some studies have looked at a spectrum of eruptive events within the system to make broad conclusions regarding the mechanics and

interworking of the volcanic system (Di Vito et al., 2016, Stock, 2016, Stock et al., 2018b), whereas others have focused on assigning timescales of recharge-to-eruption shown in Figure 1.9 (Perugini et al., 2015, Arzilli et al., 2016, Di Vito et al., 2016, Stock et al., 2016, Stock et al., 2018b, Iovine et al., 2017, Astbury et al., 2018, Pelullo et al., 2022). A range of different chronometric techniques have been used to assign these timescales each with benefits and limitations. Given the complexity of the system it is important to critically compare timescale estimates from previous studies with our own estimates in order to understand how our recharge-to-eruption timescales compare to the current understanding of the system and how they can be useful for future forecasting of eruptive events.

Studies to ascertain recharge-to-eruption timescales have focused on three eruptions at Campi Flegrei; Agnano Monte Spina (AMS) (Epoch 3A), Astroni (Epoch 3B), and Monte Nuovo. AMS was the largest of these eruptions and is the only other eruption where timescales have been deduced via diffusion chronometry using barium diffusion in sanidine phenocrysts (Iovine et al., 2017), and Fe-Mg diffusion in clinopyroxene crystals (Pelullo et al., 2022).

Two alternative techniques have been used to constrain timescales for the Astroni eruption. Recharge-to-eruption timescales have been calculated based on K-feldspar growth rate estimates of the most recently recorded crystal zone. However, the extensive variables which contribute to crystal growth rates are not considered when using this technique resulting in uncertainties over the robustness of these short ~1 h - 6 day timescales (Astbury et al., 2018). Concentration Variance Decay (CVD) has also been used to calculate timescales at Astroni, using diffusive fractionation in trace elements assessing element mobility and chemical homogenisation in melt systems. Timescales obtained indicate only tens of minutes elapsed between recharge indicated by magma mixing and eruption (Perugini et al., 2015). These timescales may be useful when predicting future eruptions however the range of variables which impact magma mixing and subvolcanic processes prior to eruption make it near impossible to recreate these system dynamics in a lab, therefore the reliability of these experiments remains uncertain.

Finally, there is only one example of an attempt to constrain recharge-to-eruption timescales at Monte Nuovo prior to this study, using K-feldspar crystal growth rates timescale estimates are between hours and days (Arzilli et al., 2016). My study suggests

that products that erupted later during the Monte Nuovo event came from a shallower magma storage region <4 km depth (see section 1.2.a). Figure 9.1 demonstrates the variation in these calculated timescales.

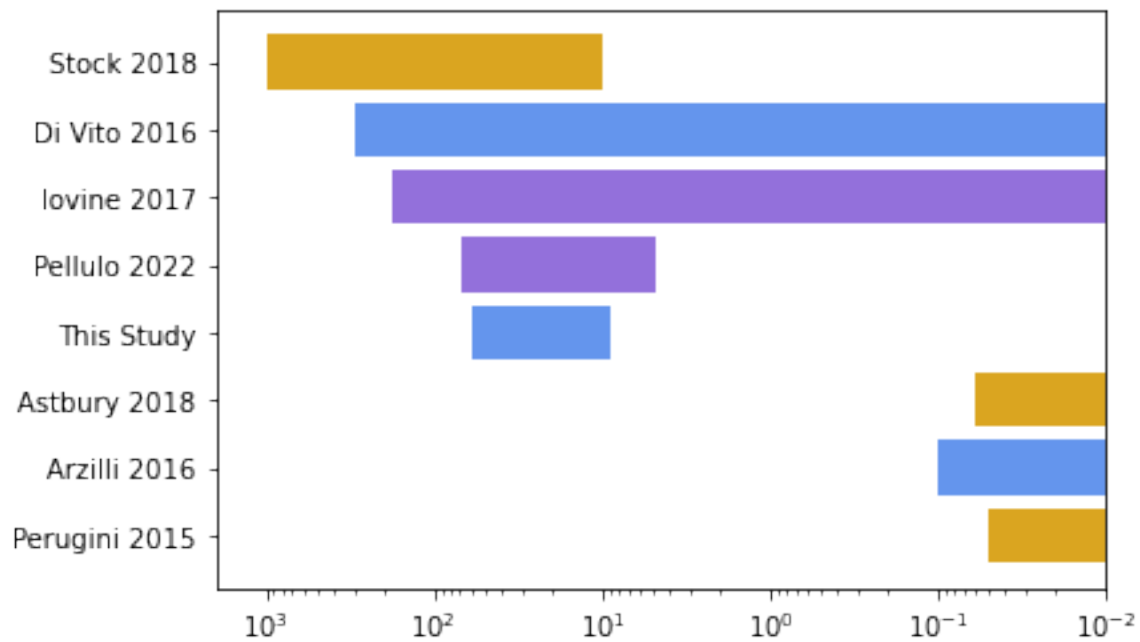


Figure 1.9. Simplified graph of timescales for pre-eruptive recharge at Campi Flegrei. Simplified graph of timescales (years) from recharge-to-eruption at Campi Flegrei. Yellow = Astroni, blue = Monte Nuovo, Purple = Agnano Monte Spina (Di Vito et al., 2016, Stock et al., 2018b, Perugini et al., 2015, Arzilli et al., 2016, Iovine et al., 2017, Astbury et al., 2018, Pelullo et al., 2022).

1.3 Experimental Methods

1.3.a. Introduction to diffusion chronometry

A variety of techniques can be used to calculate the timescales of magmatic processes, that occur over minutes to millennia. Two techniques dominate the field: diffusion chronometry and radiometric dating. Radiometric dating can be used for timescales ranging from decades (Ra) to millennia (U-Th, Ar-Ar) as well as a small window of applicability for days (Condomines et al., 2003). Unfortunately the U-series technique cannot be applied effectively to open systems because the isotopic clock is disturbed (Costa and Chakraborty, 2004). Diffusion chronometry uses the re-equilibration of crystal zones via chemical diffusion to calculate timescales of magmatic processes including storage, ascent, and eruption (Costa et al., 2020). The beauty of diffusion chronometry is it can span the full range of timescales from minutes to millennia depending on which elements and minerals are used.

Different elements in different minerals record processes from a variety of timescales, from seconds to 1000's years. Examples of simple diffusion modelling used on volcanic systems can be found in papers dating back to the 1980's (Maaløe and Hansen, 1982, Humler and Whitechurch, 1988). Simple models are one dimensional, diffusion profiles in one direction between the core and the rim of a crystal. Equation parameters are manipulated to fit a model profile to natural data and extrapolate a timescale, in early diffusion models this was done by eye (Morgan et al., 2004) now this is calculated mathematically through a model (Mutch et al., 2019). Simple diffusion models assume that diffusivity is constant and that a one-dimensional approach is adequate. Advances in experimental and analytical techniques used have increased the quality of timescale determinations dramatically over the past 30 years. This includes a higher spatial resolution when measuring compositional profiles and more precise diffusion coefficients (Turner and Costa, 2007).

In recent years, diffusion modelling has developed and is now widely applied to estimate timescales of a variety of magmatic processes, including recharge events and magma mixing, magma ascent rates, cooling rates, and crystal mush disaggregation timescales. Newer models take into consideration a wider range of variables and allow a more holistic

approach to diffusion timescales. (Mutch et al., 2019) uses Bayesian statistics to calculate the most probable diffusion timescale and associated errors using a range of input parameters. This model outputs temperature-time density plots demonstrate the exponential balance between temperature and magma storage times improving the robustness of timescale estimates.

1.3.b Element diffusion in minerals

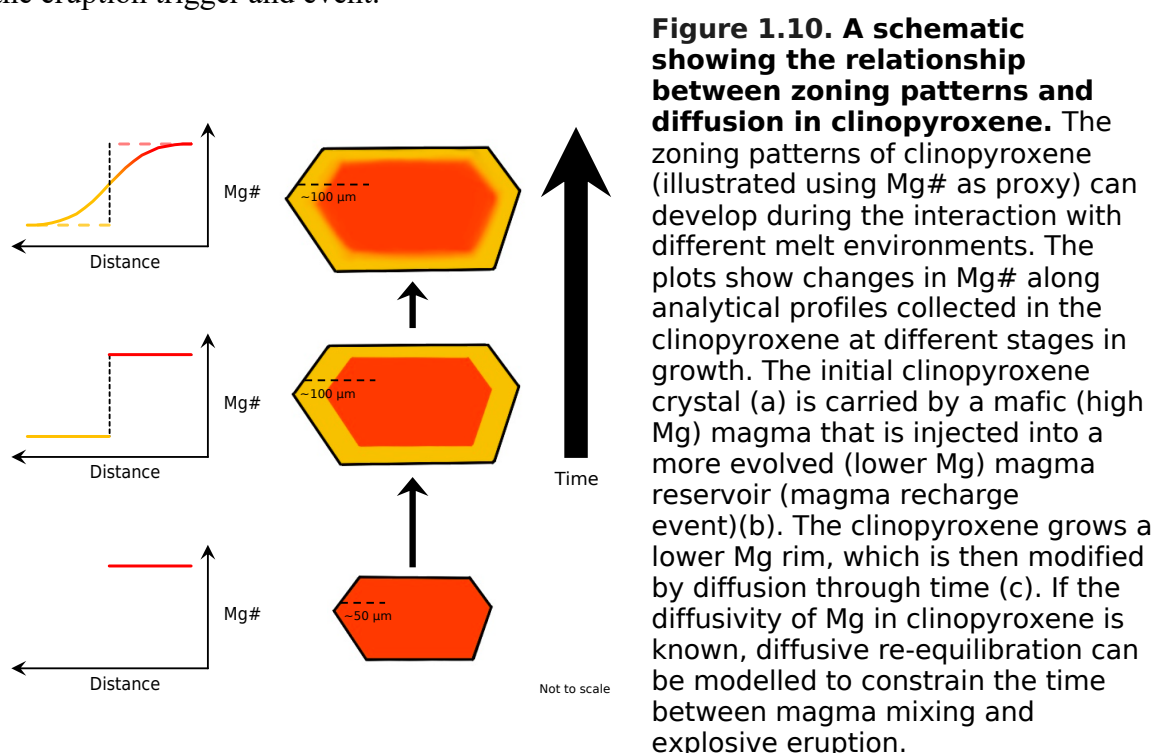
Diffusion is a kinetic process whereby the random motion of atomic-scale particles relative to other particles occurs within a defined region. The consequence of this process is a reduction in concentration gradients within that region and thus over extended time homogenisation occurs. At temperatures greater than absolute zero, all ions vibrate; some ions have more energy than others. In crystals, ions are situated in lattice sites which represent the energy minima. To move out of these sites into vacant sites, higher levels of energy are required. Diffusion therefore requires energy and vacancies, ions will jump from their wells to adjacent vacant sites or interstitial sites creating new vacancies in the wells they abandoned (Costa and Morgan, 2010).

There are two types of vacancies in ionic crystals, Schottky defect and Frenkel defect. Schottky deficits occur where multiple ions are removed from the lattice to achieve a charge balances, these are encouraged by higher temperatures. Frenkel defects force an ion into an interstitial site, creating a vacancy in its abandoned space, the charge remains balanced as the ion moves elsewhere in the lattice (Costa and Morgan, 2010). The rate of diffusion is dependent on the rate at which these vacancies are created and is dictated by; temperature, pressure, fluids (oxygen fugacity, water content), mineral compositions, element concentrations, state of strain, diffusion mechanism, crystal anisotropy (Costa and Chakraborty, 2004).

Within crystals' internal diffusion occurs, chemically distinct mineral zones re-equilibrate with one another after the crystal has grown. The zoning is caused by magmatic processes changing the surrounding melt conditions (Figure 1.10) and diffusion occurs due to the chemical gradient between zones (Costa and Morgan, 2010). The most dominant variable affecting the rate of diffusion is temperature, it is an Arrhenian relationship which scales exponentially (Costa et al., 2008). At higher temperatures atoms have more kinetic energy

available for ions to vibrate within the lattice. In any given unit of time, this increases the probability of an ion moving to a new site and creating a vacancy therefore increasing the rate of diffusion (Costa et al., 2020).

For diffusion to occur the crystal must be stored in a temperature region above the closure temperature for that mineral. In lava flows this temperature may extend beyond the time of eruption allowing crystals to record evidence of both pre and post eruptive processes. For more explosive eruptions (such as those seen at Campi Felgrei) the crystals are quenched immediately on eruption allowing crystals to preserve eruption time 0 as their rim (Costa et al., 2020). This means that diffusion across the final zone boundary at the edge of the crystal records the final magmatic processes that occur prior to eruption, and potentially the eruption trigger and event.



1.3.c Calculating diffusion timescales

The diffusivity (D) is a measure of the probability of an ion jumping into a vacancy in any given amount of time. It is related to the amount of material available and the amount of time that has passed through Fick's first law:

$$F = -D \frac{dC}{dx}$$

F , The amount of material lost per unit area, per unit time ($\text{nm}^{-2}\text{s}^{-1}$); D , Diffusivity (nm^2s^{-1}); dC/dx , Concentration, C ; gradient over distance, x (m^2s^{-1}).

Fick's second law, the rate of homogenising chemical gradients as a function of time. It is the fundamental concept used in diffusion chronometry models (Costa et al., 2020):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

t , time that a crystal spends at a given temperature; x , distance (m); C , concentration (mol/m^3).

To obtain reliable timescales we fit a model to the measured concentration profile in a natural crystal using a numerical algorithm (Costa and Morgan, 2011). A diffusion coefficient (D) describes the diffusivities of elements in different minerals, they are experimentally determined in a laboratory, using equations derived from chemical kinetic theory. (Boltzmann, 1892) determined a distribution which describes the activation energy of ions across a population that only those with the most energy are available for reaction. This led to the formation of the Arrhenius equation:

$$N = Ae^{-\Delta h/RT}$$

N , Number of molecules; A , Constant; Δh , Critical energy value; R , Universal gas constant; $8.314\text{Jmol}^{-1}\text{K}^{-1}$; T , Temperature (K).

The concepts behind diffusion are similar: diffusion rate is governed by the generation and availability of vacancies which have a high energy of formation, analogous to a high activation energy for reaction. Therefore, when experimentally determining the diffusion coefficients for different ions in different minerals, the following equation is used:

$$D = D_0 e^{-\Delta h/RT}$$

Once diffusivity measurements have been experimentally determined by comparing natural compositional changes with monitored lab experiments, for appropriate elements and

minerals, these experimentally calibrated diffusion coefficients can be inserted into diffusion models used to calculate timescales from crystal zoning patterns. The most appropriate are selected based on their geographical location relative to the natural sample and the similarity in geochemistry of the sample- usually therefore from the same system.

1.3.d. Geothermobarometry experimental methods

Diffusion chronometry is extremely temperature dependent and so geothermobarometric modelling has been used to determine the pressures and temperatures (P-T) of magma storage in which the clinopyroxene crystals grew prior to eruption. This also gives us critical information regarding the structure of the magma plumbing system prior to the Monte Nuovo eruption. A clinopyroxene-liquid melt matching geothermobarometer specifically calibrated for alkaline systems was used (Masotta et al., 2013). The geothermobarometer was calibrated through regression analysis from experimental datasets obtained by merging data from phase equilibria experimental literature data with new experimental data collected from trachytic and phonolitic starting compositions from the Campanian Ignimbrite and Mt Vesuvius (Masotta et al., 2013). The barometer equation we used was Eqn. Palk2012:

$$P(\text{kbar}) = -3.89 + 0.28 \left(\frac{X_{\text{jd}}^{\text{cpx}}}{X_{\text{Na}}^{\text{liq}} X_{\text{Al}}^{\text{liq}} (X_{\text{Si}}^{\text{liq}})^2} \right) + 0.074(\text{H}_2\text{O}) + 5.01 \left(\frac{X_{\text{Na}}^{\text{liq}}}{X_{\text{Na}}^{\text{liq}} X_{\text{K}}^{\text{liq}}} \right) + 6.39(K_D(\text{Fe} - \text{Mg})^{\text{cpx-liq}})$$

The thermometer equation we used was Eqn. Talk2012:

$$\begin{aligned} \frac{10^4}{T(^{\circ}\text{K})} = & 2.91 - 0.40 \ln \left(\frac{X_{\text{jd}}^{\text{cpx}} X_{\text{jd}}^{\text{liq}} X_{\text{Fm}}^{\text{liq}}}{X_{\text{DiHd}}^{\text{cpx}} X_{\text{Na}}^{\text{liq}} X_{\text{Al}}^{\text{liq}}} \right) + 0.038 (\text{H}_2\text{O}) - 1.64 \left(\frac{X_{\text{Mg}}^{\text{liq}}}{X_{\text{Mg}}^{\text{liq}} + X_{\text{Fe}}^{\text{liq}}} \right) \\ & + 1.01 \frac{X_{\text{Na}}^{\text{liq}}}{X_{\text{Na}}^{\text{liq}} + X_{\text{K}}^{\text{liq}}} - 0.22 \ln X_{\text{ti}}^{\text{liq}} \\ & + 0.47 \ln \left(\frac{X_{\text{jd}}^{\text{cpx}}}{X_{\text{Na}}^{\text{liq}} X_{\text{Al}}^{\text{liq}} (X_{\text{Si}}^{\text{liq}})^2} \right) + 1.62 (K_D^{\text{cpx-liq}}) + 23.39 (X_{\text{ca}}^{\text{liq}} X_{\text{Si}}^{\text{liq}}) \end{aligned}$$

The open source tool Thermobar was used to perform thermobarometric calculations (Wieser, 2022). This tool has advanced functionality making it possible to analyse thousands of crystals against thousands of melts within a short timeframe. Using this tool it is possible that one crystal point may be at equilibrium with multiple input liquids, in this instance the model calculates the average between these liquid matches to give a reasonable pressure and temperature output.

Clinopyroxene crystal point data collected by EPMA analysis (Section 2.4) was input as the clinopyroxene component. We then input glass, whole rock, and melt inclusion literature data from Monte Nuovo and all Epoch III eruptions (Arzilli et al., 2016, D'Oriano et al., 2005, Piochi et al., 2005, Stock et al., 2018b, D'Antonio et al., 1999, Smith et al., 2011b, Piochi et al., 2008, Turney et al., 2008, Pappalardo and Mastrolorenzo, 2012, Armienti et al., 1983). We used literature data from all Epoch III eruptions as there is limited liquid data for the more mafic melts from Monte Nuovo samples. Eruption times between the Epoch II eruptions and Monte Nuovo as well as the close geographical location of Monte Nuovo and Epoch III edifices within the Campi Flegrei caldera suggest they are being fed by the same part of the system from a similar time in the volcano evolution. Making the use of these liquid compositions a reasonable step to take.

The input variables used in the model were 5% pre-eruptive H₂O and an 0.2 Fe³⁺/FeT ratio equivalent to QFM+1 oxygen fugacity, values were based on previous work completed on the Campanian Ignimbrite by (Forni et al., 2018). A 2-sigma error was used and a KDError of 0.05. A total of 125136 liquid pairs were considered with a total of 1520 matches from 77 crystal points.

2. Analytical methods

This chapter contains details of the analytical methods and sample preparation techniques used within this project. New clinopyroxene compositional major and minor element data (Si, Al, Na, Mg, Fe, Ti, Cr, Mn, Ca, and K) from the Monte Nuovo eruption of Campi Flegrei. Sample CF195 (previously studied extensively by (Stock et al., 2018b)) is a pyroclastic flow deposit collected from 40°49'57.3 N, 014°05'31.1 E with an average matrix glass composition of phonolite. The sample was deposited between 3-5th Oct 1538 and is part of the upper member unit C (Smith et al., 2011b)(Figure 1.5). It was part of the final explosive phase of the eruption and so we chose to use it due to the crystals being present throughout the initial eruptive sequence in the hope they would record short timescales.

CF195 has a major phase assemblage of K-feldspar + plagioclase + clinopyroxene + biotite + apatite + magnetite. In this study we analyse the clinopyroxene crystals as they can be used to constrain temperatures, pressures, and timescales. Clinopyroxene crystals from this sample exhibit two populations which can be identified in had specimen one green and one black, as seen in other local eruptions of Campi Flegrei and Vesuvius (D'Antonio et al., 1999, Cioni et al., 1998).

2.1 Sample Preparation

The samples used in this study was previously analysed in (Stock et al., 2018b). Rock samples were crushed, homogenised, and wet sieved to remove the fine component <44 µm. The sample was then dried in an oven at ~40 °C before separating the minerals. The Clinopyroxene phenocrysts were hand picked from the 250-500 µm fraction. Clinopyroxene crystals were the mounted in epoxy resin on the (010) crystal face and then ground and polished ready for analysis. Both pucks were carbon coated to a thickness of ~30 nm prior to analysis.

2.2 Scanning Electron Microscope (SEM)

In order to navigate the samples in line with the previous analysis completed on them (Stock et al., 2018b), high resolution BSE maps were taken of the entire epoxy resin pucks using the Tescan S8152 Field effect scanning electron microscope (FE-SEM) in the iCRAG Laboratory at Trinity College Dublin (TCD). The machine was operated at 20 kV, 300 pA. Individual BSE images were collected of each crystal for the identification of crystal zoning patterns within the different phenocryst phases.

2.3 Energy Dispersive X-Ray Analysis (EDX) element maps

Energy Dispersive X-Ray Analysis (EDX) element maps of characteristic crystals were collected so that multiple compositional profiles could be extracted from the same crystal for use in diffusion modelling. This allows for more a more efficient use of lab time as profiles can be extracted using an offline PC once the map has been collected. Maps were collected using the Tescan S8152 FE-SEM in the iCRAG lab at TCD. The machine was operated at 20 kV, 7 nA with a resolution of 1024, 2 μm per pixel for a time of 20,000 μs and calibrated using a range of appropriate natural and synthetic standards (Appendix 1).

To extract the data from the EDX maps we used the Oxford instruments AZtec software version 5.1. I used an EDX homogenous clinopyroxene crystal CF195_GCPX3 and took multiple compositional profiles across the crystal using different size parameters within the linescan function to determine accuracy. Using Electron Probe Microanalysis (EPMA)

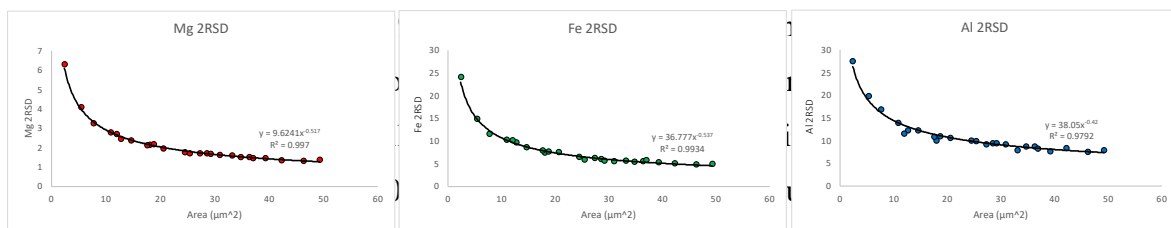


Figure 2.1. Regression analysis to assess the error of element data collected from Energy Dispersive X-Ray analysis (EDX) element maps versus area point size Regression analysis to assess the error of element data collected from Energy Dispersive X-Ray analysis (EDX) element maps versus area point size to two relative standard deviations (2RSD). EDX element data was collected from clinopyroxene crystal CF195_GCPX3. Relative standard deviations are calculated in comparison with Electron Probe Microanalysis (EPMA) data also from CF195_GCPX3. A) Mg concentration error (2RSD). B) Fe concentration error (2RSD). C) Al concentration error (2RSD).

retaining sufficient spatial precision (Figure 2.1). Therefore, when using the linescan function to extract the data a height between $\sim 12\text{-}3.5\text{ }\mu\text{m}$ was used.

2.4 Electron Probe Microanalysis (EPMA)

EPMA collected to obtain accurate and precise minor element compositions for use in geothermobarometric modelling. When extracting data from EDX maps the error is too large for reliable results when concentrations are below 0.1 wt%. Due to travel and lab restrictions during the Covid-19 pandemic EPMA data collected on my behalf by Professor Victoria Smith, University of Oxford. Samples were reground prior to electron microprobe analysis to reduce compositional alteration caused by electron beam exposure from the SEM analysis. Major and trace elements of the Clinopyroxene crystals were analysed using the JEOL JXA-8200 electron microprobe (EPMA) equipped with 5 wavelength dispersive spectrometers and an energy dispersive spectrometer at the Research Laboratory for Archaeology and the History of Art (RLAHA), University of Oxford.

Samples were coated simultaneously with standards to avoid variability in light element X-ray attenuation, and the machine was calibrated with the appropriate standards (Appendix 2) for the beam conditions. In total 35 crystals from the Monte Nuovo eruption were analysed using a 15kV, 15 nA beam at $3\mu\text{m}$. Count times on peak were 30 s for each element except for Cr (80 s). The background counts were collected for half the peak counting time either side of the peak. Over 200 spot analysis points were analysed from different compositional zones within the crystals to obtain a holistic view of each crystals compositional evolution as it grew.

2.5 Additional information

All clinopyroxene formula recalculations were calculated on a 6-oxygen basis. The Mg numbers (Mg#) was calculated using $\text{Mg}/(\text{Mg}+\text{FeT})\times 100$. Data peaks are determined using Kernel Density Estimates (KDE). Element units are atoms per formula unit (apfu), cations calculated by stoichiometry on a 6 oxygen basis.

3. Petrography

3.1 *Clinopyroxene textures*

Through both textural and compositional analysis, crystals give insights into the magmatic environments within which they grew. The clinopyroxene crystals from the CF195 sample are anhedral to euhedral dark green and black phenocrysts with a diopsidic composition, the average matrix glass composition from this deposit was phonolite (Stock et al., 2018b). Over 300 crystals were imaged via the SEM to produce high resolution BSE images. Thirty-five characteristic crystals were individually examined via EPMA point analysis (12%).

Clinopyroxene have been categorised into populations based on optical properties observed in BSE images. I identified four distinct groups which were further split into subgroups. Characteristic crystals from these groups are shown in Figure 3.1. Zoning in diopside crystals suggests compositional changes throughout growth, observable grayscale contrasts in BSE imaging of diopside crystals correlate with Fe/Mg ratios, darker grayscale has a higher Mg t%, lighter greyscale has a higher Fe wt% (Streck, 2008).

Group 1 contains normally zoned crystals, normal zoning is inferred from a dark core and lighter mantle/rim. Subgroup 1A presents rounded corners, elongated crystals with a patchy core. Subgroup 1B presents elongated crystals with euhedral cores. Subgroup 1C has euhedral crystals with zoned cores but a high contrast rim to distinguish the crystal as normally zoned. Group 2 contains crystals with reverse zoning. Subgroup 2A has a patchy evolved cores with patchy textures. Subgroup 2B presents sharp boundaries between light cores and the dark rims these crystals are anhedral and fragmented. Group 3 contains crystals with complex concentric zoning. Subgroup 3A are defined by a distinct thin dark euhedral band. Subgroup 3B are Euhedral crystals with a patchy core and a thick dark anhedral mantle followed finally by a thin light rim. Group 4 contains crystals with 'hidden zoning'. Hidden zoning has been identified by further EPMA analysis (results in section 3.2) but is not obvious from BSE images as crystals appear homogenous. Subgroup 4A shows crystals with an ultra thin light rim less than 10µm across.

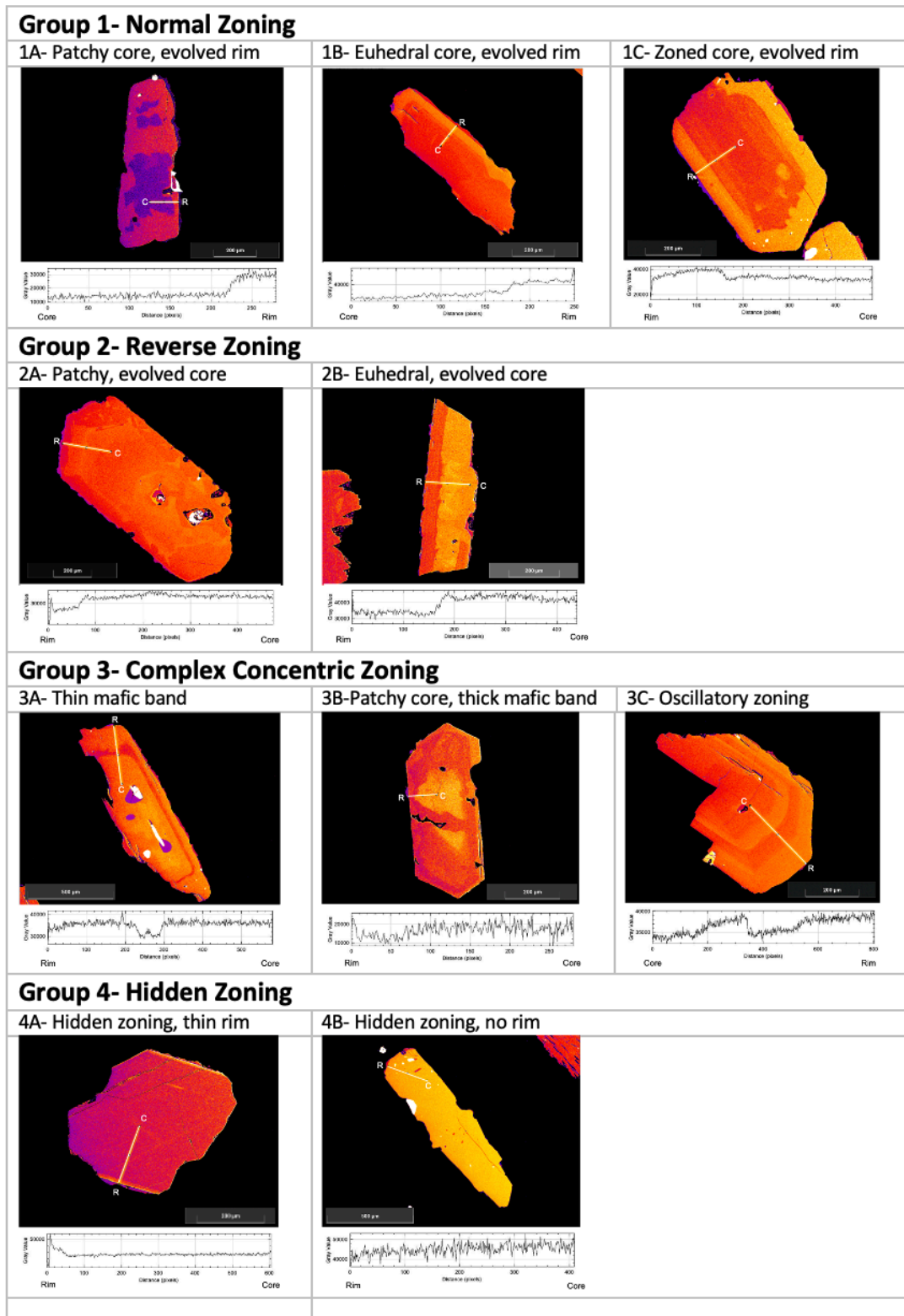


Figure 3.1. BSE images of characteristic CF195 clinopyroxene crystals for each group and subgroup BSE images of characteristic CF195 clinopyroxene crystals for each group and subgroup. 1A) normal zoning, dark patchy core, light rim 1B) normal zoning, dark euhedral core, light rim. 1C) normal zoning, dark zoned core, light rim. 2A) reverse zoning, patchy light core, dark rim. 2B) reverse zoning, euhedral light core, dark rim. 3A) complex concentric zoning, thin dark band. 3B) complex concentric zoning, thick dark mantle, patchy light core. 3C) complex concentric zoning, oscillatory zoned. 4A) hidden zoning, thin rim 4B) hidden zoning, no rim. Colours are overlain to enhance contrasts.

3.2 Clinopyroxene Geochemistry

From EPMA the Mg# range 72-93 of these crystals emphasises broad compositional heterogeneity. Trends in this heterogeneity have no obvious correlation to the colours of crystals observed in hand specimen. Geochemical analysis shows Ti, Al, FeT, and Na apfu (atoms per formula unit) have a negative correlation with Mg (Figure 3.2). Cr has a positive correlation with the Mg (Figure 3.2). Ca has no correlation to the Mg and is completely scattered (Figure 3.2). Ti has a range from 0.005-0.026 apfu. Al has a range from 0.05-0.225 apfu. Cr³⁺ has a range from 0-0.0175 apfu. FeT has a range from 0.075-0.275 apfu. Ca has a range from 0.90-0.96 apfu. Na has a range from 0.002-0.037 apfu.

From the EPMA data collected for 28 crystals three melt environments have been identified based on Mg concentration, this can most clearly be seen in the Fe/Mg plot (Figure 3.2). These three melt environments will henceforth be referred to as M1, M2, and M3. M1 is the most mafic of the environments with a mol.% range from 0.82-0.92, 29% of crystals were homogenous in this environment, whilst 82% of crystals interacted with it in some way. M2 is the intermediate environment ranging from 0.78-0.82 only 1% of crystals interacted with this environment and none grew within it homogeneously. M3 is the more evolved environment ranging from 0.73-0.78, <1% of crystals homogeneously grew within this environment but 61% of crystals interacted with this environment.

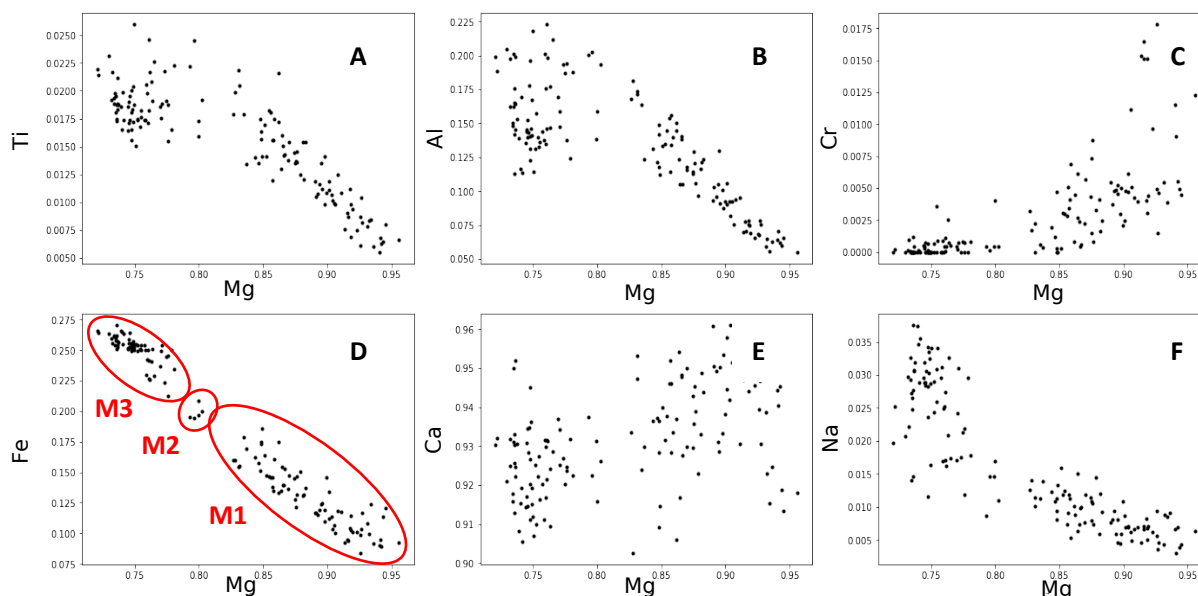


Figure 3.2. Major and minor elements vs Mg compositions of clinopyroxene EMPA point analysis. Major and minor elements vs Mg compositions of clinopyroxene EMPA point analysis, A) Ti v Mg, B) Al v Mg, C) Cr³⁺ v Mg, D) FeT v Mg, E) Ca v Mg, F) Na v Mg.

Group 1 was the most dominant crystal population showing normally zoned crystals easily observed in the BSE images. Compositional analysis of these crystals shows that they are indeed compositionally zoned with the more mafic M1 compositions in the core of the crystals and the more evolved M3 compositions at the rims. Subgroups of Group 1 all show this normal zoning trend regardless of rim thickness and diffusivity of the core-rim boundary. Compared to the whole crystal population (grey points, Figure 3.3) the rims of Group 1 crystals cluster around the lower end of the observed Ti and Al compositions with the majority lying between 0.016-0.021 apfu and 0.125-0.175 apfu respectively. There is a very shallow positive gradient between Mg and Ca, cores have Ca concentrations between 0.92-0.96 apfu, rims overlap with concentrations between 0.90-0.94 apfu (Figure 3.3).

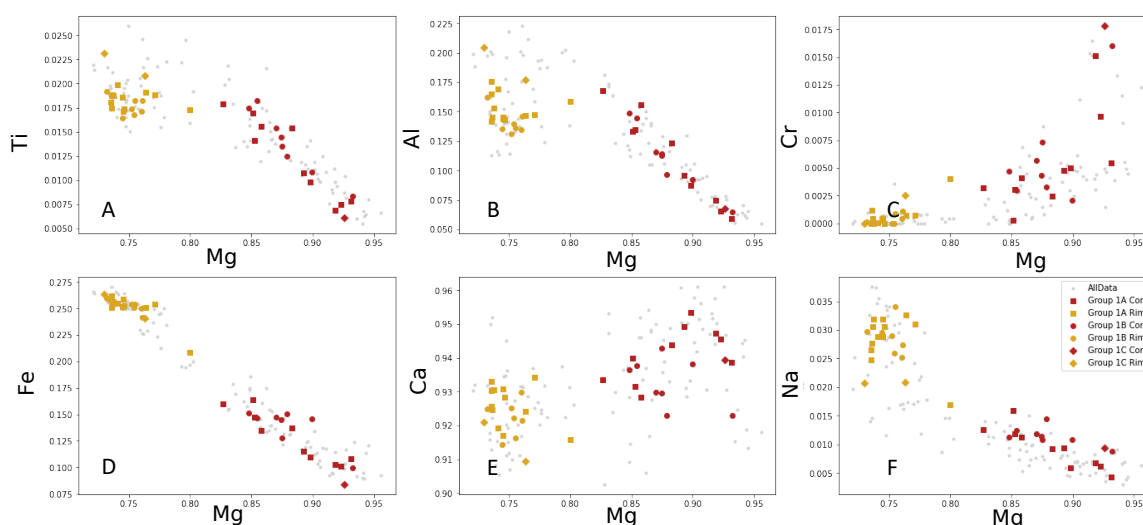


Figure 3.3. Major and minor elements vs Mg compositions of clinopyroxene EMPA point analysis for Group 1. Major and minor elements vs Mg compositions of clinopyroxene EMPA point analysis for Group 1. Gray points = all data, Red points = core concentrations, orange = rim concentrations. A) Ti v Mg, B) Al v Mg, C) Cr³⁺ v Mg, D) FeT v Mg, E) Ca v Mg, F) Na v Mg.

Group 2 zoning patterns are more compositionally complex than those of Group 1. Cores and rims are not distinguishable. This complex zoning is reflected in the BSE images of Subgroup 2A (Figure 3.4). Figure 3.4 shows Subgroup 2B which has a more obvious reverse zoning pattern and this is reflected in the compositional analysis of the crystals. The rims and mantles of these crystals have more mafic M1 and M2 compositions. Compared to the whole crystal population (grey points, Figure 3.4) crystals from Subgroup 2A have lower Na concentrations with a maximum concentration of 0.017 apfu and higher Al concentration with core compositions at ~0.2 apfu.

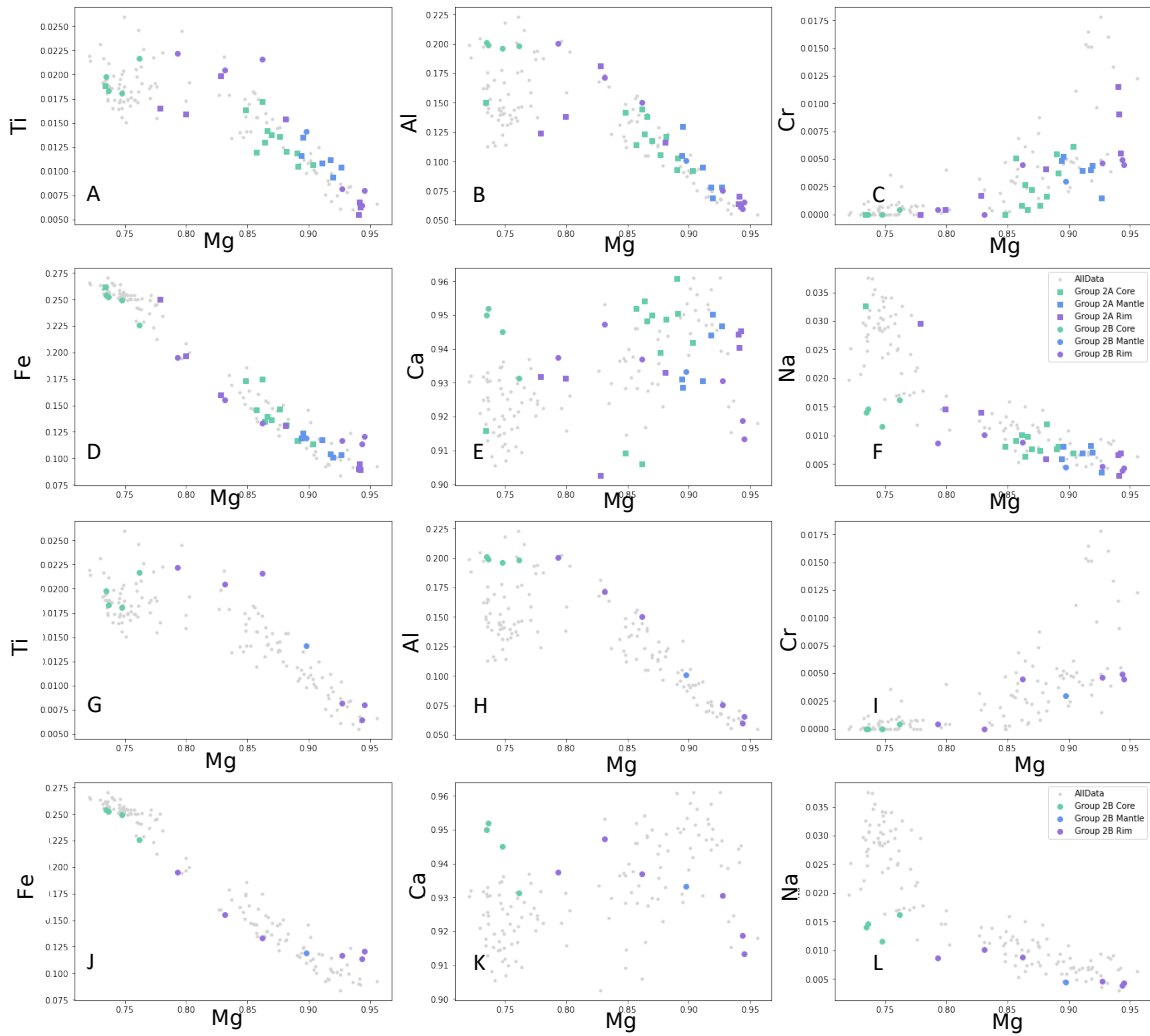


Figure 3.4. Major and minor elements vs Mg compositions of clinopyroxene EMPA point analysis for Group 2. Major and minor elements vs Mg compositions of clinopyroxene EMPA point analysis for Group 2. Gray points = all data, green points = core concentrations, blue points = mantle concentrations, purple = rim concentrations. A-F plot all points from Group 2 A) Ti v Mg, B) Al v Mg, C) Cr³⁺ v Mg, D) FeT v Mg, E) Ca v Mg, F) Na v Mg. G-H plot points from Subgroup 2B only G) Ti v Mg, H) Al v Mg, I) Cr³⁺ v Mg, J) FeT v Mg, K) Ca v Mg, L) Na v Mg.

As the name entails, Group 3 ‘Complex concentric zoning’ has the most complex compositional results. There are also limited analysis per zone making zoning systematics difficult to discern. Subgroup 3A (Figure 3.5) is the simplest to interpret with the core and rim compositions being in the M3 environment as expected from the textural analysis (Section 3.1). Some measurements from the thin dark band observed in BSE images (Figure 3.1) have also recorded this more evolved composition. However, due to the thickness of the band in some crystals it is understood that this is a potential analytical error whereby the point size is larger than the band it is measuring, or the point was calibrated slightly off

the thin dark band when measuring took place. Subgroup 3B is the most complex subgroup, there is no real pattern to the compositional variations within the crystal regarding the positions of analysis in the core, mantle, or rim as observed in Figure 3.5 Subgroup 3C shows oscillatory zoning in BSE images, geochemical analysis shows only the outer rim of the crystals have a more evolved composition M3. These crystals though presenting an oscillatory texture, chemically appear normally zoned. Compared to the entire crystal population (grey points, Figure 3.5) Subgroup 3C crystals have very low levels of Cr no higher than 0.0015 apfu.

Group 4 crystals appear homogenous in BSE images however when geochemically analysed they are not (Figure 3.6). Compositions from these crystals span M1, M2, and M3. All crystals in this group show low levels of Na across all melt environments with a maximum Na 0.016 apfu. Subgroup 4A does show a normal zoning trend (figure X) however, the sample size from this group is too small to draw conclusions.

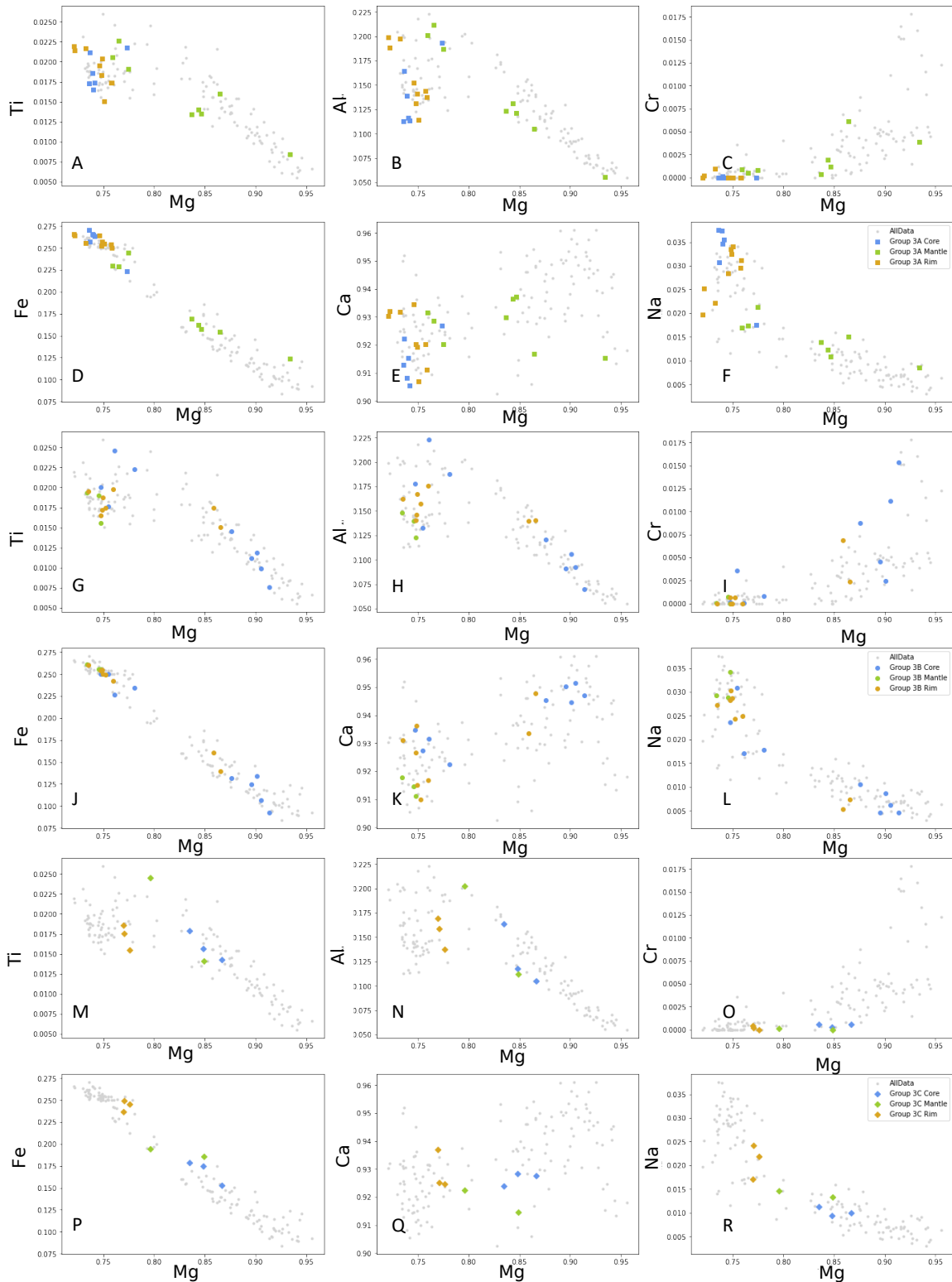


Figure 3.5. Major and minor elements vs Mg compositions of clinopyroxene EMPA point analysis for Group 3. Major and minor elements vs Mg compositions of clinopyroxene EMPA point analysis for Group 3. Gray points = all data, blue points = core concentrations, green points = mantle concentrations, yellow = rim concentrations. A-F plot all points from Subgroup 3A, A) Ti v Mg, B) Al v Mg, C) Cr³⁺ v Mg, D) FeT v Mg, E) Ca v Mg, F) Na v Mg. G-H plot points from Subgroup 3B, G) Ti v Mg, H) Al v Mg, I) Cr³⁺ v Mg, J) FeT v Mg, K) Ca v Mg, L) Na v Mg. M-R plot points from Subgroup 3C, M) Ti v Mg, N) Al v Mg, O) Cr³⁺ v Mg, P) FeT v Mg, Q) Ca v Mg, R) Na v Mg.

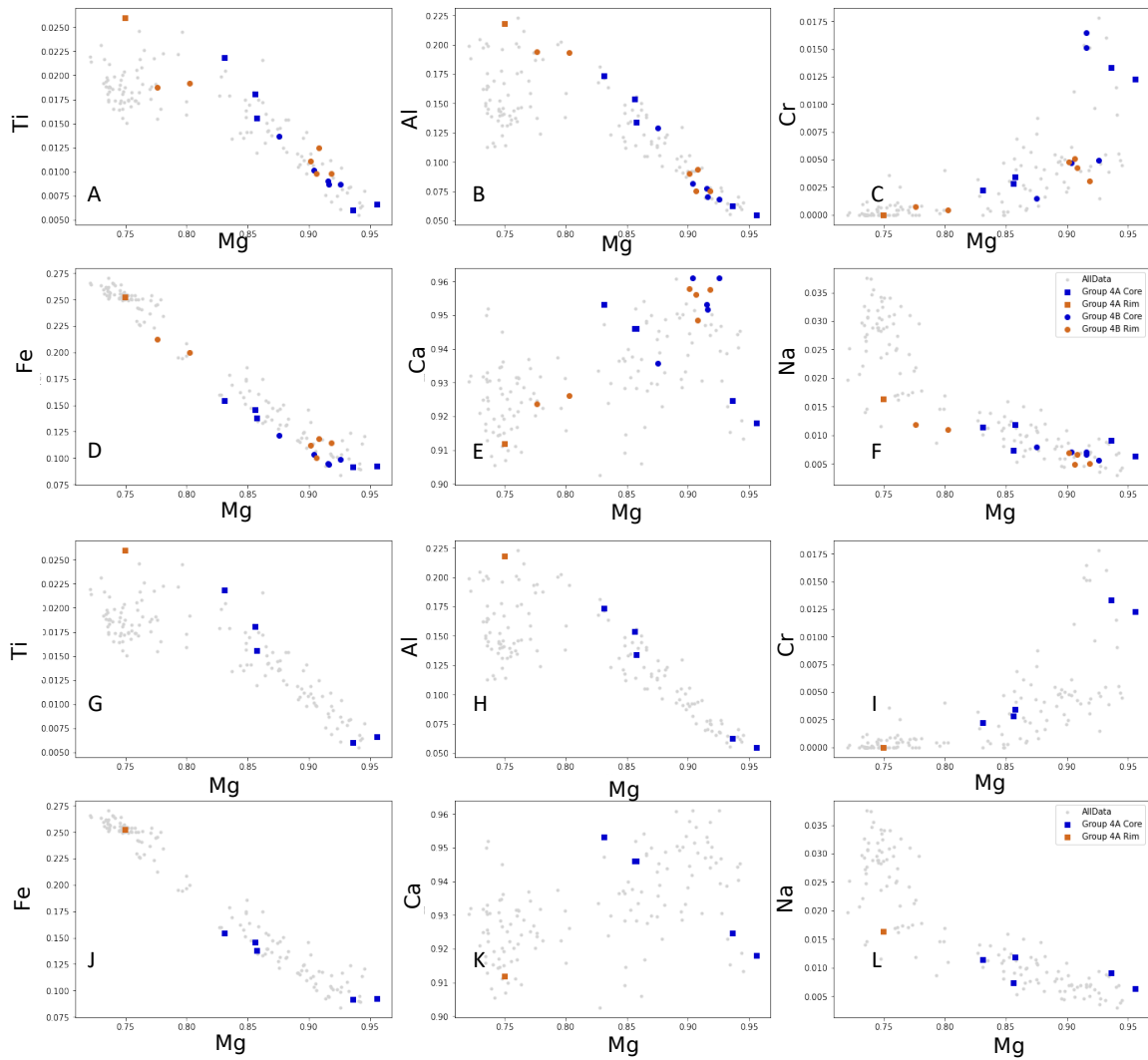


Figure 3.6. Major and minor elements vs Mg compositions of clinopyroxene EMPA point analysis for Group 4. Major and minor elements vs Mg compositions of clinopyroxene EMPA point analysis for Group 4. Gray points = all data, blue points = core concentrations, orange points = rim concentrations. A-F plot all points from Group 4 A) Ti v Mg, B) Al v Mg, C) Cr³⁺ v Mg, D) FeT v Mg, E) Ca v Mg, F) Na v Mg. G-H plot points from Subgroup 4B only G) Ti v Mg, H) Al v Mg, I) Cr³⁺ v Mg, J) FeT v Mg, K) Ca v Mg, L) Na v Mg.

3.3 Petrography discussion

Group 1 are normally zoned crystals with M1 cores and M3 rims, normal zoning indicates the crystals grew as they moved into progressively cooler and more evolved portions of the magmatic plumbing system. As per a normal geothermal gradient this is likely to be upwards. Sodium and Al are preferentially incorporated into the clinopyroxene structure as

pressure increases. The negative correlation between Mg and both Na and Al in Group 1 indicates a decrease in pressure and there from movement to a shallower part of the system as the magma becomes more evolved (Putirka, 2008, Blundy et al., 1995, Putirka et al., 1996). The depletion of Na and Cr in the rim suggests a period of fractional crystallisation following magma recharge (Coote and Shane, 2018) and plagioclase formation which is evidence of magma mixing/contamination (Streck, 2008).

The elongated crystals with rounded edges and diffuse core-rim boundaries seen in Subgroup 1A suggests the crystals have been exposed to different melt conditions and evidence of open system processes and diffusional equilibration (Streck, 2008). Subgroup 1B have a defined euhedral core-rim boundary indicating that the crystals are potentially younger than Subgroup 1A and havent been exposed to such extreme changes in melt conditions. These crystals are ideal candidates for diffusion modelling as they present a clear zone boundary between M1 and M3 with visible evidence of diffusion in BSE images (Figure 3.1). The core-rim boundary observed in Subgroup 1C is analogous to that observed in Subgroups 1A and 1B where it is caused by a compositional change in the surrounding magma from M1 to M3 either by influx of new magma, or by movement of the crystal from one storage region to another. However, visible oscillations in the M1 core of these crystals suggest localised changes in the melt variables such as changes in fO_2 proportions within the reservoir (Streck, 2008).

Group 2 represents reversed zone crystals, a positive correlation between Mg/Cr indicates that this zoning is due to a more mafic magma being introduced to the melt environment rather than localised changes in the storage conditions (Ubide et al., 2019).

Group 3 are complex concentrically zoned euhedral crystals with variations between M1, M2 and M3 compositions throughout their structure, demonstrating mafic-silicic-mafic melt interactions either through crystals being transported to different melt regions or by injections of new mafic magmas into the system that then evolve. Subgroup 3A has a thin mafic band of M1 composition is likely caused by an M1 magma injection into the system. The thin band suggests that this sudden mafic melt surrounding the crystal did not remain for long. Through magma mixing or crystal transfer the crystals was rapidly moved into a more evolved environment. This was a more gradual transfer change than the initial injection likely due to the melt around the crystal homogenising with the new magma

moving in that direction at some point during their growth. Some crystals do pass through the M2 composition on their way from M1 to M3 however, the majority of crystals have M3 as their rim composition. Overall this supports that as crystals grow they are moving upwards through the crust into more evolved magmas as the melt undergoes fractional crystallisation along the liquid line of descent and a normal geothermal gradient. A schematic of the magma system is shown in Figure 3.8.

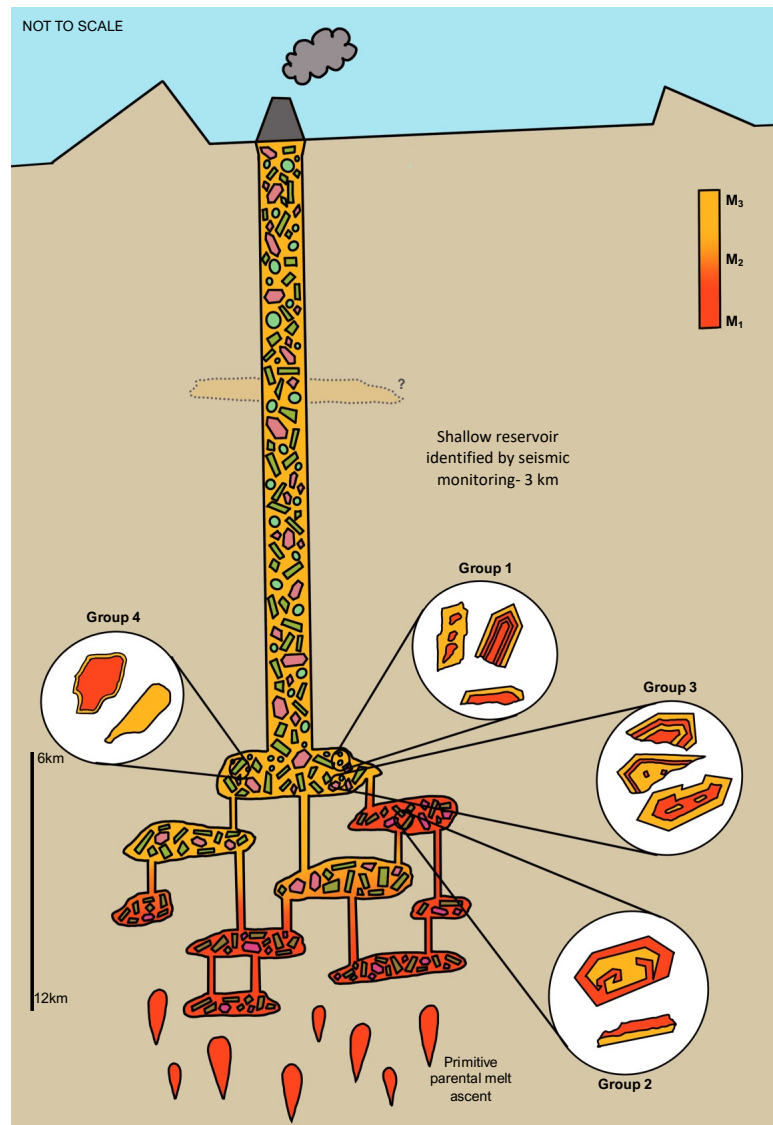


Figure 3.8. A schematic of the Campi Flegrei plumbing system. A schematic of the Campi Flegrei magma system as interpreted by detailed petrology of clinopyroxene crystals from the Monte Nuovo 1538 eruption. The shaded upper region represents a suggested shallow storage region from literature however we have no evidence for in this study. Colour intensity correlates to the melt composition as categorised by M1, M2 and M3 melts. Green crystals represent plagioclase, pink crystals represent clinopyroxene, proportions of both are not relative to what is observed.

4. Geothermobarometry

4.1 Geothermobarometry results

Figure 34.1 highlights the liquids that showed equilibrium matches with our input clinopyroxene data. Melts which matched with our clinopyroxene crystals are dominantly derived from Monte Nuovo input melts and the Monte Sant'Angelo melts from Epoch III. Input liquid matches are broadly more mafic in composition ranging from 0.65-1.76 MgO wt%. Of the input liquids they are also less alkaline ranging from 10-13.5 K₂O+Na₂O wt%. Input liquid matches are more Ca and Ti rich with CaO ranging between 2.2-4.7 wt% and 0.4-0.8 wt% respectively.

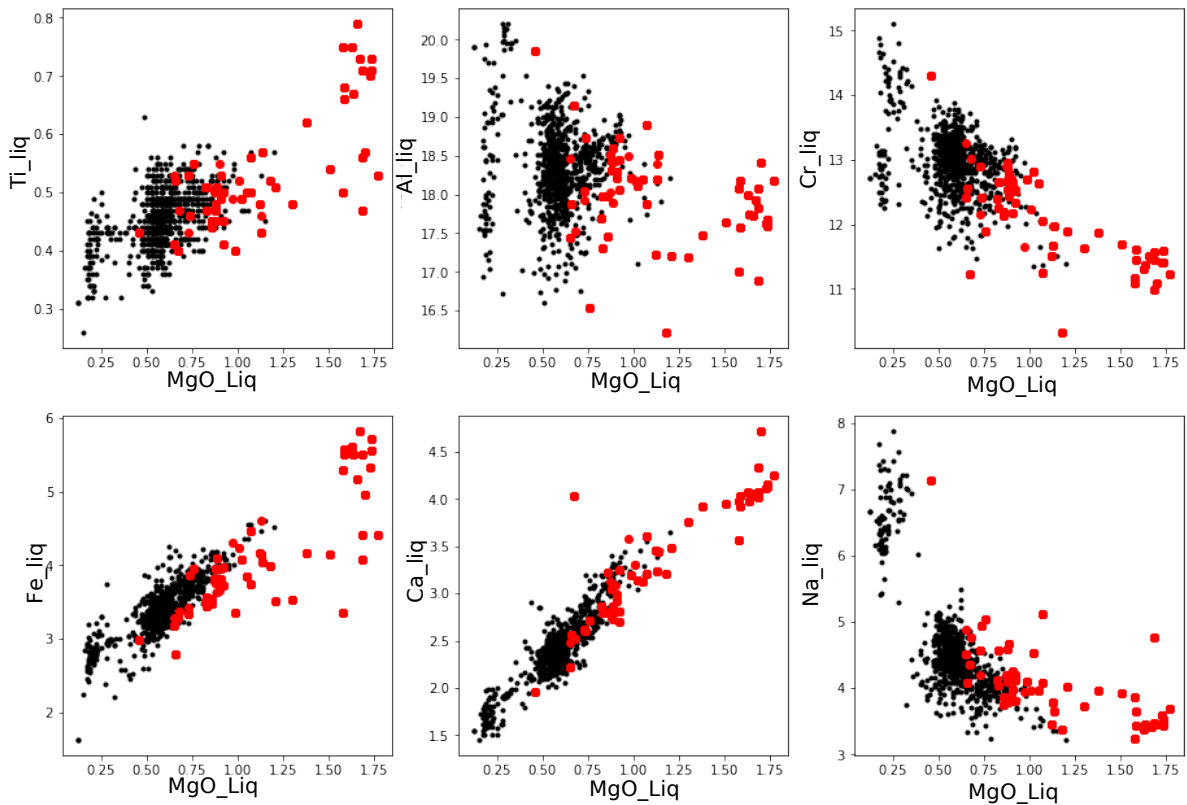


Figure 4.1. Geothermobarometry melt matches. Major and minor elements vs Mg compositions of Campi Flegrei Epoch III literature data. Black points = all input data, Red points = melts which matched with clinopyroxene input data. A) TiO₂ /MgO, B) Al₂O₃ /Mg, C) Cr₂O₃/MgO, D) FeO_t/MgO, E) CaO/MgO, F) Na₂O/MgO.

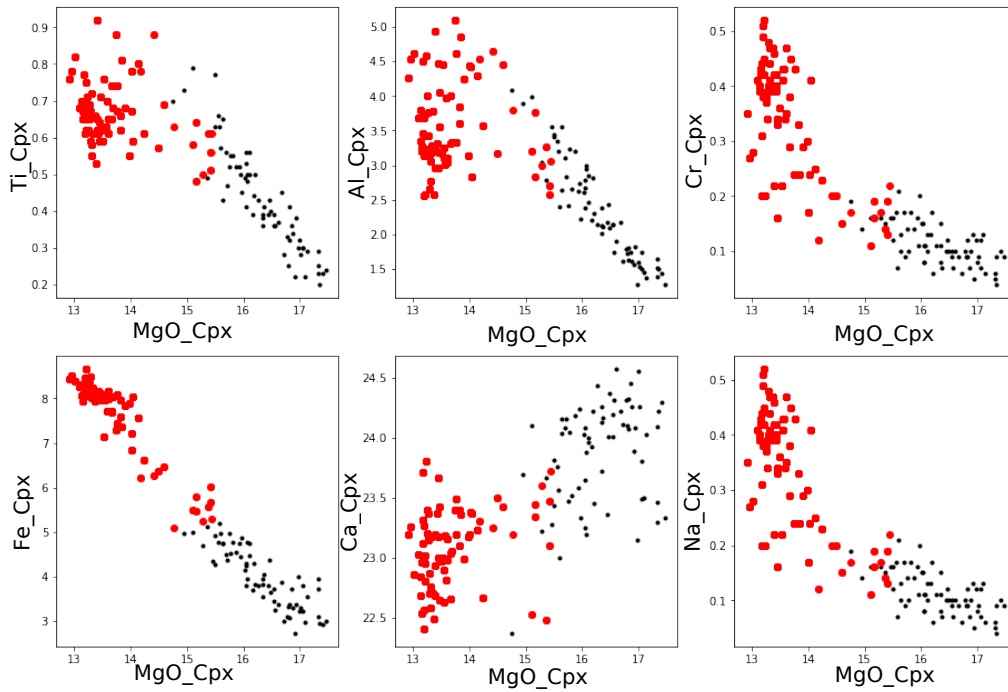


Figure 4.2. Geothermobarometry crystal matches. Major and minor elements vs Mg compositions of CF195 clinopyroxene crystals. Black points = all input data, Red points = crystals which matched with liquid input data. A) $\text{TiO}_2 / \text{MgO}$, B) $\text{Al}_2\text{O}_3 / \text{Mg}$, C) $\text{Cr}_2\text{O}_3 / \text{MgO}$, D) FeO / MgO , E) CaO / MgO , F) $\text{Na}_2\text{O} / \text{MgO}$.

Figure 4.2 shows the clinopyroxene crystals which matched with the above discussed melts. From our interpretations in section 3 we can see that most of the crystal matches are from the M3 environment, which has the more evolved, less Mg rich composition between 73-78 Mg#.

The KDE estimates from the modelled geothermobarometry results show a peak for the more evolved crystals Mg# ~74 corresponding to the M3 environment, and another peak showing the temperature of formation at ~984-989 °C (Figure 4.3). These same crystals also gave output pressures of 1.4-2.4 kbar which can be converted to depth using a crustal density of 2.3 gcm⁻³ after (Rosi and Sbrana, 1987) giving a depth of 6-11 km (Figure 4.4).

The standard error of estimate for temperatures and pressures calculated using the Masotta et al. (2013) geothermobarometer for alkali systems are 18.2 °C and 1.15 kbar respectively. The analytical errors used when calculating the error of the geothermobarometer are analogous to the techniques used to collect geochemical data in this study. It is therefore reasonable that the errors from using this barometer for my study are the same.

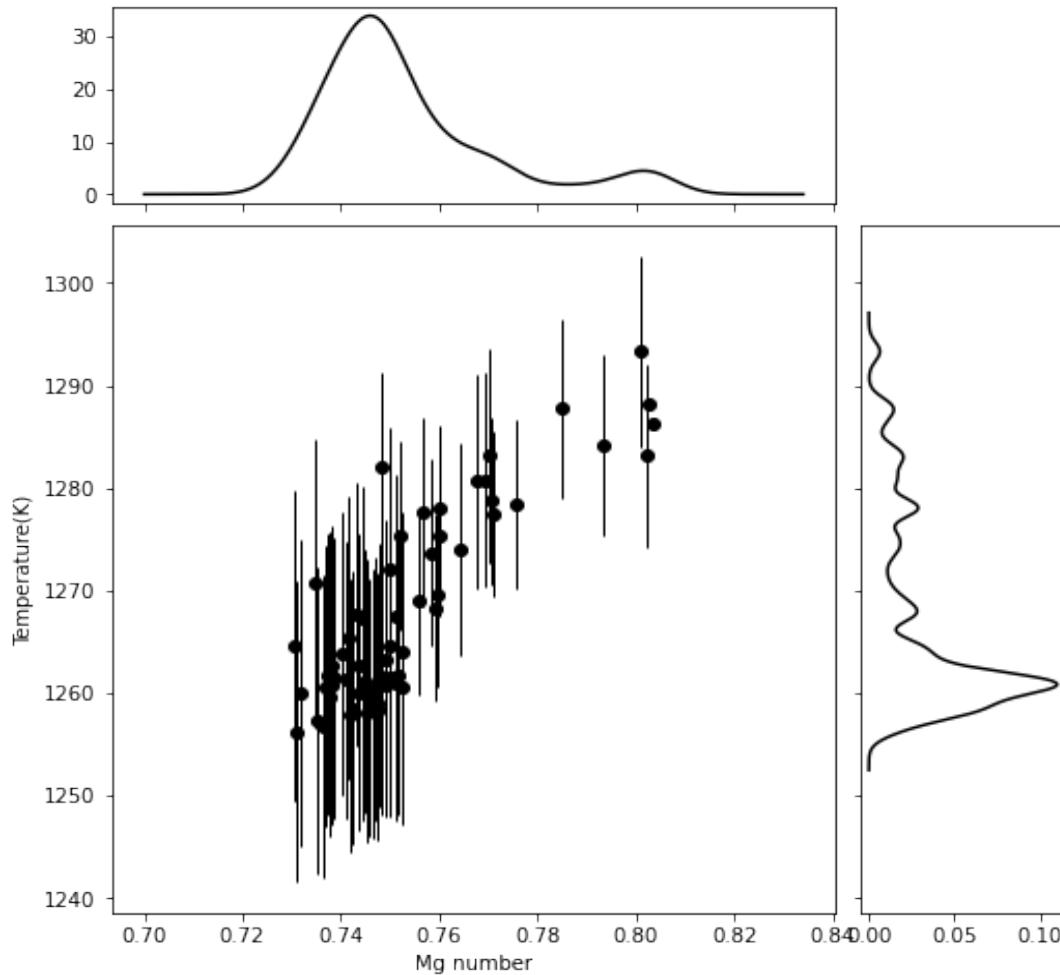


Figure 4.3. Geothermobarometry results temperature versus Mg#
Geothermobarometry results temperature versus Mg#. Kernel Density estimates above and right determine the statistical significance of output crystals compositions and calculated temperatures of crystallization.

4.3 Geothermobarometry discussion

The melt matches from the geothermobarometric modelling that came from non-Monte Nuovo eruptions originate from the Monte Sant'Angelo eruption, this edifice is < 2km from the Monte Nuovo. Of the liquids input into the model the equilibrium matches found were more Mg rich 0.65-1.76 MgO wt%. Some melts have anomalous compositions which lie outside the main clusters (Figure 4.1) however, these outlier compositions were collected from melt inclusions from within my CF195 clinopyroxene crystal samples, and so it is expected for these crystals to form from these anomalous melts which they enclose. This also proves the validity of our method.

Of the melts input into the Thermobar tool it was the more mafic (higher in Mg-Fe) that

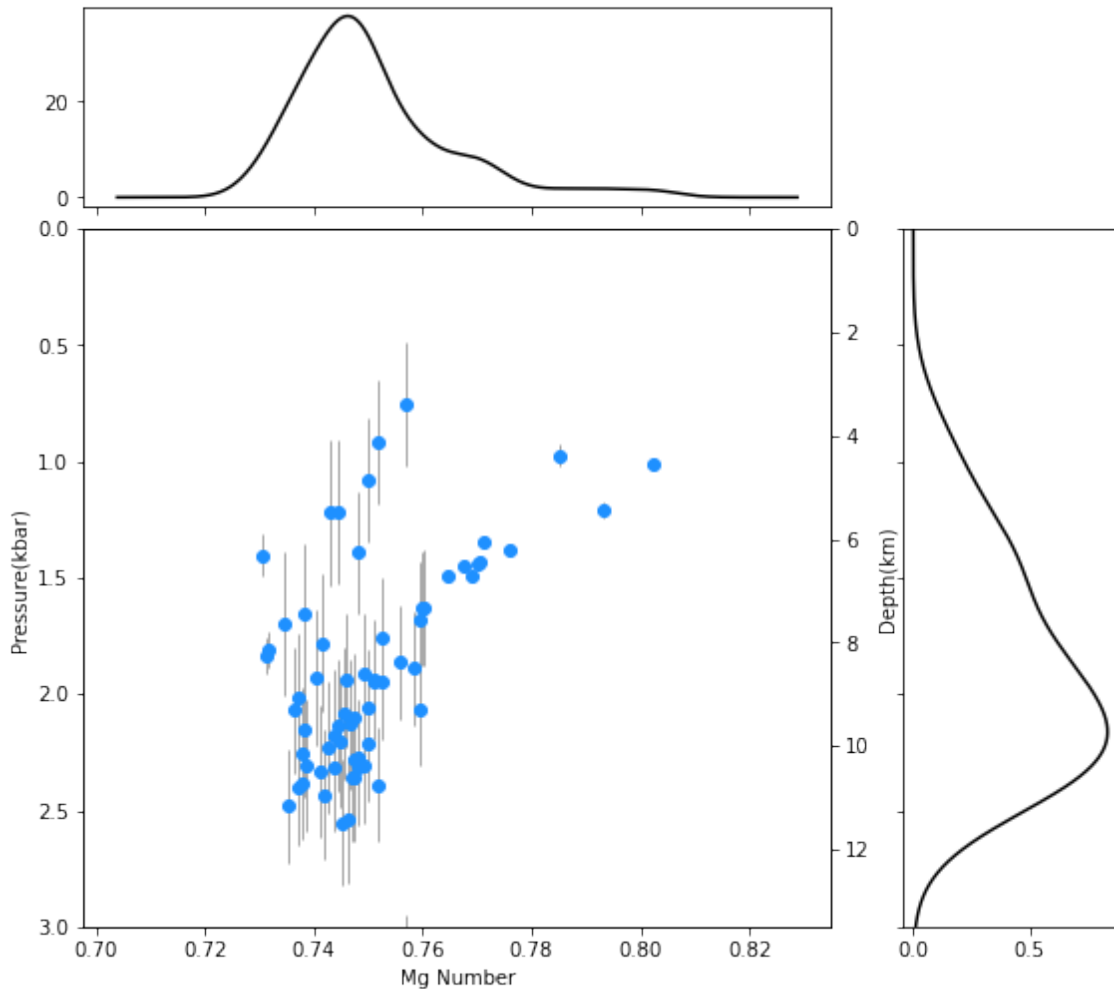


Figure 4.4. Geothermobarometry results pressure/depth versus Mg#

Geothermobarometry results pressure/depth versus Mg#. Kernel Density estimates above and right determine the statistical significance of output crystals compositions and calculated pressures of crystallization. Depths calculated using $P = \rho gh$.

matched with the input crystals. As seen in Figure 4.1 there is a large proportion of more evolved melts that do not match with any of the input crystals. Clinopyroxene comes onto the liquidus at around 1150 °C and actively crystallises down to around 900 °C, after which the clinopyroxene is still stable but doesn't crystallise in such large relative proportions (Brey and Green, 1977). At this point other crystals continue forming within the melt however, clinopyroxene is unlikely to record the further evolution of the melt at these lower temperatures (Brey and Green, 1977). Assuming a normal geothermal gradient these more evolved liquids (0-0.65 wt% MgO), which do not match with the input crystals are likely lower temperature melts which reside higher in the system, undetectable by geothermal barometric modelling of clinopyroxene crystals. There are two potential

explanations for the location of these melts within the system; firstly these melts may be residing in the shallow storage region < 3 km deep identified by seismic tomography and melt inclusion data (Section 1.2.a and references therein). Alternatively, these melts are residing in the upper part of the deeper storage system as an evolved “roof zone” such as that identified in the Bushveld complex, South Africa (Cawthorn, 2013).

The input crystals matched using the Thermobar tool are mostly the more evolved M3 crystals, we do not have a significant number of matches from the M2 or M1 environments to discern statistically significant temperature or pressure estimates for these regions. This is an expected result as the input melts are fractionation products of more mafic liquids within the system. These more mafic crystal compositions have formed within the more mafic melts which are located deep within the system. Crystals are entrained within erupted melt but these primitive mafic melts from which they originate do not erupt. This analysis means we have three potential melts;

1. The most mafic melt which does not erupt but was the growth environment for the M1 and M2 clinopyroxene crystals.
2. The intermediate melt, identified in our geothermobarometric results as a storage region between 6-11 km depth at a temperature 984-989 °C, where the M3 crystals grew.
3. The evolved melt 0-0.65 wt% MgO identified in the literature whole rock, melt inclusion, and glass data (Section 4.2) which has no crystal matches and so is likely <900 °C and stored at a currently undetermined shallower depth.

The temperatures of crystallisation ~984-989 °C calculated using the geothermobarometric modelling are within error of the temperatures of melt storage calculated by other studies (e.g. Pelullo et al. (2022), Astbury et al. (2018)). Depths calculated agree with the identification of a deep storage region ~6-11 km beneath the Campi Flegrei caldera (see section 1.2.a and references therein). These parameters are only applicable to the M3 crystal compositions. The rims of Group 1, Subgroup 3C, and Subgroup 4A, and the core of Subgroup 2B. For recharge-to-eruption diffusion to have occurred within this temperature/pressure range the rim of the crystal is the M3 environment as diffusion occurred making Group 1, Subgroup 3C, and Subgroup 4A crystals the most appropriate recharge-eruption timescales via diffusion chronometry (Section 5).

The crystals do not display evidence of crystallisation at shallow depths, suggesting that the erupted magmas did not undergo prolonged storage at the depth of recent bradyseismic activity. Hence, our data agree with previous studies (Stock et al., 2018b) which have suggested that recent Campi Flegrei eruptions are fed by magmas ascending directly from the mid–lower crust and undergo minimal interaction with magmas that have stalled at shallow depths. Analogous to other systems such as the Galapagos Wolf Volcano (Stock et al., 2018a)

5. Diffusion Modelling

5.1 Diffusion modelling experimental methods

In this study the compositional gradient between Mg-Fe is assessed using diffusion coefficients calculated by using the expression provided by (Müller et al., 2013):

$$D^{\text{Fe-Mg}} = 2.77 \pm 4.27 * 10^{-7} \exp\left(\frac{-320.7 \pm \frac{16\text{kJ}}{\text{mol}}}{RT}\right) \text{m}^2/\text{s}$$

Where R is the gas constant and T is the temperature in Kelvin.

The diffusion coefficient was calculated along the C-axis of the crystal, consequently compositional transects in this study were also taken along the C-axis. Both initial and boundary conditions need to be appropriately chosen prior to modelling. Key variables influence the rate of diffusion across this chemical boundary which must be considered to validate how robust the calculated timescales are. Two key variables which can influence calculated timescales by orders of magnitude are temperature and crystal growth. In this study a temperature of ~984-989 °C calculated via geothermobarometric modelling (Section 4) was input into the model. The clinopyroxene point compositions which successfully matched with the Epoch III and Monte Nuovo melt compositions grew in the more evolved M3 environment. It is reasonable to infer, assuming a normal geothermal gradient and considering the normal zoning texture exhibited by the crystals analysed, that the temperature range in which these evolved crystal rims grew is that of the final magmatic environment and therefore the temperature at which diffusion occurred. The crystal growth component to diffusion is more difficult to incorporate into the model. Figure 5.1 shows prominent decoupling between Mg# and Al, this same trend can be seen in ~70% of

analysed crystals. Decoupling between fast diffusing elements (Fe-Mg) and slow diffusing element (Al) indicates growth dominated zonation. Due to time constraints of this study the growth component was not incorporated into the diffusion model therefore timescales calculated are maximum timescales.

The aim of this study is to correlate diffusion timescales with pre-eruptive signals recorded in historical chronicles of Monte Nuovo, the final compositional zone boundary closest to the rim of the crystal gives the final movement of the crystal prior to eruption (Figure 5.1). This is the boundary across which I took a compositional transect from the EDS element maps (Section 2.3). Due to the maps recording the major and minor element concentrations

across the face of the entire crystal, only

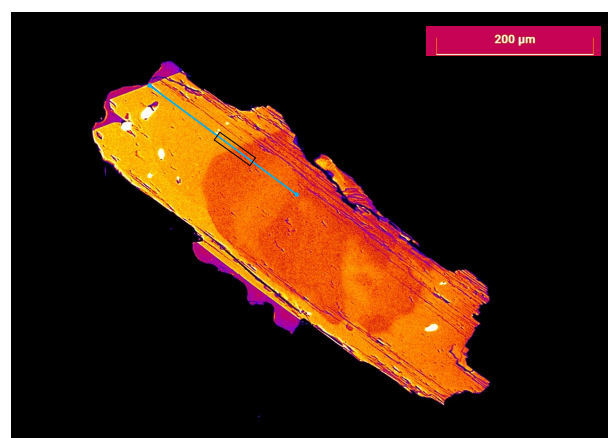
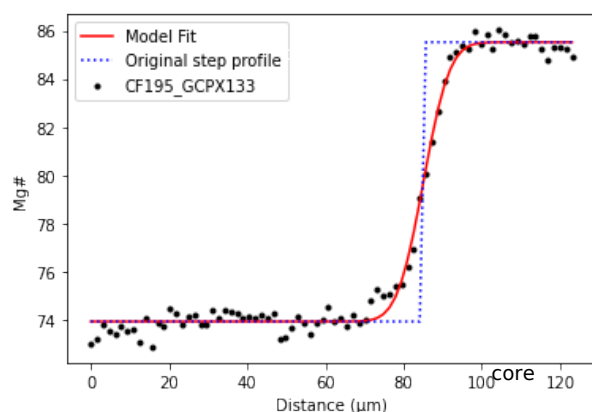
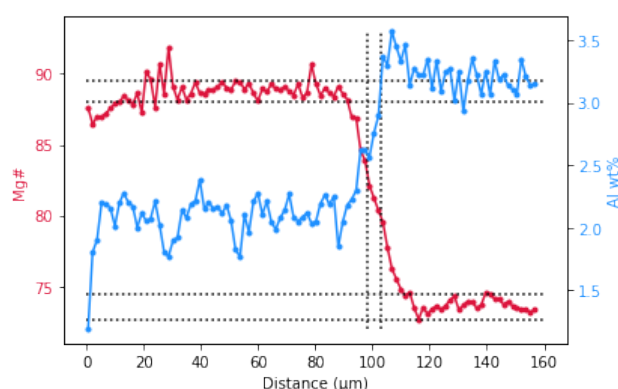


Figure 5.1. Diffusion modelling step profile experimental methods crystal CF195_GCPX133.

A) CF195_GCPX133 BSE image showing orientation of profile drawn following the C-axis. Blue line represents the full extent of profile drawn and data collected. Black box represents the approximate area of the data that was used in the diffusion model.



B) Distance (μm)/Mg# plot of CF195_GCPX133. Black points = Raw data collected from profile. Blue dash = theorised original profile before diffusion occurred. Red = model fit to profile.



C) Distance (μm)/ Mg and Al. This figure shows decoupling between the two elements suggesting growth was a large factor in the diffusion across the zone boundary.

one transect was required from each crystal as it was easy to visually identify and avoid artefacts which may influence the compositional data during acquisition. All transects (rim-core) were taken across a normally zoned boundary from the M3 to M1 environment. The majority of these transects were taken from Group 1 crystals (n= 16) however, a small number were taken from Subgroup 3C/4A (n= 3) as they had a good final zone boundary along the C-axis with compositional zone from the M3-M1 environment (rim-core). In total n= 19 number of crystals used in the diffusion study.

The diffusion model used was developed for Olivine Fe-Mg diffusion and adapted for clinopyroxene Fe-Mg diffusion by Mutch et al. (2019). Alongside standard step-profile diffusion modelling it also incorporates Bayesian statistics to robustly characterise the uncertainties in the diffusion chronometry by calculating the probability of different variables based on the degree of certainty of an event. As well as calculating a timescale it also gives the probability of that timescale versus other variables such as temperature in giving the most likely scenario from which reasonable conclusions can be drawn. For each geochemical profile analysed a level of uncertainty is calculated for each parameter, this is then displayed as a normal distribution to see what the most likely value for each parameter is. An example of this output can be seen in Figure 5.4.

Profile	Time (years)	Temperature (°C)
CF195_CPX8	68±35	987
CF195_CPX29	46±24	987
CF195_CPX40	58±32	987
CF195_CPX65	28±15	986
CF195_CPX67	32±17	986
CF195_CPX84	94±51	986
CF195_CPX140	71±35	986
CF195_CPX164	256±117	989
CF195_CPX224	9±5	987
CF195_GCPX5	49±24	988
CF195_GCPX22	25±12	986
CF195_GCPX48	172±76	986
CF195_GCPX75	253±113	985
CF195_GCPX83	42±22	987
CF195_GCPX87	50±25	986
CF195_GCPX116	286±128	984
CF195_GCPX118	31±16	988
CF195_GCPX125	187±87	987
CF195_GCPX133	28±17	990

Table 5.2. Table of median results from diffusion modelling per crystal

5.2 Diffusion modelling results

Table 5.2 shows the results from the diffusion modelling including the median timescale for each crystal as well as the median temperature of the zoning modelled. Figure 5.3 shows a histogram that estimates the temperature of M3 where rims formed and diffusion occurred. Temperatures are calculated based on the input temperature range as well as Bayesian statistics performed for each crystal to calculate the most likely temperature at which each crystal formed. An example of this output for CF195_GCPX133 is shown in Figure 5.4. KDE peaks for the median temperatures calculated from each crystal suggest that the crystals formed at a temperature $\sim 987\text{-}988^\circ\text{C}$.

Figure 5.5 is a histogram of the most likely timescales calculated from the Monte Nuovo eruption shows a significant peak shown by the KDE ~ 36 years prior to eruption. Whilst it is important to remember that this timescale is the maximum timescale as growth was a factor in the development of compositional profiles and not differentiated from the diffusion process by this model, this timeline is consistent with the start of the period of uplift in 1502 noted in historical chronicles (Di Vito et al., 1987).

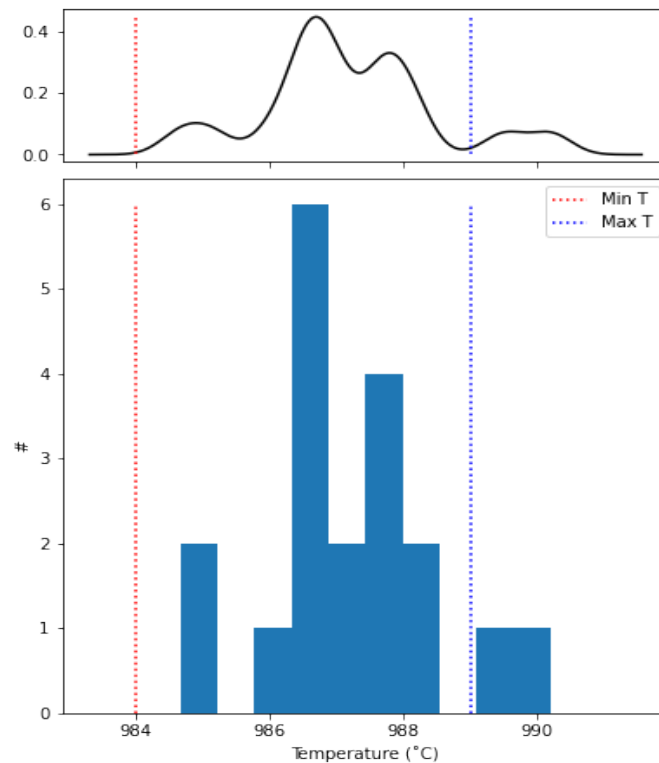


Figure 5.3. Histogram showing the temperature of crystallization calculated using diffusion modelling. Min and max dashed lines indicate the input parameters calculated from the geothermobarometric modelling (Section 4).

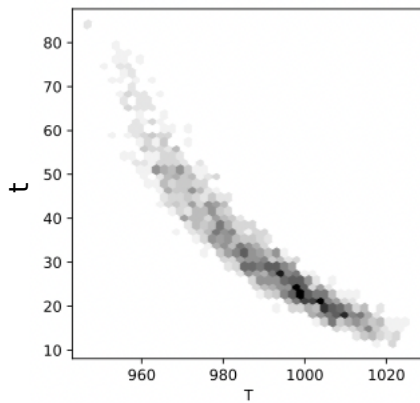


Figure 5.4. Temperature-time density plot for CF195_GCPX133 intensity of the greyscale indicates the probability of the temperature calculated being the temperature that the crystal formed in. Using the median value from this data we have a robust temperature estimate of crystallisation under which the diffusion was occurring.

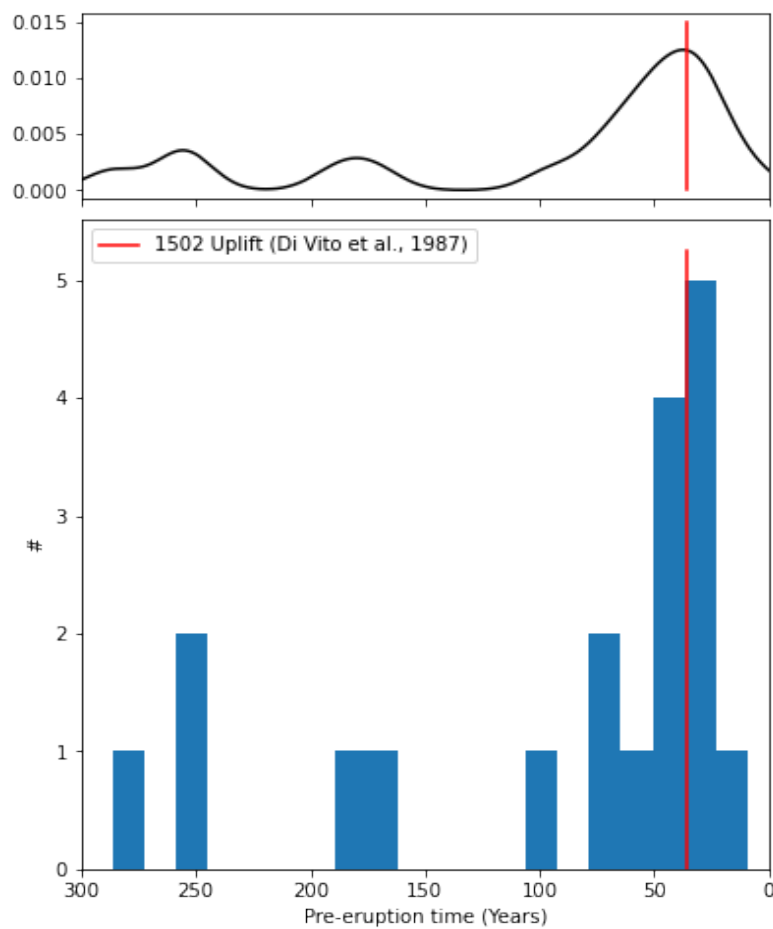


Figure 5.5. Histogram showing the recharge-to-eruption timescales of diffusion. The KDE plot indicates a peak 36 years prior to eruption. The red line shows the time uplift began and was documented in prehistoric chronicles (Di Vito et al., 1987).

5.3 Diffusion modelling discussion

When calculating timescales via diffusion chronometric modelling, varying the temperature can systematically dramatically change the results. The use of Bayesian statistics within the diffusion model allowed us to refine the temperature range calculated via the clinopyroxene melt match geothermobarometry (Section 4). This crystallisation temperature of $\sim 987\text{--}988^\circ\text{C}$ is within error of other studies which calculate the temperature of Campi Flegrei magmas (e.g. (Pelullo et al., 2022, Astbury et al., 2018)) and also lies comfortably within the temperature range established by the thermobarometry (red and blue lines in Figure 5.3).

Our diffusion modelling records the Fe-Mg diffusion across the normally zoned M1-M3 boundary core-rim, as discussed in Section 3 this change is likely caused by the crystals moving from one melt environment to another. Figure 5.5 demonstrates that this transfer occurred ~ 36 years before the 1538 eruption. As discussed in Section 1.2.b there have been a variety of techniques used to assign timescales to the recharge-to-eruption rate at Campi Flegrei. Other diffusion studies at Campi Flegrei assign timescales to the Agnano-Monte Spina (AMS) eruption from Epoch III (Pelullo et al., 2022, Iovine et al., 2017). Although this is a significantly larger eruption (DRE 0.9 km^3 (Orsi et al., 2009)) in comparison to Monte Nuovo (DRE $<0.1\text{ km}^3$ (Rosi and Sbrana, 1987)) both studies give recharge-to-eruption timescales of <60 years. Given the scale of the Monte Nuovo eruption is significantly smaller than the AMS eruption it is reasonable to suggest that the period of recharge prior to eruption was shorter. Therefore, a recharge-to-eruption timescale in the order of decades prior to eruption seems consistent across diffusion studies carried out on Campi Flegrei eruptions.

The recharge-to-eruption ~ 36 year timescale correlates with the start of observed uplift within Pozzuoli detailed in historical chronicles (Di Vito et al., 1987). This suggests that the movement of clinopyroxene crystals from the more mafic M1 magma to the more evolved M3 magma was the result of a recharge event which instigated the beginning of a final uplift phase prior to the 1538 CE eruption. This is corroborated with studies from Dvorak and Gasparini (1991) who concluded that magma injection inducing expansion of the underlying magma storage region causes the episodes of rapid uplift observed at Campi Flegrei. It is suggested that the most intense inflation of magma occurs as magma from a

deeper reservoir ~8-12 km deep injects material into the speculated shallow storage region ~3 km deep (Caliro et al., 2014), this study does not support this. Though it is entirely possible that magma recharge into a shallow reservoir coincided with the recharge of magma we have observed, our barometric data suggests that the recharge event that caused the 1502 uplift occurred within the deeper magma storage region ~6-11 km deep at Campi Flegrei.

6. Conclusions and future work

6.1 Conclusions

This study identifies through detailed petrological analysis that prior to the 1538 eruption of Monte Nuovo clinopyroxene crystals were transferred from a more mafic M1 environment to a more evolved M3 environment. This M3 environment formed as a result of the melt undergoing fractional crystallisation along the liquid line of descent as well as magma mixing and contamination. This recharge event correlates with a period of gradual uplift which began ~36 years prior to the eruption within Pozzuoli detailed in historical chronicles (Di Vito et al., 1987). This magma recharge occurred in a deep storage region ~6-11 km beneath the Campi Flegrei caldera and was ~984-989 °C as determined by geothermobarometric modelling. A recharge-to-eruption timescale in the order of decades prior to eruption is consistent across diffusion studies carried out on Campi Flegrei eruptions.

6.2 Future work

This study is just a small window into the events of the 1538 Monte Nuovo eruption, and there is still future work to be done. To continue untangling the sequence of events there are numerous directions I would like to take the research further. To gain a more holistic view of the entire Monte Nuovo eruption sequence samples from different deposits of the eruptive sequence need to be analysed as well as more mineral populations within those samples.

Samples from earlier in the eruptive sequence are more likely to give indications of events

that trigger the eruption. The clinopyroxene crystals used in this study did not match with the most evolved melt compositions input into our barometer. Assuming a normal geothermal gradient this melt is likely higher in the system and thus the first to be erupted from the volcano. Due to its more evolved composition, it is also likely to be a cooler melt, because of this it is likely that it is not favourable for clinopyroxene to grow in this environment and instead other minerals would preferentially form. Therefore, it is reasonable to suggest that to detect the potential shallow storage region detected in seismic surveys via geothermobarometric analysis of crystals and assign shorter timescales that align with events immediately preceding the eruption, more evolved minerals should be analysed such as plagioclase.

To understand how the volcano behaves prior to eruption and understand patterns in its pre-eruptive behaviour it is also important to study more than one eruption. From the now three existing diffusion studies over two different eruptions we have established a recharge-to-eruption timescale in the order of tens of years. By applying these techniques to other Campi Flegrei eruptions we may be able to determine the average recharge-to-eruption rate for Campi Flegrei eruptions and determine whether the subsequent size of eruption is reflected in this timescale as hinted by the timescales assessed in this study.

Finally, our timescale is only the maximum timescale calculated through diffusion modelling. As previously stated in Section 5, the growth rate has a large influence on diffusion and vastly affects the timescales calculated. In further work, I will be adding this variable to the diffusion model to give more robust recharge-to-eruption timescales for each crystal analysed. This additional component will be included in published work from this study but was not included in this thesis due to time constraints.

7. Bibliography

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Appendix 1- EDX calibration standards

- Aluminium (Chromite)
- Calcium (Calcite)
- Chromium (Chrome-Diopside)
- Iron (Magnetite)
- Magnesium (Olivine)
- Manganese (Rhodonite)
- Nickel (Pentlandite)
- Phosphorous (Apatite)

- Potassium (Orthoclase)
- Silicon (Diopside)
- Sodium (Jadeite)
- Sulfur (Pentlandite,)
- Titanium (Rutile)
- Zinc (Sphalerite)
- Zirconium (Cubic Zirconia)

Appendix 2- EMPA calibration standards

- Silicon (Wollastonite)
- Calcium (Wollastonite)
- Iron (Pyrite)
- Magnesium (Periclase)
- Chrome (Chromium)
- Aluminium (Jadeite)
- Sodium (Jadeite)
- Manganese (Fowlerite)
- Titanium (Rutile)
- Potassium (Orthoclase)