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Geochemical fingerprinting of intermediate to distal tephra layers within pre-Campanian Ignimbrite stratigraphic sequences: evidence for volcanic sources active in Campania in the 40 - 200 ka time span

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Abstract

The wide half-graben depression represented by the Campanian Plain, in Southern Italy, has been, and continues to be, a site of intense explosive volcanism since at least 300 ka. Because of this long-lasting and voluminous activity, the products of the most ancient eruptions have often been eroded or buried by deposits from those that occurred over the last 40 ka. Thus, the stratigraphic record of hundreds of thousands of years of volcanic activity is difficult to access. The recent rapid urbanization and the closure of almost all the quarries where the ancient products were exposed, further contributed to the reduction in the number of successions, whose exposure is limited throughout the territory. Moreover, the pervasive, intense alteration characterizing the outcropping products makes the analysis of fresh glass challenging, discouraging studies concerning this time-window. On the other hand, both marine and continental ultra-distal successions provide a good record of at least a hundred of well characterized Campanian tephra older than the Campanian Ignimbrite eruption (~ 40 ka). This implies that the knowledge of the recent activity occurred at Campi Flegrei and Somma-Vesuvius is sufficiently thorough to contribute effectively to the volcanic hazard assessment, whereas the frequency and features of the ancient volcanism are still poorly known. This Ph.D. thesis aims to refine the Campanian tephra lattice contributing to bridge the gap between the very limited knowledge about the pre-Campanian Ignimbrite volcanic record in proximal-intermediate settings and the abundant findings in distal and ultra-distal settings, investigating the pyroclastic deposits outcropping at intermediate distances from the potential volcanic sources.

To cope with the paucity of well-exposed, unaltered successions, we integrated tephra layers from both outcropping and drilled sequences. Three boreholes in which previous studies had highlighted the presence of pre-CI pyroclastic deposits were selected allowing us to cover almost all the potential direction of dispersal of a Neapolitan volcanic activity. Also, some poorly defined portions of the San Gregorio Magno Basin (Southern Campania) lacustrine succession were re-investigated to refine the tephra record. Establishing a correlation between proximal and distal successions is often complicated by the different methodological approach generally used; in fact, most of the geochemical data provided on proximal deposits are produced on whole rocks and not directly comparable with the glass chemical data available for distal tephra layers. For this reason, we decided to set up a method, also suitable for

tephrostratigraphic studies, made up of successive steps pointing to provide a complete lithological, geochemical (major and trace elements) and chronological characterization ($^{40}Ar/^{39}Ar$) of the volcanic units investigated. Moreover, we also explored the potential of using the radiogenic isotopes composition of tephra layers as a correlative tool providing for most of the studied units the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ contents.

This work provides new insights to the largely incomplete reconstruction of the pre-Campanian Ignimbrite volcanism. Beside the finding of previously unknown eruptive events ranging in age between 40 and 200 ka, we also were able to recognize some peculiarities in the geochemistry of ancient products. In fact, while the geochemical features of the products emplaced in the Late Pleistocene seem to be quite similar to those of post-CI Phlegraean deposits, the late Middle Pleistocene tephra markers identified here are quite typical. The recognition of widely spread tephra markers not only in the well-known time span ranging between 90 and 110 ka but also around 158 and 175 ka has shed light on a hitherto little-known slice of the Campanian volcanic history. All the new outcomes were widely supported by the use of the radiogenic isotopes composition of the juvenile fractions, which in some cases proved essential to the proper identification and correlation of tephra layers.

Aim of the study and structure of the thesis

The volcanic history of the Campanian Plain can be dated back to ~ 2 Ma, the age determined for the fingerprints of a basaltic to andesitic calc-alkaline activity, buried under a pile of sediment 1,300 m thick, found in the Parete well (Caserta - Di Girolamo, 1978). However, the features and timing of these early stages of volcanic activity are still unknown. Similarly, the growth of the Somma-Vesuvius, as we know it today, only began after the Campi Flegrei caldera-forming Campanian Ignimbrite eruption (ca. 40 ka), but evidence of a much older (at least ca. 360 ka - Jashemsky, 2002) volcanic activity in the same area is inferred from the Trecase 1 geothermal well (Brocchini et al., 2001). Instead, the oldest volcanic products from the Campi Flegrei caldera in proximal outcrops correspond to the > 150 ka Ischia island activity and the oldest age obtained for proximal outcropping products of the continental sector dated back to ca. 78 ka (San Martino lower tephra in Scarpati et al., 2013). At least five ancient ignimbrites outcropping at intermediate distance from the volcanic sources in the Campanian Plain and at the foot slopes of the limestone reliefs that border it are reported by De Vivo et al. (2001) and Rolandi et al. (2003). These findings further shift the age of the outcropping volcanic products to nearly 290 ka. However, the very few outcrops of pre-Campanian Ignimbrite products often consist of strongly altered deposits and their general poor state of preservation prevents in many cases both the precise field description and the geochemical characterization of the juvenile fragments. The reasons for the lack of outcrops of such ancient products are manifold. The Campanian volcanic area is a still active volcanic zone, therefore the products of the numerous volcanic eruptions occurred at Campi Flegrei and Somma-Vesuvius and the emplacement of voluminous ignimbritic eruptions such as the Campanian Ignimbrite (39.85 ± 0.14 ka $^{40}Ar/^{39}Ar$ dating - Giaccio et al., 2017b), Masseria del Monte Tuff (29.3 ± 0.7 ka $^{40}Ar/^{39}Ar$ dating - Albert et al., 2015, 2019) and Neapolitan Yellow Tuff (14.9 ± 0.4 ka $^{40}Ar/^{39}Ar$ dating – Deino et al., 2004) caused burial and/or erosion of the preceding products. What is more, at least two of these highly-explosive Campi Flegrei eruptions were associated to caldera collapses that produced the displacement and the sinking of the older products. As many other cities, also Naples, Pozzuoli and their neighbourhoods in the last decades have experienced an intense and often uncontrolled expansion of the urbanized area that has contributed to the obliteration of the already scarce number of outcrops. This intense urbanization also affected most of the urban centres in the Campanian Plain, where the older products has been studied. Moreover, the introduction of stricter laws for quarrying activities at the end of the last century led to the abandonment of many quarries along whose walls the products of the older volcanic activity were exposed. Nowadays most of the quarries are no longer in use and have been gradually filled in with alluvial sediments (and sometimes even used as landfills) and closed preventing any further study on these successions.

On the other hand, the great boost given in the last decades by the Quaternary research to the use of tephrostratigraphy as a tool to provide high-resolution records for paleo-environmental and archaeological reconstructions shed new light on the fragmentary history of the pre-Campanian Ignimbrite volcanism. Indeed, further clues to the ancient activity of this volcanic area have emerged from the tephrostratigraphic records of distal and ultra-distal Early/Middle to Late Pleistocene marine and lacustrine sedimentary successions. The impossibility to correlate each of these distal findings to a proximal counterpart because of the almost complete lack of both good outcrops and geochemical analyses on the ancient products, which when performed are almost never referred to the glass fraction, led to generically attribute them to Campi Flegrei in virtue of the major element geochemical composition (e.g. Paterne et al., 1986; Wulf et al., 2004 among the others). Assuming that their geochemical features similar to the post-Campanian Ignimbrite products of Campi Flegrei testify to a Campanian origin, the occurrence of about a hundred eruptive events is pinpointed by distal and ultra-distal tephra layers. This evidence could meaningfully backdate the onset of the highly explosive volcanic activity in Campania and supply useful information to increase the knowledge about its frequency. Thus, beyond tephrostratigraphy and tephrochronology, the proper identification and correlation of distal ash layers with proximal pyroclastic deposits can aid in the reconstruction of the spatial distribution of the products increasing our ability in evaluating the volcanic hazard. In fact, some of these tephra layers are spread as far as the Balkans and Greece testifying to the occurrence of highly explosive volcanic eruptions throughout the Middle-Late Pleistocene.

As it has just been highlighted and will be explained in more detail in the Introduction, the knowledge of the Campanian volcanic history is largely unbalanced. Geochemistry and eruptive features of the products emplaced after the Campanian Ignimbrite and, even more, the Neapolitan Yellow Tuff eruptions at Campi Flegrei, as well as the Somma-Vesuvius products, are well-known and contribute effectively to the volcanic hazard assessment. In contrast, the pre-CI volcanic history is represented by a few widespread main tephra markers and many reports of distal occurrences without a proximal counterpart. Thus, the largely incomplete proximal-intermediate record contrasts with a tephra-rich distal record that testifies to a large number of events in the Campanian Plain volcanism.

Under this premise, it seems clear that an attempt should be made to bridge this gap. For this reason, a new field investigation in the Campanian Plain and at the foot slopes of the limestone reliefs surrounding it was carried out to recover new accessible outcrops and overcome the inaccessibility of most of the previously studied successions. Most of the efforts were focused on the eastern and northeastern sectors of the plain, taking into account the main dispersal direction of umbrella clouds of Plinian and sub-Plinian eruptions from Neapolitan sources. To cope with the scarce number of outcrops and with their poor exposure we decided to integrate the field data with those produced on the pyroclastic products embedded within drilled successions, which are supposed to ensure better preserved and more continuous records. The three boreholes selected were drilled at different distances from the potential volcanic sources and in different directions from the potential source. In fact, the San Marco Evangelista borehole (SME – Santangelo et al., 2010) is located in the northern sector of the plain, in the Caserta area, the Camaldoli della Torre borehole (CdT – Di Renzo et al., 2007) on the southern slopes of Somma Vesuvius and the Sarno San Vito borehole in the eastern sector, in the Sarno alluvial Plain (Santo et al., 2019). The selection of these successions allowed us to cover almost all the potential directions of dispersal of an ancient explosive activity from the Neapolitan area. In addition to the intermediate outcropping and drilled successions, we also selected some poorly defined intervals of the distal San Gregorio Magno Basin succession (SGM - Munno and Petrosino, 2007). This strategy aims to maximize the potential results despite the very limited data available trying to rationalize the fragmentary knowledge and even the miscorrelations that characterise the pre-Campanian Ignimbrite volcanism and the related tephra.

In addition to this integration between buried and outcropping sequences, we had to face some difficulties inherent in the products we were working on. Given the scarcity of available outcrops, and their poor state of preservation, which makes the deposits of the so called "ancient ignimbrites" (De Vivo et al., 2001; Rolandi et al., 2003) very similar to each other, a careful and accurate stratigraphic study was combined with the assessment of the geochemical composition of the products in order to avoid misinterpretations due to the association of different deposits only on the basis of their field characteristics. To this aim, a multi-methodological approach was carried out (Figure 1). As previously stated, the common feature of the juvenile fractions of the pre-CI products is a pervasive alteration. During the preparation of the samples for the geochemical analyses, an accurate selection of the glass fragments was performed in order to be sure to work on the least altered products and on all types of juveniles present in the deposit. The glasses extracted from the tephra layers were chemically characterized in terms of major elements using the SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectroscopy). Although, the tephrostratigraphic correlation of distal tephra layers has been traditionally based on the major element composition, in the last decade many tephrostratigraphic studies have deepened the geochemical fingerprinting of the glass fragments providing data on the trace element composition. In addition to better characterizing the products of the eruptions, trace elements can provide important information about the volcanic source and can help us overcome the obstacle of changes in major element content caused by alteration also relying on fluid-immobile trace elements ratios. Therefore, we selected the samples for Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS) on the basis of their relevance in the stratigraphic reconstruction, of the availability of glass fragments suitable (in terms of size) for this technique and not affected by alteration. Comparing our stratigraphic and geochemical results with the previous literature, we also decided to carry out $^{40}Ar/^{39}Ar$ age determinations on sanidine crystals extracted from some crucial volcanic units.

It is worth noting that one of the latest advances in the fingerprinting of tephra layers is the assessment of the isotopic composition of Sr and Nd of the juvenile fragments. The main application of this approach is related to the possibility of distinguishing the volcanic source that emplaced the tephra layer. However, the still unexplored potential of the application of the Sr and Nd isotopic composition as a correlative tool supporting tephrostratigraphy needs to be further deepened. For this reason, and with the additional aim of enriching the almost non-existent comparative database for proximal pre-Campanian Ignimbrite deposits, most of the volcanic units were also characterized in terms of their radiogenic isotopes composition.

The Ph.D. project is part of the FUTURE research project (FUcino Tephrochronology Unites Quaternary REcords - PRIN 2017) framework. It is a granted PRIN (No. 20177TKBXZ_003; G. Zanchetta: coordinator; M. D’Antonio, B. Giaccio and D. Palladino, UR responsible) supported by MIUR (Italian Ministry of Education, University and Research) and co-funded by DFG (German Research Foundation - grant WA 2109/16). The project involves national and international institutions such as the Universities of Pisa, Rome-Sapienza, Naples-Federico II,

Cologne and LSCE-Paris Saclay and IGAG-CNR, IGG-CNR, INGV-OV research institutes. The main objective of the project is to obtain a high-precision tephrochronological record, supported by $^{40}Ar/^{39}Ar$ dating, for the Fucino lacustrine succession. As a part of the University of Naples Federico II UR, this Ph.D. thesis accomplishes the role of deepening the knowledge about the pre-CI volcanic history from the Campanian volcanic sources providing the complete characterization of tephra levels.

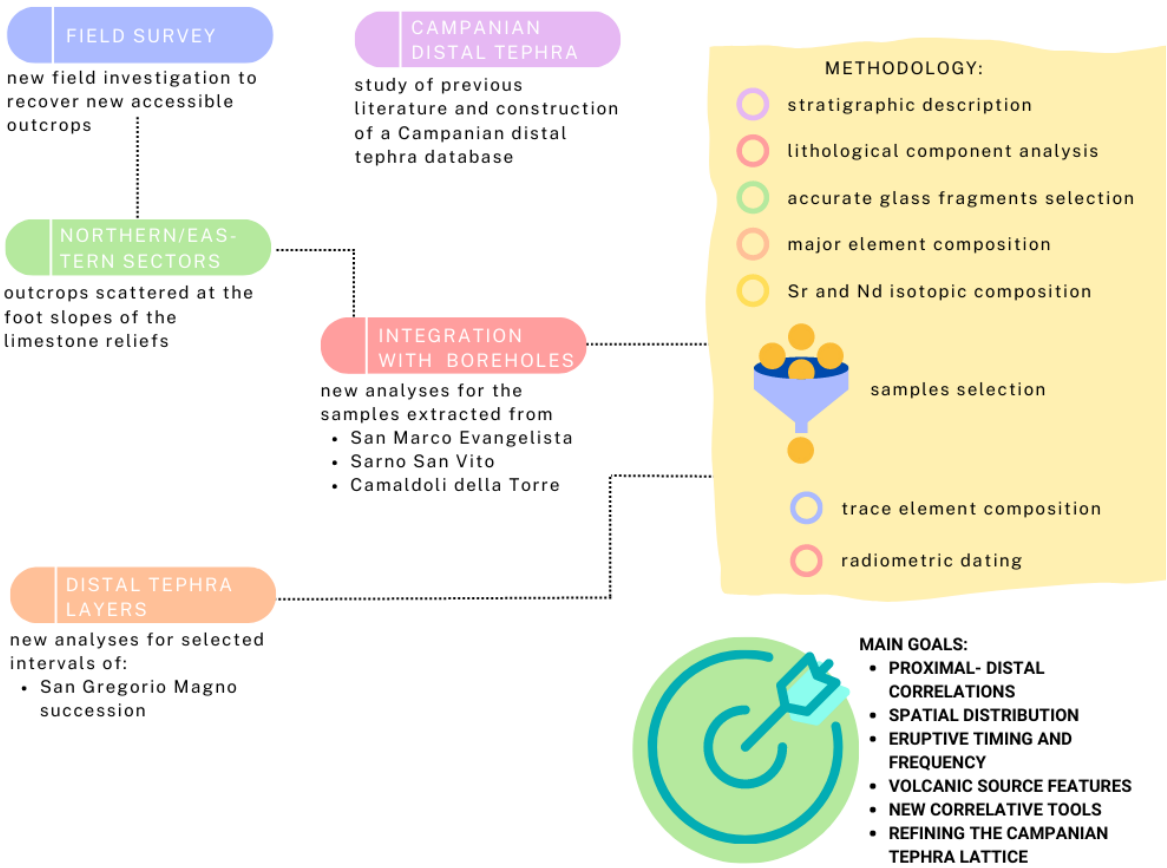

Figure 1 - Flow chart evidencing the main steps of the strategy developed for the Thesis.

The thesis is divided into different chapters, the content of which is articulated as follow:

- Chapter 1: the first chapter is devoted to an introduction that deals with the main aspects of tephrostratigraphy and then summarises the pre-Campanian Ignimbrite volcanic records in proximal, intermediate and distal (and ultra-distal) settings. Moreover, the few previous applications of the radiogenic isotopes composition to tephrostratigraphic investigations are outlined.

- Chapter 2: the second chapter explains the multi-method approach used during the investigation. It also explains the reasons for the selection of samples for the trace element and isotopic analyses.

- Chapter 3: the third chapter is devoted to the summary of the samples used during this study. In particular, section 3.1 reports a brief summary of the description of the Camaldoli della Torre, San Marco Evangelista and San Gregorio Magno drilled successions, already investigated by other authors and here re-analysed.

- Chapter 4: the fourth chapter reports the results of the analyses carried out on the samples. Each section is sub-divided into different sub-sections, according to the age of the studied tephra layers (from 39 to 120 ka: Late Pleistocene; from 130 to 200 ka: late Middle Pleistocene).

- Chapter 5: the fifth chapter is dedicated to the discussions. In the first part (section 5.1) the pre-CI record in the Late Pleistocene is investigated. During this period the emplacement of some of the most important and well-studied Campanian tephra markers occurred. This part of the thesis concerns the time span ranging between ca. 39 to ca. 121 ka. The interpretation of the results allowed us to make interesting observations about the tephrostratigraphic correlation of the analysed tephra layers with distal and ultra-distal markers. Some remarks are also made on the isotopic composition and the source of the volcanic products emplaced between 39 and 121 ka.

The second part (section 5.2) deals with the tephra layers older than 130 ka. The oldest sample analysed has an age of about 185 ka. This time span is poorly known, especially in areas proximal/intermediate with respect to the volcanic sources. In this part of the thesis, I have contributed to deepen the knowledge about the late Middle Pleistocene volcanic activity in the Campanian Plain by increasing the data about the frequency of large eruptive events. The interpretation of the results allowed me to present several previously unknown volcanic events. In addition, some comments are made on the isotopic composition and the source of the volcanic products emplaced between 130 and 185 ka.

- Chapter 6: in the last chapter of the thesis, conclusions and main outcomes about the whole investigation are reported.

1. Introduction

2. Methods

During this study we carried out a new field investigation on the foothills of the limestone reliefs surrounding the Campanian Plain to recover new accessible outcrops. In fact, a great number of the previously studied outcrops are now inaccessible. Moreover, as already highlighted, the products of the pre-CI activity in the Campanian Plain are scattered and poorly exposed. To cope with this problem, we decided to work also on tephra levels embedded within the successions of 3 boreholes drilled in different localities of the Campanian Plain. The 3 drilled sites are located at different distances from the potential volcanic sources, respectively at Camaldoli della Torre (CdT – Di Renzo et al., 2007), on the southern slopes of Somma-Vesuvius, and in medial-distance sites in Sarno alluvial Plain (Santo et al., 2019) and at the foot slopes of the limestone reliefs in the Caserta area (San Marco Evangelista – SME – Santangelo et al., 2010). The location of the drilling sites in different direction from the potential source, being located to the north, south and east from them, allowed us to cover almost all the potential dispersion paths of an ancient explosive activity from Neapolitan area. Moreover, we re-sampled some intervals of the San Gregorio Magno (SGM) succession (Munno and Petrosino, 2007). Although some of those successions had been already investigated in the past, we felt it was necessary to carry out a detailed tephra analysis, using modern techniques and in the light of more than a decade of new results. The main purpose was to obtain a fully comparable data set in order to find some important tephra markers missing from the record and to better define poorly constrained intervals.

To use the tephra layers as a tool of correlation between proximal/intermediate outcrops and distal records, it is necessary to obtain a lithological and geochemical characterization of the studied levels. This is even more important taking into account the lack of knowledge that affects the pre-CI volcanic record. To this aim, a multi-methodological approach was carried out applying some of the best practices summarised by Wallace et al. (2022) and references therein. The glasses extracted from the tephra layers were chemically characterized in term of major elements using the Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS). For selected samples, the most important and crucial to define the record, we also provided trace element compositions by the means of Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS). Since the traditional geochemical characterization alone is often not able to provide sufficient information to define the volcanic source that produced the investigated level, the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ were determined on glasses and minerals thanks to the use of the Multi-Collector Thermal Ionization Mass Spectrometry (TIMS). Using isotopic compositions, we also would like to assess potential changes in the volcanic sources over time. Since the mineral fraction of tephra could be partly inherited (i.e., xenocrystic) so that it might not reflect the isotopic composition of the magma, we preferred to collect the glass juvenile fraction by hand picking for isotopic determinations, in the case of samples containing abundant and fresh glass. Finally, to better constrain outcropping successions and boreholes, we selected 10 samples to carry out $^{40}Ar/^{39}Ar$ age determinations on sanidine crystals.

Applying the described multi-analytical approach to samples from both outcropping sections and drilled successions we attempted to consolidate the tephra framework in the poorly constrained scenario of the pre-CI volcanic activity in the Campanian Plain.

In the first stages of the research, during the study of the previous contributions to the pre-Campanian Ignimbrite tephrostratigraphic framework, it was considered necessary to rationalize the geochemical data previously produced on the tephra layers to allow comparison of the investigated volcanic units with literature data. To this aim, a geochemical database containing major and trace elements, and when available radiogenic isotopes composition, of Campanian tephra layers was built. The database currently consists of at least 280 Excel® sheets, which in the future could be easily exported in Access® to allow fast and complex querying. For the sake of completeness and to avoid inheriting miscorrelations, the database also includes records of tephra layers from volcanic sources other than Campanian for the time interval outlined in section 1.2.3. Each Excel® sheet is identified and labelled as follows: age of the tephra layer, name of the eruption, volcanic source. The structure of the sheet contains in the first column the reference paper from which the data were obtained (also marked with a different colour for each reference) and in the second column the name of the sample. In the case of previously unknown eruptions or tephra layers ascribed to an uncertain source, the name of the sheet retains the sample identification code and the chronostratigraphic position attributed to it by the authors. Given the heterogeneity of the data available in the literature, when individual point glass analyses were available, they have been included in the database, while where the only data available was the average composition, this is given next to the sample name. To ensure the completeness of this database, it is clearly necessary to keep it updated with new published data and new attempts to refine pre-existing correlations.

2.1 Sample pre-treatment

Samples collected from the Sarno San Vito, San Marco Evangelista and San Gregorio Magno boreholes and in the field were dry sieved at 1φ interval sieves, cleaned with ultrasonic probe and dried at 60 °C. For some samples, containing a large amount of fine ash/clay fraction, the cleaning step was repeated several times. Sometimes, even these additional steps were not enough because of the high alteration degree of the levels.

For samples from Camaldoli della Torre borehole (except for CdTj 204.5, CdTg 214.4, CdTf 217.2, CdTc 222.7, CdTc 227.6, CdTc 229.4 samples) the authors that originally investigated the drilled succession (Di Renzo et al., 2007) only made available for the new analyses some coarse fragments of the juvenile fraction. For this reason, the pumice fragments were gently crushed with the help of an agate mortar and pestle. The crushed fractions were repeatedly sieved at 1φ interval during crushing, cleaned with ultrasonic probe and dried at 60 °C. Some samples (i.e.: CdTj 204.5, CdTg 214.4, MAD_AEU_A-5, MAD_AEU_A-6, MAD_AEU_B-2b, MAD_AEU_B-3a and MAD_AEU_A-1 basal ash) were partially or completely lithified or cohesive and were disaggregated using H_2O and dried at 60 °C before dry sieving.

All the different grain size fractions thus obtained (from 101 samples) were observed at the optical stereomicroscope for a semi-quantitative evaluation of lithological component distribution and the preparation for chemical analyses. Six samples resulted from the pre-treatment were not prepared for the chemical analyses because: - three were sub-samples of largely sampled units; - one was almost totally made up of lithic fragments; - two were represented by a lithified ignimbrite, and fresh glass fragments were not found after pre-treatment. Total grain size analysis and relative percentage by weight were not assessed because many samples were either aggregated or highly altered.

2.2 Major element compositions

To compare and correlate the chemical composition of the investigated tephra layers with that of the tephra horizons found in marine cores of the Mediterranean Sea and in lacustrine ultra-distal successions, individual point analyses on juvenile glass fraction must be carried out. In order to obtain a comparable database, containing major and trace elements data, all the samples (from levels already analysed in the SGM and SME cores and from the new sampling) were prepared through hand picking of fresh glasses under the optical stereomicroscope.

At least 30 juvenile fragments extracted from the +2φ fraction of ninety-seven samples were picked up and mounted in epoxy resin and suitably polished to be characterized in terms of major element composition through SEM-EDS technique. For five of these samples the absence of fresh glasses precluded the successful outcome of the analysis.

The Scanning Electron Microscope (SEM) is an instrument that uses a focused beam of electrons emitted from an electron gun to produce high-resolution and high-zoomed images of a sample (Figure 2.1 A). The electrons of the incident beam interact with the sample surface and its atoms giving information about its topography and composition. The beam has an energy typically ranging between 0.2 and 40 keV and is focused by condenser lenses making the spot range from 0.4 to 5 nm in diameter. During the interaction between the electron beam and the sample, several electromagnetic radiations are generated, such as secondary electrons, backscattered electrons, Auger electrons, characteristic X-rays and visible light. Secondary electrons can be used to produce very high-resolution images because, in virtue of their very low energies and brief mean free path in the sample, they emerge from the very top portion of the specimen. Backscattered electrons have higher energy and emerge from deeper portions of the sample producing lower-resolution images. However, they can provide information about the distribution of elements with different atomic number in the sample; in fact, materials with higher atomic number return a brighter image. When the SEM is equipped with an X-ray energy dispersion spectrometer (EDS) and, as it is possible for modern SEMs, a wavelength dispersion spectrometer (WDS), a quantitative determination of the chemical components of the sample can be obtained. The SEM is capable to analyse even very small samples that need to be coated with a conductive layer of carbon or gold (in the present case, we used carbon) facilitating the removal of electrical charges from the sample, which could interfere with the image formation.

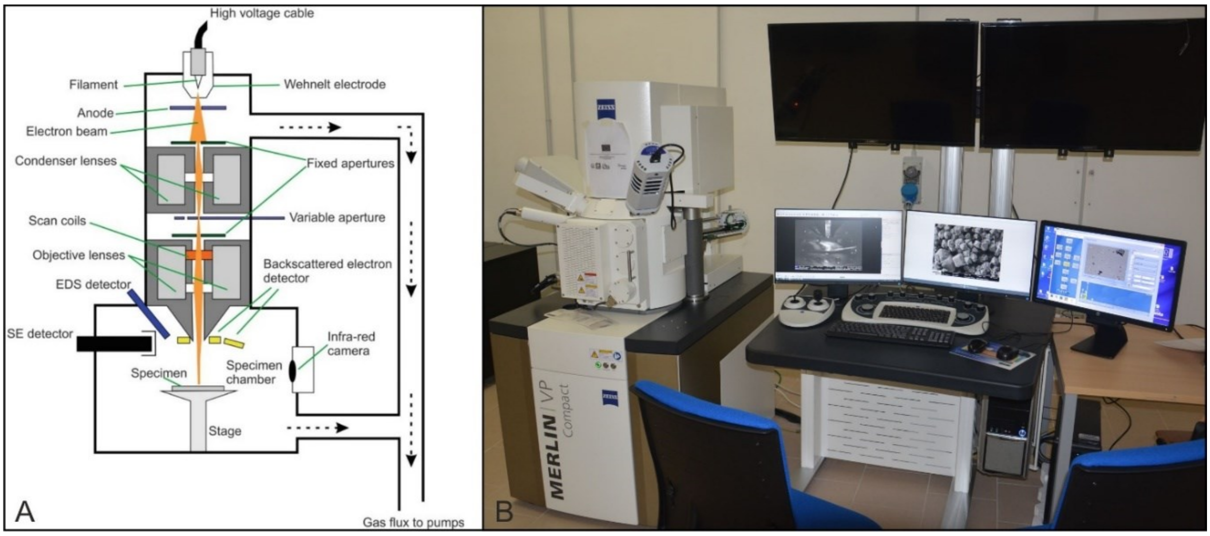

Figure 2.1 – A: sketch of the main parts of an SEM-EDS; B: Field Emission Scanning Electron Microscope (SEM) at DiSTAR – Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse – University of Napoli Federico II. From Petrosino et al. (2023).

The analyses were carried out at the DiSTAR SEM laboratory (University of Naples Federico II) (Figure 2.1 B). The micro-analytical measurements were performed using a Field Emission Scanning Electron Microscope (FESEM) Zeiss Merlin VP Compact, used together with an X-ray energy dispersion spectrometer (EDS) and an X-ray wavelength dispersion spectrometer (WDS), equipped with four analytical crystal(s). EDS operating conditions were 15-kV primary beam voltage, 60-mA filament current, 10-s acquisition time and variable spot size. The quant optimization was carried out using cobalt (FWHM–full width at half maximum peak height- of the strobed zero = 60–65 eV). The INCA version 4.08 software was employed to perform the correction for matrix effects. The software uses the XPP correction routine, based on a Phi-Ro-Zeta approach. Primary calibration was performed using international mineral and glass standards. Individual analysis of glass shards with total oxide sums lower than ~ 95% were excluded. Standards of the international set labelled USNM were used as follows: Anorthoclase 133,868 for Si, Na and Al, Microcline 143,966 for K, Fayalite 85,276 for Mn, Anorthite 137,041 for Ca and Hornblende 143,965 for Fe, Mg and Ti. Precision was <5% for SiO_2, Al_2O_3, K_2O, CaO and FeO, and around 10% for the other elements. Precision and accuracy were assessed using the rhyolitic Lipari obsidian ID3506 and basaltic Laki 1783 CE tephra (Kuehn et al., 2011) as secondary standards. Na and Cl were also tested in WDS, with 15-kV primary beam voltage, 60-mA filament current, 8.5 work distance, 300-120 micron aperture, 20-s acquisition time and variable spot size.

2.3 Trace element compositions

Trace element analyses of selected samples were performed at the Department of Physics and Geology, University of Perugia on the same juvenile fragments mounted on epoxy resin prepared for the SEM-EDS analyses. Samples selection was determined by three main factors: a) relevance of the tephra layer to the preliminary stratigraphic reconstruction; b) availability of glass fragments suitable (in terms of size) for the Laser Ablation technique and unaffected by alteration; c) homogeneity of major element composition of the sample: for samples covering a wide range of composition it is necessary to map them prior to the trace element analysis. Unfortunately, it is not always possible with small glass fragments such as those we handled.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is a powerful micro-analytical technique used to provide high sensitivity analyses (down to ppb level) on solid samples. This technique is applied in a wide range of study fields such as archaeometry, biology, geology and so on. A focused laser beam is used to "ablate" a portion of the sample surface, creating an aerosol transported by a carrier gas to the ICP-MS instrument. Here the vaporized sample is ionized by the Inductively Coupled Plasma torch and the excited ions are analysed by the Mass Spectrometry instrumentation (Petrelli et al., 2007a; 2007b; 2008; 2016). Major elements, such as Si and/or Ca, can be acquired together with trace elements and this is particularly useful in the case of analyses of loose glass fragments to recognize the potential different composition of the several glasses mounted in the epoxy resin. A frequent complication during the tephra analysis is represented by the possible presence of micro-crystals into the glass fragments. The occurrence of microlites close to the ablation pit of a glass shard to be analysed might result in a mixed composition. To avoid or limit this effect, we used a laser diameter of 15, 20 or 25 µm. The acquisition time for the samples and the standards was 30 s.

The instrumentation is represented by a Teledyne/Photon Machine G2 LA device equipped with a two-volume ANU HelEx 2 cell coupled with a Thermo Scientific quadrupole-based iCAP Q ICP-MS device (Figure 2.2). Before each analytical session, the operating conditions were optimized by continuous ablation of international reference standard NIST SRM 612 to provide maximum signal intensity and stability for the ions of interest, while suppressing the formation of oxides (ThO^+ /Th^+ below 0.5%). The U/Th ratio was also monitored and maintained close to 1. The stability of the system was evaluated based on ^{139}La, ^{208}Pb, ^{232}Th

and ^{238}U by a short-term stability test consisting of five acquisitions (1 min each) on a linear scan of international reference standard NIST SRM 612. The glasses object of this study were analysed by using a circular laser beam with a diameter of 15, 20 or 25 µm, depending on the type and size of the glass fragments, a frequency of 8 Hz and a laser density on the sample surface of 3.5 J cm−2. The NIST SRM 610 reference material was used as a calibrator, and ^{29}Si as an internal standard. The USGS BCR2G reference material was analysed as unknown to provide a quality control (the analyses of the standard are reported in Appendix 3.2). Under these operating conditions precision and accuracy are better than 10% for all elements. Further details on the instrumentation are reported in Petrelli et al. (2016).

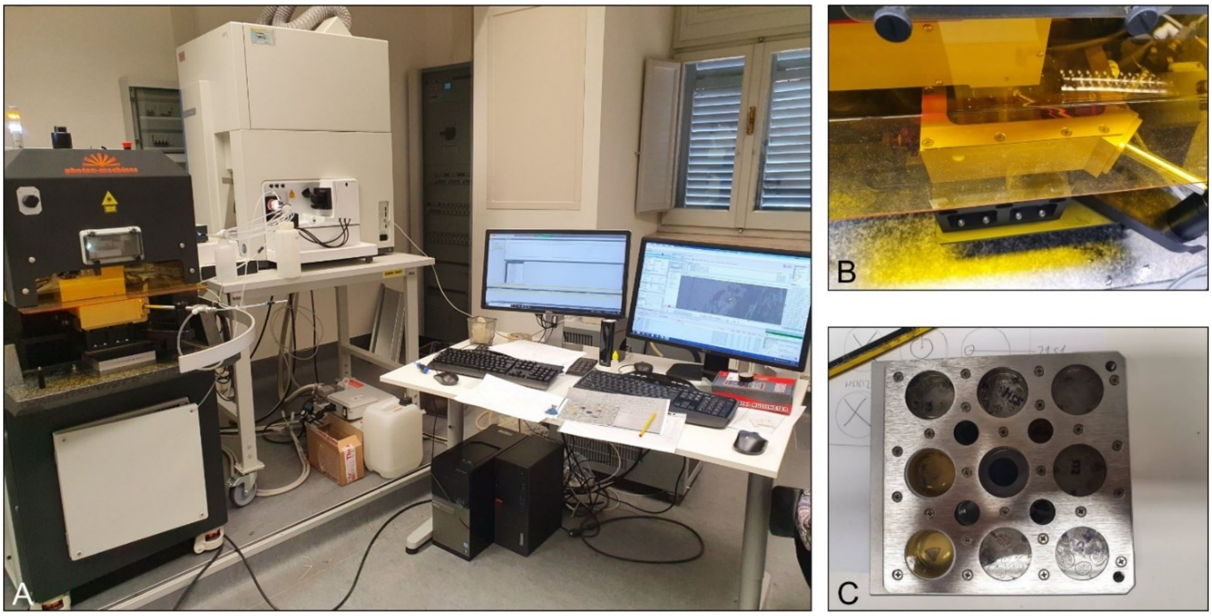

Figure 2.2 – A: Teledyne/Photon Machine G2 equipped with a Two-Volume ANU (Australian National University) HelEx 2 cell at Department of Physics and Geology, University of Perugia; B: sample holder into the HelEx II 2-Volume Tunable LA-ICPMS Cell; C: sample holder for round chips of 1 and ½ inches.

2.4 Sr and Nd isotopes

For samples selected for isotopic analyses, an aliquot of glass fragments or crystals (pyroxene or feldspar) was hand-picked under an optical stereomicroscope (Figure 2.3 A, B). At least 0.05 g of material (weighted through a high-precision analytical balance - Figure 2.3 C) were selected in the case of volcanic glasses and pyroxene crystals and 0.02 g in the case of feldspar crystals and successively washed in an ultrasonic bath using Milli-Q® water. The entire procedure for the isotopic analyses was carried out in an ISO 6 class clean room at Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR, University of Naples Federico II). In particular, the use of a Plexiglas laminar flow hood equipped with two

HEPA filters was necessary to guarantee a clean working environment during all the steps from sample pre-treatment, through dissolution, to Sr-Nd separation from the matrix.

The first step of the procedure involves leaching of the separated volcanic glasses and crystals with Suprapur® grade 6 N HCl for 10’ on a hot plate at ca. 80 °C, and then the rinsing with Milli-Q® water (18.2 MW resistivity) for 5’ on a hot plate (Figure 2.3 D, E). This first step was repeated three times to eliminate possibly present secondary carbonate. The leached samples were solubilized using three successive acid mixtures (Suprapur® grade HF-HNO_3-HCl); the first acid attack is prolonged for two days, the other two for one day each.

Sr and Nd were separated from the matrix through conventional cation-exchange chromatographic techniques on quartz columns filled with either AG® 50W-X8 (for Sr and Rare Earth Elements) or Ln Spec® (for Nd) resins and using diluted Suprapur® grade HCl as eluent (Figure 2.3 F – further details are described in Arienzo et al., 2013). During the period of chemistry processing, the blank for Sr was ~100 pg, negligible compared to the average Sr content of the studied materials, estimated to be in the range ~ 1 - 1,000 ppm based on literature data and trace element analyses (Fedele et al., 2009; Di Renzo et al., 2007). In such a clean laboratory no determination for Nd blank was deemed to be necessary. The samples were loaded on a previously outgassed tungsten filament (Figure 2.3 G, H, I). The isotopic composition of Sr and Nd was determined in the same laboratory through Thermal Ionization Mass Spectrometry (TIMS) techniques using a Thermo Scientific Triton Plus® mass spectrometer (Figure 2.4 A).

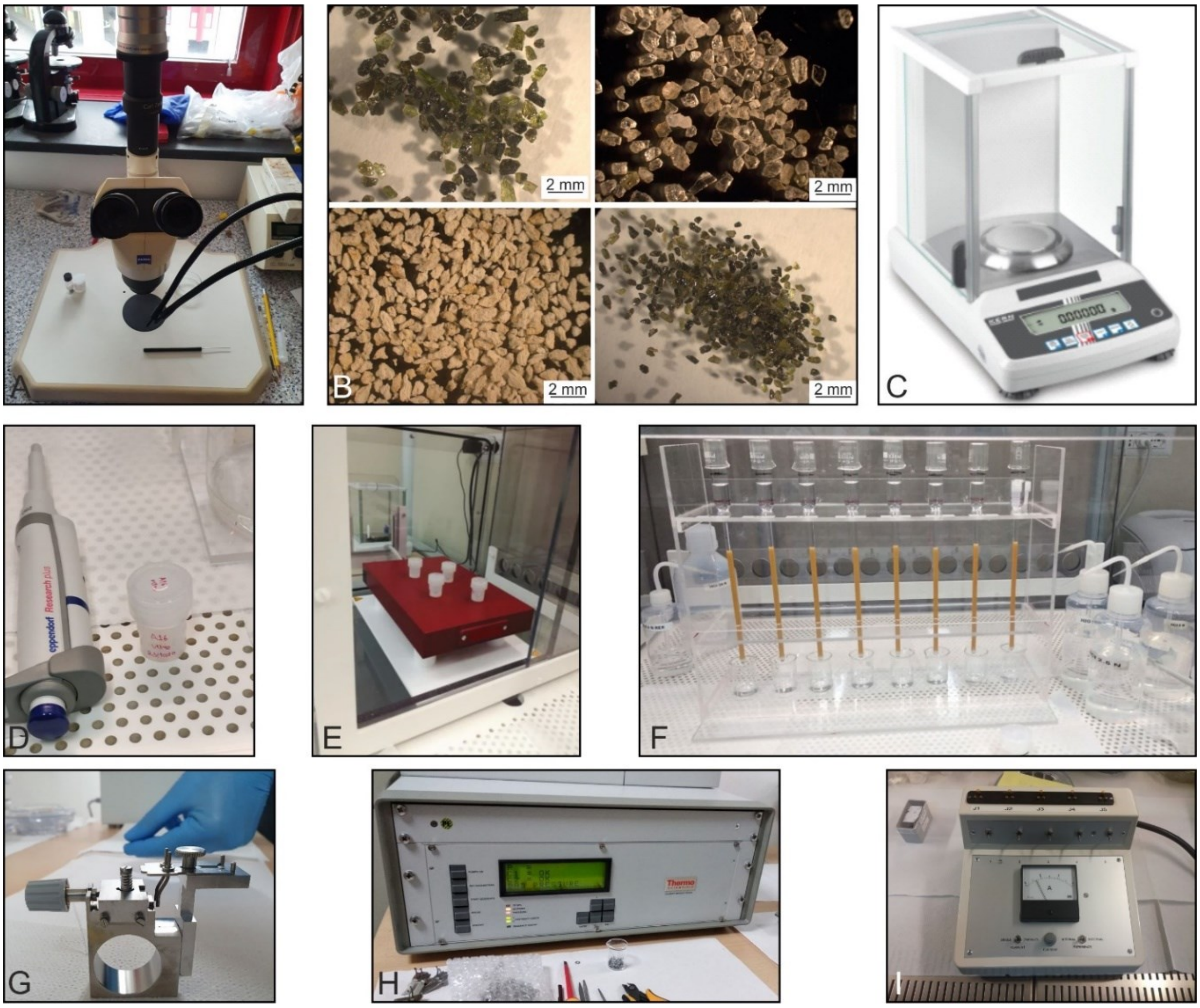

Figure 2.3 – The figure shows the main steps for the preparation of the samples to the isotopic analysis. A: optical stereomicroscope used to select juvenile or crystal fractions; B: examples of selected glasses and crystals; C: high-precision analytical balance; D: pipette and Savillex® vials used in the clean room; E: PFA-coated, acid-resistant hot plate, with Savillex® vials on top for sample digestion; F: chromatographic columns filled with cation exchange resin used to separate Sr and REE from samples; G: tool for the welding of the tungsten ribbon on steel supports; H: filament degassing unit; I: filament sample loading unit.

The TIMS, used in geochemistry, geochronology, environmental and planetary geochemistry, is an instrument that measures isotopic ratios with high precision and accuracy (Figure 2.4 B). The ions are created by the passage of a current into metal ribbons (made up of tungsten, tantalum or rhenium) under high vacuum. Then, the ions are accelerated across an electrical potential gradient (up to 10 KV) – always under vacuum – to a magnetic field where they are separated according to their M/C (mass to electric charge ratio). These different-mass beams are directed into collectors that convert them into voltage. By comparing signals (voltages) of different ion beams, precise isotope ratios are provided.

The Triton Plus is equipped with one fixed and eight adjustable Faraday cups to acquire simultaneously several ion beams in static mode. 2σmean, i.e., the standard error with N = 150, was better than ± 0.000009 for both Sr and Nd measurements. In-run isotopic fractionation was corrected through normalization of measured $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios to $^{88}Sr/^{86}Sr$ = 8.37521 and $^{146}Nd/^{144}Nd$ = 0.7219, respectively. During the period of analysis, replicate measurements of NIST–SRM 987 ($SrCO_3$) and JNdi–1 international reference standards were carried out to check for external reproducibility, 2σ (σ is the standard deviation of the standard results, Goldstein et al., 2003), obtaining the following mean values: $^{87}Sr/^{86}Sr$ = 0.710251 ± 0.000013 (N = 34) for NIST–SRM 987; $^{143}Nd/^{144}Nd$ = 0.512095 ± 0.000006 (N = 67) for JNdi–1. The measured Sr and Nd isotope ratios were normalized to the recommended values (Zhang and Hu, 2020) of NIST–SRM 987 ($^{87}Sr/^{86}Sr$ = 0.710248 ± 0.000012 (σ)) and JNdi–1 ($^{143}Nd/^{144}Nd$ = 0.512107 ± 0.000012 (σ)) standards, respectively.

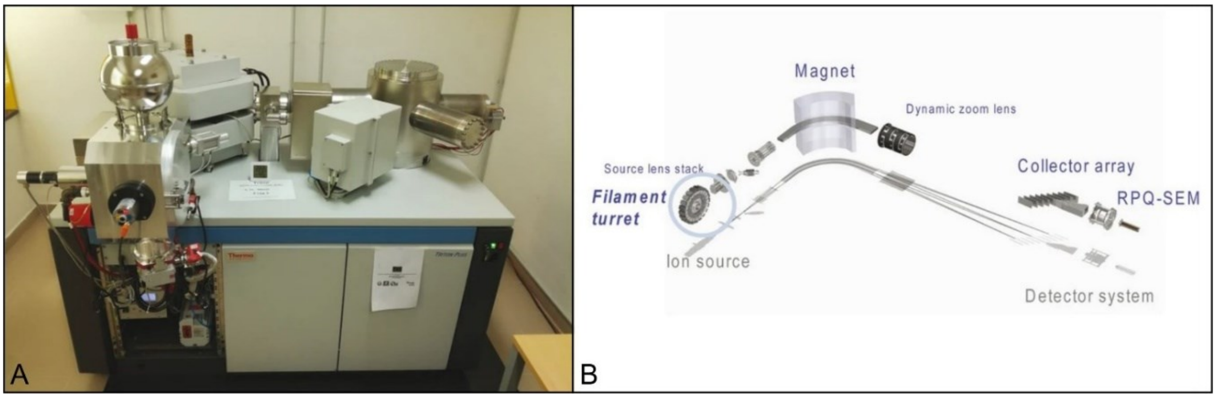

Figure 2.4 - A: Triton Plus® thermal ionization mass spectrometer at DiSTAR – Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse – University of Napoli Federico II; B: technical scheme of the Triton Plus®. From D'Antonio et al. (2023).

2.5 $^{40}Ar/^{39}Ar$ dating

The $^{40}Ar/^{39}Ar$ dating method is a variant of K/Ar geochronology and it is very versatile because it allows to date a wide-ranging variety of K-bearing materials that refer to a very large time span (from a few thousand years to the age of the solar system itself, in virtue of the 1.248 × 10^9 yr half-life of ^{40}K). It is based on the radioactive decay of ^{40}K to ^{40}Ar, which naturally occurs. Magma, during an eruption, equilibrates with the atmospheric argon and K remains within its crystals. Once the magma has solidified, the ^{40}Ar begin to accumulate by continuous decay of the ^{40}K and, unless alteration or metamorphic processes occur, it is retained within the rock. Both K/Ar and $^{40}Ar/^{39}Ar$ techniques are based on the same principle, with differences in the method of measurement applied. In the first case, the two elements (K and Ar) are measured separately on two different aliquots of the sample. The time since the crystallization is obtained by measuring the ratio between the ^{40}Ar accumulated and the ^{40}K remaining, the half-life of ^{40}K (1.248×10^9 yr) being known. Instead, the ^{40}Ar/^{39}Ar technique, which is the most used nowadays, requires only one aliquot of sample. The potassium contained in the samples is irradiated with neutrons in a nuclear reactor to produce ^{39}Ar from ^{39}K. The conversion is performed by bombarding them with ^{235}U causing ^{39}K to absorb a neutron and eject a proton becoming ^{39}Ar (Kelley, 2002; Renne, 2006). The age determination requires the measurement of ^{40}Ar produced by the radioactive decay of ^{40}K and of ^{39}Ar produced by the irradiation of the same aliquot of sample, allowing the age to be calculated from the argon isotopes ratio (Twyman, 2007). By co-irradiating a standard of well-known age (in our case the 1.1864 Ma Alder Creek sanidine - Jicha et al., 2016) it is possible to define the irradiation parameter *J*. Then, the sample is loaded into an ultrahigh-vacuum system where it is subject to fusion. The resulting gases are purified and introduced in a static gas-source mass spectrometer for isotopic analysis (Schaen et al., 2020).

The two main modes for evaluating ^{40}Ar/^{39}Ar are the laser step-heating and the single-crystal total fusion (Lee, 2015). In laser step-heating, a laser beam characterized by a large-diameter progressively heats single crystals following a series of steps of increasing temperature until the crystal is completely melted and fused into a glass bead. The argon isotopes released by the heating during each step are analysed in a mass spectrometer to obtain an ^{40}Ar/^{39}Ar age for each. The use of a defocused beam is essential to uniformly heat the entire crystal in each step. The complete sequence of steps allows to obtain an ^{40}Ar/^{39}Ar apparent age spectrum. This mode can be used when the sample pertains to a rock that may have cooled slowly or been affected by metamorphism or local heating to clarify potential age gradients within rock crystals. In single-crystal total fusions, a single mineral crystal is completely melted in one step by a laser using a focused or slightly defocused beam. The result is an ^{40}Ar/^{39}Ar age for the crystal deduced by the released argon isotopes analysed in a mass spectrometer. This age is identical to the integrated age that would be obtained from an ^{40}Ar/^{39}Ar apparent age spectrum. This mode is most used when the dating material is available in a limited amount of sample, when the crystal sizes are very reduced, or when the study is focused on the provenance of crystals that may come from a variety of source rocks of different ages. The data are presented in the form of a probability density diagram of total fusion age versus relative probability.

Fresh sanidine crystals were hand-picked from selected samples to obtain the $^{40}Ar/^{39}Ar$ age of ten tephra levels determined from laser fusion of single crystals. The analyses were conducted at the Geochronology Laboratory of University of Wisconsin–Madison.

3. Materials

A preliminary field survey carried out in the frame of this thesis and the results of previous research mostly for unpublished master's theses (e.g. Costantini, 2015; Penna, 2016) showed that the entire pyroclastic products outcropping in the area to the south of the Campania Plain and corresponding to the Sorrento Peninsula and the valleys that shape it are affected by such a strong alteration as to prevent the analysis of the glass fragments. For this reason, most of the efforts were focused on the eastern and northeaster sectors of the plain between Caserta and Moschiano (AV).

Along with outcropping successions studied at Valle di Maddaloni ("Piano delle Crete" locality), Maddaloni S. Salvatore sanctuary, Maddaloni quarry, Polvica quarry, Acqua Feconia and San Giovanni del Palco (Taurano), we decided to include tephra levels from some boreholes to cope with the paucity of well-exposed pre-CI products. We selected three drilled sediment cores to be included into the framework of the thesis and some samples from the San Gregorio Magno borehole. The location of the studied outcrops and drill holes is reported in Figure 3.1 and Table 3.1.

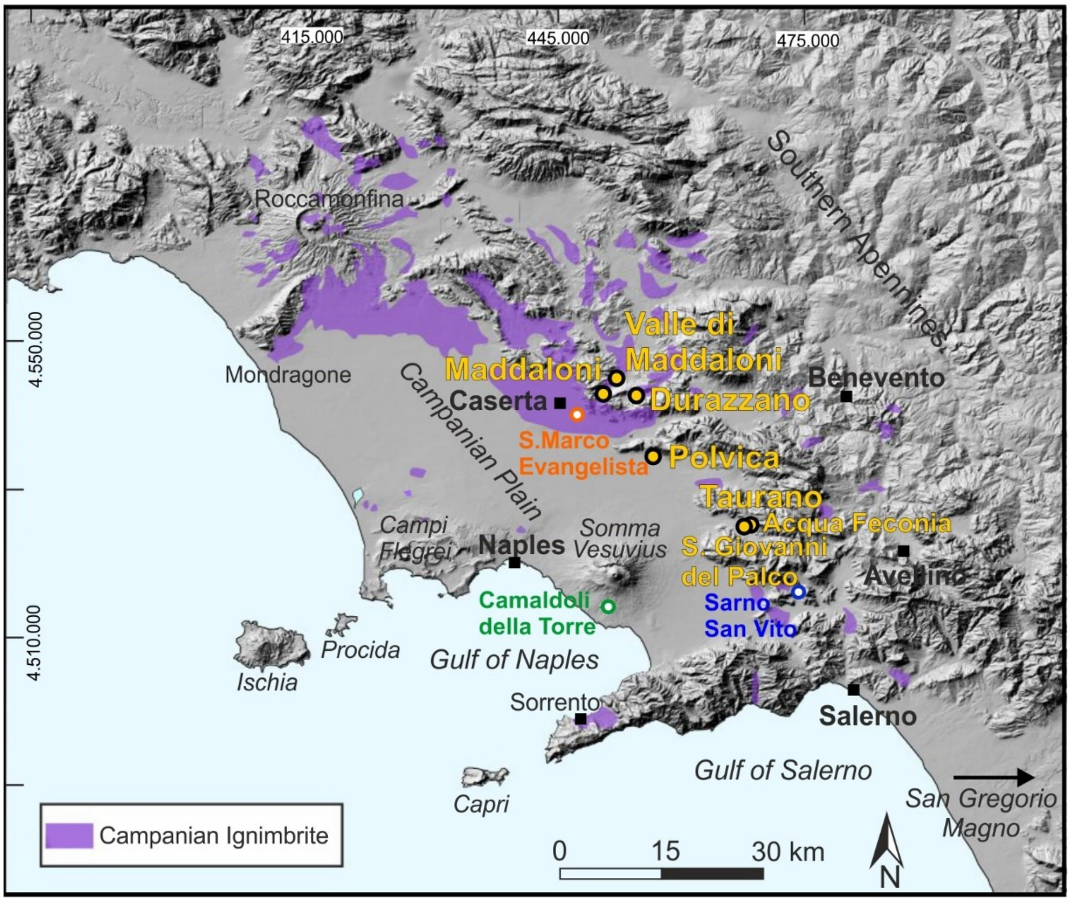

Figure 3.1 - Location of studied outcrops (yellow circles) and drill holes (white circles with coloured outline) sites.

Table 3.1 - Summary of the studied drillholes and outcropping successions location.

Succession type	Location	Latitude	Longitude

During the field survey 49 samples from 7 localities were collected. Where variations in the grain-size or in the colour of clasts could be identified, two or more samples were taken from the same volcanic unit. The samples comprise both clast supported and matrix supported tephra layers characterized by a thickness between ~ 1 cm and ~ 3.5 m. Moreover, 52 samples from 4 boreholes were selected for this study. Almost all the investigated samples are characterized by a medium to high alteration degree of the juvenile fragments. The whole Sarno San Vito cored succession was here studied for the first time and the samples containing primary tephra layers were selected for geochemical analyses. Also, samples from the previously studied boreholes of Camaldoli della Torre (Di Renzo et al., 2007) and San Marco Evangelista (Santangelo et al., 2010) were included in this new analytical phase together with 8 samples from some poorly defined intervals of the distal San Gregorio Magno Basin succession (Munno and Petrosino, 2007). Six out of these eight samples come from the original sampling of Munno and Petrosino (2007), while two new horizons were sampled for the first time (SG 39.60 and SG 37.65) to try and find possible correlatives of the products found in the field. As already highlighted in section 2.1, for samples from Camaldoli della Torre borehole (except for CdTj 204.5, CdTg 214.4, CdTf 217.2, CdTc 222.7, CdTc 227.6, CdTc 229.4 samples) we only received from the authors that originally investigated the drilled succession (Di Renzo et al., 2007) some coarse fragments of the juvenile fraction that we gently crushed with the help of an agate mortar and pestle. Since the Camaldoli della Torre, San Marco Evangelista and San Gregorio Magno drilled successions were already described in the previously quoted papers, in the next section (3.1) we report a brief summary of their description. Twenty-one samples were selected for the trace element analyses and forty-two for Sr and Nd isotopic composition. In particular, for the radiogenic isotopes composition analysis, where possible, we worked on a hand-picked fraction of selected glass fragments. For most of the samples extracted from the Sarno San Vito borehole two different fractions were selected (glass, where possible, and feldspar/pyroxene or feldspar and pyroxene).

In Table 3.2, the summary of the investigated tephra layers and the analyses performed on each of them is reported.

*Table 3.2 - Summary of the investigated tephra layers and type of analysis performed on the glass fragments extracted. For Camaldoli della Torre samples the depth of recovery in the drill hole is denoted by the name of the sample. * crushed pumices fraction.*

		Analysis			
Succession	**Sample (depth for drill holes m b.g.l.)**	**Major elements (SEM-EDS)**	**Trace elements (LA-ICP-MS)**	**Sr-Nd isotopes**	**^{40}Ar/^{39}Ar**
San Marco Evangelista	SEP 0 (36.5)	x			
San Marco Evangelista	SEP 1 (40.20)	x			
San Marco Evangelista	SEP 2 (41.20)	x			
San Marco Evangelista	SEP 3 (43)	x		x	
San Marco Evangelista	SEP 4 (48.9)	x	x	x	x
San Marco Evangelista	SEP 4a (49.4)	x			
San Marco Evangelista	SEP 5 (61)	x			
San Marco Evangelista	SEP 6 (67)	x			
San Marco Evangelista	SEP 7 (base of SEP6)				
San Marco Evangelista	SEP 8 (70.50)	x			
Camaldoli della Torre	CdTj 204.5	x			
Camaldoli della Torre	CdTi 211.9*	x			
Camaldoli della Torre	CdTi 212.6*	x			
Camaldoli della Torre	CdTh 213.1*	x			
Camaldoli della Torre	CdTg 214.4	x	x		x
Camaldoli della Torre	CdTg 215.3*	x		x	
Camaldoli della Torre	CdTf 216.4*	x			
Camaldoli della Torre	CdTf 217.2	x		x	
Camaldoli della Torre	CdTd 219.4*	x	x	x	
Camaldoli della Torre	CdTc 222.7	x			
Camaldoli della Torre	CdTc 227.6	x	x	x	
Camaldoli della Torre	CdTc 229.4	x			
Camaldoli della Torre	CdTa 232.5 light*	x			
Camaldoli della Torre	CdTa 232.5 dark*	x			
Camaldoli della Torre	CdTa 238.5*	x	x	x	X
Sarno San Vito	SAT 21 (6.00)	x		x	
Sarno San Vito	SAT 22 (10.20)	x		x	
Sarno San Vito	SAT 23 (14.50)	x		x	
Sarno San Vito	SAT 24 (17.80)	x		x	
Sarno San Vito	SAT 25 (22.60)			x	
Sarno San Vito	SAT 30 (34.50)	x		x	
Sarno San Vito	SAT 31 (35.10)	x		x	
Sarno San Vito	SAT 32 (37.80)	x		x	
Sarno San Vito	SAT 33 (39.20)	x		x	
Sarno San Vito	SAT 34 (39.70)	x	x	x	
Sarno San Vito	SAT 35 (39.80)	x		x	
Sarno San Vito	SAT 36 (40.30)	x		x	
Sarno San Vito	SAT 38 (43.10)	x		x	
Sarno San Vito	SAT 40 (44.70)	x	x	x	

Sarno San Vito	SAT 47 (57.70)	x		x	x
Sarno San Vito	SAT 52 (75.80)	x		x	
Sarno San Vito	SAT 53 (77.70)	x		x	x
Sarno San Vito	SAT 54 (78.70)			x	
Sarno San Vito	SAT 55 (79.80)			x	
San Gregorio Magno	S13 (22.70)	x			
San Gregorio Magno	S12 (24.30)	x			
San Gregorio Magno	S9 (27.90)	x	x		
San Gregorio Magno	SG 37.65	x			
San Gregorio Magno	SG 39.60	x		x	
San Gregorio Magno	S8 (40.90)	x		x	
San Gregorio Magno	S7 (41.75)	x			
San Gregorio Magno	S6 (43.80)	x			
Valle di Maddaloni	MAD$_A$ EU$_B$-3b	x		x	
Valle di Maddaloni	MAD$_A$ EU$_B$-3a	x			
Valle di Maddaloni	MAD$_A$ EU$_B$-2b	x			
Valle di Maddaloni	MAD$_A$ EU$_A$-6bisG				
Valle di Maddaloni	MAD$_A$ EU$_A$-6bisD	x	x	x	x
Valle di Maddaloni	MAD$_A$ EU$_A$-6bisB	x			
Valle di Maddaloni	MAD$_A$ EU$_A$-5	x			
Valle di Maddaloni	MAD$_A$ EU$_A$-4	x			
Valle di Maddaloni	MAD$_A$ EU$_A$-3	x	x	x	
Valle di Maddaloni	MAD$_A$ EU$_A$-2	x			
Valle di Maddaloni	MAD$_A$ EU$_A$-1	x	x	x	
Valle di Maddaloni	MAD$_A$ EU$_A$-1 basal ash	x			
Maddaloni Sanctuary	MAD$_B$ EU$_C$-7	x			
Maddaloni Sanctuary	MAD$_B$ EU$_C$-6b	x			
Maddaloni Sanctuary	MAD$_B$ EU$_C$-6a	x			
Maddaloni Sanctuary	MAD$_B$ EU$_C$-5d	x			
Maddaloni Sanctuary	MAD$_B$ EU$_C$-5b				
Maddaloni Sanctuary	MAD$_B$ EU$_C$-5a	x			x
Maddaloni Sanctuary	MAD$_B$ EU$_C$-4	x			
Maddaloni Sanctuary	MAD$_B$ EU$_C$-3	x	x	x	
Maddaloni Sanctuary	MAD$_B$ EU$_C$-2b	x			
Maddaloni Sanctuary	MAD$_B$ EU$_C$-2a	x			
Maddaloni Sanctuary	MAD$_B$ EU$_C$-1c	x			
Maddaloni Sanctuary	MAD$_B$ EU$_C$-1a				
Maddaloni quarry	MAD$_C$ EU$_A$-1	x			
Durazzano	DUR$_4$EU$_C$-10b	x			
Durazzano	DUR$_3$EU$_C$-11b cohesive	x			
Durazzano	DUR$_3$EU$_C$-11b	x			
Durazzano	DUR$_2$EU$_A$-2	x			
Durazzano	DUR$_3$EU$_C$-11a	x			x
Polvica quarry	CP6	x	x		
Polvica quarry	CP4	x			
Polvica quarry	CP3	x			

Polvica quarry	CP2	x			
Polvica quarry	CP1	x	x	x	
Acqua Feconia	AF$_5$ EU$_C$-2	x	x		
Acqua Feconia	AF$_3$ EU$_C$-1	x		x	x
Acqua Feconia	AF$_4$ EU$_B$-1b	x	x	x	
Acqua Feconia	AF$_4$ EU$_B$-1a				
Acqua Feconia	AF$_4$ EU$_A$-4				
Acqua Feconia	AF$_4$ EU$_A$-2				
Acqua Feconia	AF$_4$ EU$_A$-1				
San Giovanni del Palco	TAU 4	x	x	x	
San Giovanni del Palco	TAU 3b	x			
San Giovanni del Palco	TAU 3a	x	x	x	
San Giovanni del Palco	TAU 2d	x	x	x	
San Giovanni del Palco	TAU 2c	x		x	
San Giovanni del Palco	TAU 2a	x	x	x	
San Giovanni del Palco	TAU 1	x	x	x	x

3.1 San Marco Evangelista, Camaldoli della Torre and San Gregorio Magno boreholes

3.1.1 San Marco Evangelista

The San Marco Evangelista (SME) borehole (Santangelo et al., 2010) was drilled in 2003 in the neighbourhood of San Marco Evangelista (Caserta, Southern Italy – Figure 3.1) in the frame of the CARG Project in order to investigate the deposits underlying the Campanian Ignimbrite products. The location of the drilling site was at 32 m a.s.l. on the floor of a disused quarry from which the CI was exploited in the past; the sediment core was 80 m long (Figure 3.2). Santangelo et al. (2010) combined micropaleontologic, macropaleontologic and tephrostratigraphic studies to provide a paleogeographical reconstruction of the studied area during the last 200 ka. The CI products occur at a depth of 2 m below the ground level (under reworked material) and until a depth of 35 m. They are separated by a paleosol from 15 m of pyroclastic deposits called by the authors "Pre-Campanian Ignimbrite volcanic unit" (tephra layers from SEP0 to SEP4/4a) ranging from 49.40 to 34.80 m below the ground level and made up of pyroclastic silt and sand layers alternating with paleosols. This unit is separated from the "Lower volcanic unit" by 10 m of fossiliferous clays and silts (the "Upper fossiliferous unit"). The "Lower volcanic unit" (tephra layers from SEP5 to SEP8) is made up of gravel and sandy layers with a high content in pyroclastic material. Santangelo et al. (2010) carried out individual point glass analyses on pyroclastic layers from the drill hole. At least 8 pyroclastic layers were recognized embedded to lacustrine to marshy deposits and marine horizons, whose age was constrained through a $^{40}Ar/^{39}Ar$ age determination and stratigraphic data, between 39 and 150 ± 10 ka. However, the authors themselves do not consider the result of the age determination to be very reliable because of the partial alteration affecting the sample, as evidenced also by the wide range of error. Several unknown explosive events attributed to Campanian Plain volcanism were identified and some tentative correlations with the deposits found along the border of the CF caldera by Pappalardo et al. (1999), at the foot slopes of the Apennine chain by Di Vito et al. (2008), in distal drill holes as Monticchio (Wulf et al., 2004) and San Gregorio Magno (Munno and Petrosino, 2007) and in deep sea sediment cores (Paterne et al., 1986) were proposed. The description of the borehole, provided by Santangelo et al. (2010) is summarized in Table 3.3.

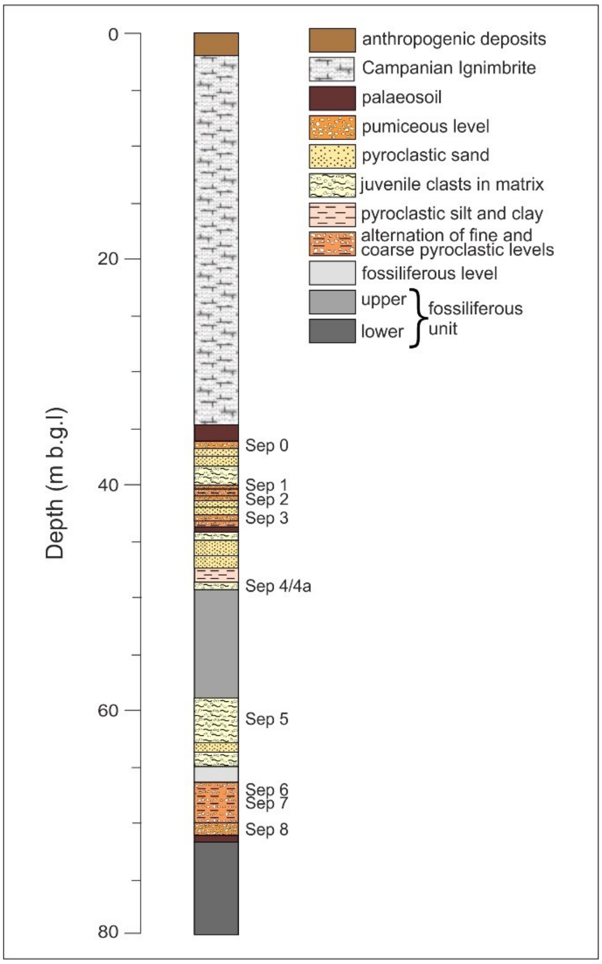

Figure 3.2 - Stratigraphy of the sequence drilled in San Marco Evangelista modified from Santangelo et al. (2010).

Table 3.3 – Description of the lithology of the San Marco Evangelista (SME) borehole as deduced from Santangelo et al. (2010).

Borehole	Depth (m)	Tephra sample	Sampling depth (m)	Lithology
SME	80.00/72.00	-	-	Lower fossiliferous unit: white, grey and beige coarse to fine sands, very rich in well-preserved mollusc shells. The sand is poorly sorted and has a pyroclastic origin. Thin layers of fine gravel, made up of reworked pumice and scoria fragments, some millimetres in diameter, are scattered along the sandy sequence.
	72.00/71.30	-	-	Dark brown paleosol rich in organic matter.
	70.50/70.10	SEP8	70.50	40 cm of coarse-grained, well sorted, pumice-rich level. The juvenile fraction is made up of sub-angular and vesiculated pumice fragments with maximum size of 2 cm. The rare lithic fragments have a maximum size of 1 cm.
	70.10/66.60	SEP6/7	67.00 and 68.50	350 cm of poorly sorted, fine sand-sized layer with dark scoria fragments made up of sub-rounded juveniles with maximum size of 2 cm. During the new analytical phase, we decided not to investigate SEP7 sample again because of the great predominance of lithic fragments.
	66.50/65.00	-	-	Fine silty-sand layer with fossil fragments.
	65.00/62.90	-	-	Dark gravels rich in pumice and scoria fragments.
	61.00/59.00	SEP5	61	200 cm of poorly sorted, fine sand-sized layer with sub-rounded grey and dark pumice and scoria fragments with maximum size of 3 cm, interpreted by the authors as a PDC deposit emplaced in a continental environment.
	59.00/49.40	-	-	Upper fossiliferous unit: fossiliferous clays and silts ranging in colour from white to light beige.
	49.40/45.35	SEP4a SEP4	49.40 48.90	The basal part (Sep 4a: 49.40) is represented by 5 cm of well-sorted, sub-angular dark scoria fragments with maximum size of 1 cm. The unit continues with a 400 cm thick, poorly sorted, sand-sized brownish-grey layer with pumice and scoria fragments reaching up to 5 cm in diameter. The juvenile fragments are sub-rounded; this portion of the unit can be interpreted as a PDC deposit.
	44.50/43.50	-	-	Brown paleosol.
	43.00/42.60	SEP3	43.00	40 cm of well-defined, well sorted, reverse-graded pumiceous level. The juvenile fraction is made up of sub-angular pumice fragments with maximum size of 2 cm. The rare lithic fragments have a maximum size of 1 cm.
	41.20/40.90	SEP2	41.20	30 cm of well-defined, well sorted pumiceous level. The juvenile fraction is made up of sub-angular and vesiculated pumice fragments with maximum size of 1 cm. Lithic fragments are rare.
	40.20/39.60	SEP1	40.20	60 cm of well-defined, well sorted pumiceous level made up of sub-angular and vesiculated pumice fragments with maximum size of 1 cm and rare lithic fragments with maximum size of 0.5 cm.

40.60/38.50	-	-	Sandy matrix-rich pyroclastic deposit ascribed to the emplacement of a PDC.
36.50/36.20	SEP0	36.50	30 cm of well-defined, well sorted, reverse-graded pumiceous level. The juvenile fraction is made up of sub-angular and vesiculated pumices with maximum size of 2 cm.

3.1.2 Camaldoli della Torre

The Camaldoli della Torre (CdT) borehole (Di Renzo et al., 2007) was drilled near the town of Torre del Greco (in the Vesuvius area) to install a strain-meter for the surveillance network of the Italian Istituto Nazionale di Geofisica e Vulcanologia (INGV). The cored sequence is a 240 m long alternation of lava flows and pyroclastic deposits investigated by the authors to increase the knowledge about the volcanic and magmatic history of the Vesuvian area (Figure 3.1). Most of the pyroclastic layers were attributed to Paleo-Somma explosive activity, several to unknown Campi Flegrei explosive events and only a few were tentatively correlated with some pyroclastic layers already found by Pappalardo et al. (1999) along the rims of the Campi Flegrei caldera. The portion of the core above the CI products is represented by a sequence of lava flows, PDC and fallout deposits with an origin from Somma-Vesuvius eruptions or Campi Flegrei main volcanic events (Figure 3.3). The CI products, comprising the basal fallout and the PDC deposit and drilled between 186 and 202.9 m, are separated by the pre-CI units by a brown, 2 m thick paleosol. Di Renzo et al. (2007) chemically and isotopically characterized the whole rocks from the 10 pyroclastic units embedded to paleosols, lacustrine and marine deposits found below the CI. The absence of the MIS5e marine deposits, expected at the borehole site, allowed the age of these layers to be constrained between 39 and ca. 130 ka.

The description of the borehole, provided by Di Renzo et al. (2007) is summarized in Table 3.4.

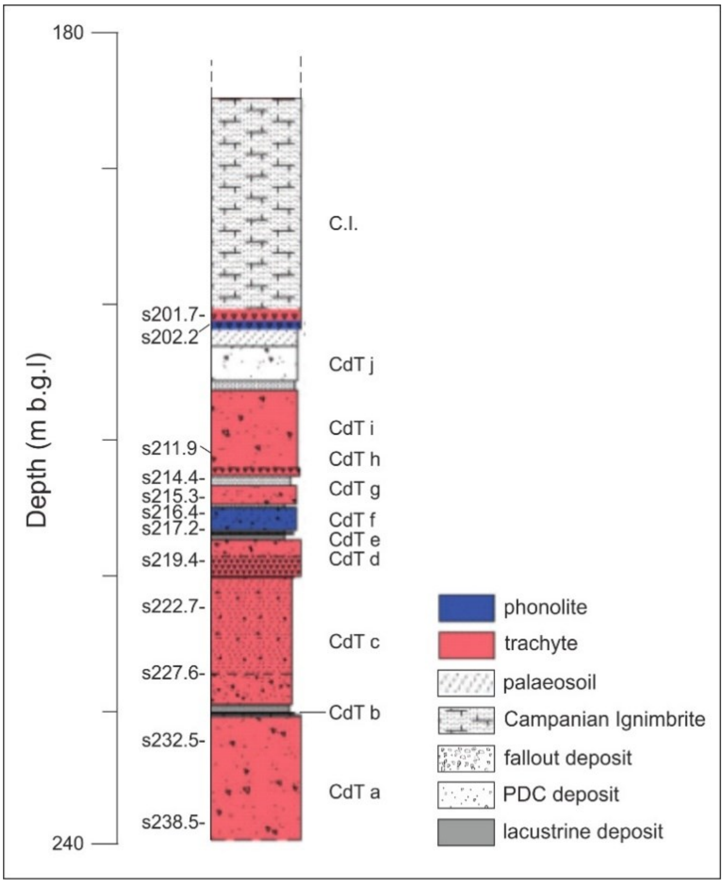

Figure 3.3 – Portion of the drilled sequence of the Camaldoli della Torre borehole below the Campanian Ignimbrite products (modified from Di Renzo et al., 2007).

Table 3.4 – Description of the lithology of the Camaldoli della Torre (CdT) borehole as deduced from Di Renzo et al. (2007).

Borehole	Depth (m)	Tephra sample	Sampling depth (m)	Lithology
CdT	240.00/231.00	CdTa	238.50 and 232.50	Pale grey, massive fine ash deposit embedding grey, well-vesiculated, subrounded pumice lapilli (maximum size 6 cm). Lithics are cm-sized lava fragments. The authors suggest that the unit is a PDC deposit from a Vesuvian eruption, based on its thickness and sedimentological characteristics.
	231.00/230.90	-	-	Thin paleosol.
	230.90/230.70	CdTb	-	Normal-graded, grey coarse ash deposit embedding mm-sized angular, well-vesiculated pumice and lava fragments interpreted as a distal pyroclastic fallout of uncertain provenance. No samples from this unit were provided for the new analytical phase.
	230.70/230.10	-	-	Lacustrine deposit.
	230.10/220.70	CdTc	229.40, 227.60 and 222.70	Sequence of grey, laminated, fine to coarse ash levels locally enriched in pumice lapilli (maximum size 2.5 cm), dense glass fragments (mm sized) and lava fragments. The pumice lapilli are subrounded. Between 227.9 and 230.1 the deposit is a massive fine ash. The unit is interpreted as a PDC and fallout deposit of uncertain provenance.
	220.70/220.60	-	-	Pale brown paleosol.
	220.60/218.10	CdTd	219.40	Grey to yellowish massive, cohesive, coarse ash containing mm-sized pale grey to whitish pumices and subordinately lava fragments. The basal portion of the unit is a poorly sorted, pumice lapilli fallout deposit. The unit is interpreted as a PDC and a minor fallout deposit of uncertain provenance
	218.10/217.40	CdTe	-	5 cm thick fallout level with mm-sized, white pumice fragments embedded in a lacustrine deposit. It is interpreted as a distal fallout deposit of uncertain provenance. No samples from this unit were provided for this new analytical phase.
	217.40/215.70	CdTf	217.20 and 216.40	Grey to brownish, massive to laminated, fine to coarse ash deposit. The unit contains white, angular, well-vesiculated, cm-sized pumiceous lapilli and subordinately mm-sized lava fragments. The basal portion of the deposit is made up of lithic-rich thin levels. The unit is interpreted as a pyroclastic fallout deposit from Campi Flegrei.
	215.70/215.50	-	-	Lacustrine deposit.
	215.50/214.20	CdTg	215.30 and 214.40	Alternating fine and coarse ash with minor lapilli beds. The ash beds are grey to yellowish, massive and contain pumice fragments with maximum size of 1.8 cm; the lapilli layers are made up of angular, well-vesiculated pumice fragments and rare lava fragments. The unit is interpreted as a sequence of PDC and minor fallout deposits from Campi Flegrei.

214.20/213.40	-	-	Lacustrine deposit.
213.40/212.90	CdTh	213.10	Whitish, massive, clast supported deposit made up of angular, well-vesiculated pumice lapilli, subordinately mm-sized scoria and lava fragments. The unit is interpreted as a fallout deposit from Campi Flegrei.
212.90/207.20	CdTi	212.60 and 211.90	Yellowish-grey, massive fine to coarse ash embedding mm to cm-sized clasts scattered or concentrated in beds mainly made up of pumice fragments. The deposit in the interval between 207.2 and 211.2 m is deeply altered; in finer beds there are accretionary lapilli. The juvenile fragments are represented by angular pumice fragments and dense obsidian-like glass fragments. The rare lithic fraction is made up of mm-sized lava fragments. This unit is interpreted as PDCs and minor fallout deposit from Campi Flegrei.
207.20/206.50	-	-	Lacustrine deposit.
206.50/204.00	CdTj	204.50	Grey, laminated, fine-ash deposit embedding pumiceous lapilli scattered or concentrated in beds and subordinately obsidian-like dense glass fragments. The pumice fragments are angular to subrounded, grey and variably vesiculated, the glassy clasts are often altered and wrapped by a patina of secondary calcite. It is interpreted as a PDC deposit from Campi Flegrei.

3.1.3 San Gregorio Magno

The San Gregorio Magno (SGM) borehole (Ascione et al., 2003; Munno and Petrosino 2007; Petrosino et al., 2019) was drilled in December 2000 in the depocenter of the Pantano of San Gregorio Magno, a polje (a tectonic-karst basin) formed in the Middle Pleistocene (Aiello et al., 2007). The sediment core is about 61 m long and did not reach the bedrock (Figure 3.4); the drilled sequence is mainly represented by silty levels with alternating thin clay levels and sparse fine to coarse sandy levels. 21 tephra layers, mainly sand-sized, have been recognized by Munno and Petrosino (2007) and then some marker tephra re-analysed in terms of trace element and isotopic composition by Petrosino et al. (2019). Since the lake was reclaimed at the end of the 19th century, the age of the sediments ranges between very recent times to more than 240 ka; in fact, the S4 tephra layer, at 51.90 m depth, was $^{40}Ar/^{39}Ar$ dated at a weighted mean age of 239 ± 8 ka (Ascione et al., 2013). Along the core, the 21 primary tephra layers (S1-S21) have been recognized as distal fallout deposits using as a discriminant the percentage of glass fragments, the almost complete lack of limestone lithic fragments and the sharpness of the basal contact.

From the entire sediment core drilled in the Pantano of San Gregorio Magno and chemically characterized (individual point glass analyses) by Munno and Petrosino (2007) we re-analysed the S9, S12 and S13 tephra layers from the upper portion of the succession (highlighted in red in Figure 3.4) embedded between S8 and S14 tephra layers in order to try to find the main tephra markers that were still missing in the record defined by the authors, after the acquisition of a dataset that is fully comparable with that obtained on newly sampled tephra layers. S14 tephra is related to C-22 (91.8 ± 1.2 ka - lastly re-dated in Monaco et al., 2022a) tephra marker; S9 was correlated by the authors with a tephra found by Paterne (1985) in the KET 80-04 core at 1083 cm depth (extrapolated age of 123.0 kyr BP). Moreover, we also re-analysed the S6, S7, and S8 tephra layers from the lower portion of the succession and sampled for the first time two new horizons (SG 39.60 and SG 37.65) in the 30-40 m depth interval, which had not been previously investigated because of the very small thickness of these sandy levels and the absence of a sharp basal contact with the underlying clays (samples highlighted in red in Figure 3.4) to try and find possible correlatives of the products found in the field in the context of the present work.

The description of the borehole, provided by Munno and Petrosino (2007) is summarized in Table 3.5.

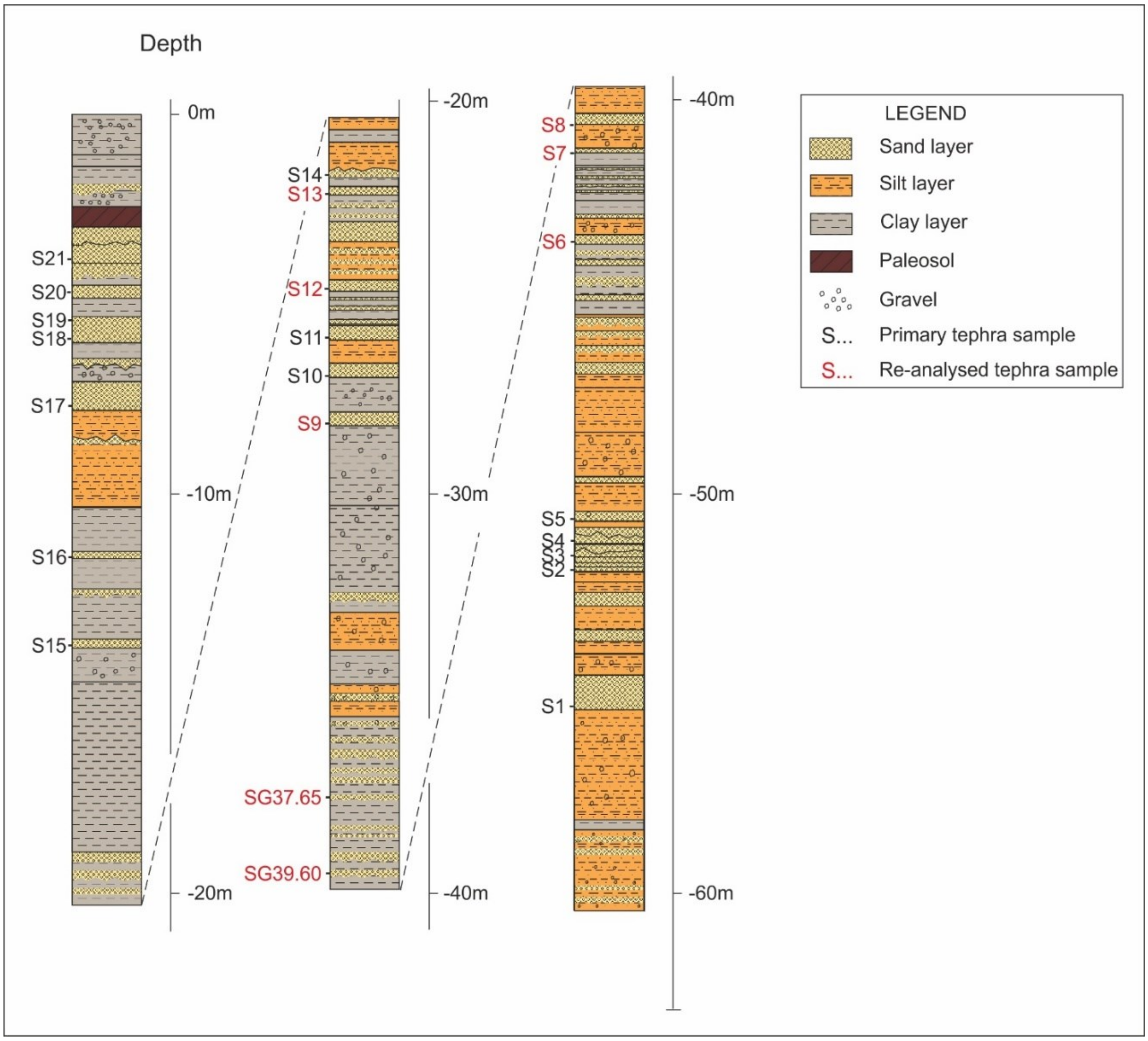

Figure 3.4 - Stratigraphic sequence of the San Gregorio Magno basin drill hole (modified from Petrosino et al., 2019). The re-investigated and re-sampled tephra layers are highlighted in red.

Table 3.5 – Description of the lithology of the San Marco Evangelista (SME), Camaldoli della Torre (CdT) and San Gregorio Magno (SGM) boreholes as deduced from Santangelo et al. (2010), Di Renzo et al. (2007) and Munno and Petrosino (2007), respectively.

Borehole	Depth (m)	Tephra sample	Sampling depth (m)	Lithology
SGM	60.30/56.10	-	-	Alternating silty, sandy and black clay sediments.
	56.10/55.50	S1	56.00	Grey silty sand-sized tephra layer containing pumice fragments and glass shards. The lithic component is made up of rare lava fragments.
	55.50/52.70	-	-	Alternating dark silty sediments, rare scattered fine gravels and sandy sediments.
	52.70/52.60	S2	52.70	Sand-sized tephra layer with maximum fragment size of 0.1 mm. It is made up of well-vesiculated pumice fragments (with ovoid vesicles) and rare limestone lithic fragments. Crystals are feldspar, biotite, green clinopyroxene and very rare brown clinopyroxene.
	52.60/52.35	-	-	Yellowish silty sands.
	52.35/52.00	S3	52.35	Dark silty pyroclastic sand with well-vesiculated pumice fragments (with ovoid vesicles) and rare lava and limestone lithic fragments. Crystals are feldspar, biotite and green clinopyroxene. The maximum size of clasts is 0.1 mm.
	52.00/51.90	-	-	Whitish silty sands.
	51.90/51.80	S4	51.90	Yellowish pyroclastic sand containing mainly pumice fragments and subordinately well-preserved glass shards. It contains a great amount of feldspar and rare green clinopyroxene crystals. The lithic component is made up of rare lava fragments.
	51.80/51.20	-	-	Whitish silty sands and greenish silts.
	51.20/50.70	S5	50.90	Whitish pyroclastic sand (maximum size of 0.1mm) mainly made up of pumice and rare lava lithic fragments. The crystal fraction is represented by feldspar, green clinopyroxene and rare brown clinopyroxene.
	50.70/43.90	-	-	Alternating dark clay and greenish-grey sandy silts.
	43.90/43.70	S6	43.80	Pyroclastic sand that contains vesiculated scoria and rare pumices as juvenile fragments and lava fragments as lithic. The crystal fraction is made up of feldspar and green clinopyroxene. The maximum diameter of clasts is 0.5 mm.
	43.70/41.75	-	-	Alternating dark silty clay sediments, rare scattered fine gravels and sandy sediments.
	41.75/41.70	S7	41.75	Whitish pyroclastic sand made up of pumice fragments and glass shards, with a minor amount of crystal grains.

41.70/40.70	-	-	Dark sandy silt and dark silty clay.
40.70/39.90	S8	40.90	Dark sandy pyroclastic silt with vesiculated scoria, minor pumice and lava fragments of maximum size of 0.5 mm. Feldspar, brown clinopyroxene and opaque make up the crystal component.
39.90/28.00	-	-	Alternating coarse sand, dark clay layers and scattered fine gravels.
28.00/27.80	S9	27.90	Dark grey pyroclastic sand embedding pumice, glass shards and lava lithic fragments. The maximum size of the elements is 0.5 mm. Crystals are mainly feldspar with a minor amount of green clinopyroxene.
27.80/26.00	-	-	Alternating dark clay sediments, rare scattered fine gravels and sandy sediments.
26.00/25.70	S10	25.90	Pinkish fine pyroclastic sand with maximum size of 0.5 mm containing glass shards and very rare lava fragments. The crystal fraction is represented by sanidine and green and brown clinopyroxene.
25.70/25.10	-	-	Clayey silt.
25.10/24.80	S11	25.00	Greyish fine pumiceous sand (maximum size of 0.5 mm) that contains well-preserved glass shards, rare pumice fragments and rare lava lithic fragments. Crystals are feldspar, green clinopyroxene and rare brown clinopyroxene.
24.80/24.40	-	-	Alternating silty sand and sandy silt layers.
24.40/24.35	S12	24.30	Pyroclastic sand with maximum size of 0.5 mm, mainly made up of glass shards, rare pumiceous and lava lithic fragments. The crystal fraction is represented by sanidine and rare biotite.
24.35/22.70	-	-	Alternating silty sands, clay and fine sands.
22.70/22.60	S13	22.70	Greenish pumiceous sand (maximum size of 0.5 mm) containing glass shards, subordinately pumice fragments and rare lava lithic fragments. Crystals are sanidine, biotite and opaques.
22.60/22.55	-	-	Brown clay.
22.55/22.20	S14	22.50	Greenish pumiceous sand containing pumice and rare lava lithic fragments. The crystal fraction is represented by feldspar, rare green clinopyroxene, opaques and biotite.
22.55/0.00			Alternating dark clay sediments, rare scattered fine gravels and sandy sediments intercalated with 7 tephra layers younger than 91.8 ± 1.2 ka (age of C-22 tephra marker lastly re-dated in Monaco et al., 2022a correlated with S14 tephra layer).

4. Results

5. Discussion

6. Conclusions and implications

As extensively evidenced during the development of this research project, the pre-Campanian Ignimbrite volcanic history is represented by a few widespread main tephra markers and many reports of distal occurrences for which a proximal counterpart has not been identified to date.

Despite the considerable difficulties encountered in the study of the pre-Campanian Ignimbrite deposits at intermediate sites, mainly due to the paucity of accessible outcrops and to the high degree of alteration that characterises these deposits, our combined approach on outcropping and drilled successions has produced some interesting results that have contributed to the refinement of a Campanian tephra lattice for the 200-40 ka. The main conclusions are briefly summarized here:

- The oldest dated products relate to SAT53 sample from the Sarno San Vito borehole. The products of the lithified ignimbrite retrieved at the bottom of the cored succession (SAT54 and 55 samples) have an age >184.5 ± 2.1 ka, compatible with the Moschiano Ignimbrite (184.7 ± 3.7 - Rolandi et al., 2003). However, the lack of fresh glass fragments in these samples prevented individual point glass analyses. Similarly, for the ancient ignimbrites outcropping in the area of the Sorrento Peninsula (Seiano Ignimbrite and Piano di Sorrento Ignimbrite), which are prone to strong alteration, we could not analyse the major element chemical composition of the juvenile fractions. Moreover, in the Durazzano area, our new field survey together with the geochemical analyses and the radiometric dating provided for the pyroclastic deposits currently outcropping has shown that they belong to the Campanian Ignimbrite products and not to the Durazzano Ignimbrite. We identified the type-section for the so called Taurano ignimbrite (158.3±3 Ka – Giaccio et al., 2017a) at the Piano delle Crete site (Valle di Maddaloni). Despite being pervasively argillified, these deposits were almost the only ones pertaining to ancient ignimbrites from which fresh juvenile clasts could be extracted, allowing for the first time the acquisition of chemical data on glass fragments from an outcrop of the Taurano Ignimbrite. These data confirm the wide compositional variability previously inferred from its distal and ultra-distal counterparts.
- This work identifies for the first time 3 well-defined eruptive events occurring in the late Middle Pleistocene between 180 and 160 ka, attributed to a "Campi Flegrei-like"

Neapolitan volcanic source and for which a comprehensive glass characterization is presented.

- The eruption, here called San Giovanni del Palco, although not directly dated, is well constrained between 167 and 180 ka by two $^{40}Ar/^{39}Ar$ dated eruptions. We have attributed to this eruption the fallout unit that forms the base of the two successions outcropping at Valle di Maddaloni and San Giovanni del Palco, characterised by a vertical colour change from whitish to dark grey, reflecting the change in the dominant juvenile fragments from pumice to dense scoria fragments. The chemical composition of the glasses changes from phonolite to tephriphonolite. The products of this volcanic event are also found as PDC deposits in the Sarno San Vito and San Marco Evangelista core sequences. A widespread distal counterpart relates to this event, for which we pointed out the correspondence with the Ionian Sea marker C-49 of Paterne et al. (2008). In virtue of its finding in ultra-distal settings it could be a good Mediterranean marker for the MIS6e-6d transition.
- As far as the chemistry of the products emplaced during the late Middle Pleistocene (between 200 and 130 ka) is concerned, we identified two different trachytic clusters: a) trachytic Phlegraean-like tephra with K_2O/Na_2O >1.5; b) trachytic tephra with a clear Ischia-type signature (CaO wt% ca. 1, K_2O/Na_2O ca. 1). Between 175 and 167 ka the two trachytic trends coexist in several studied horizons, both found in field outcrops and extracted from drilled sequences, testifying to penecontemporaneous activity at Ischia and a "Campi Flegrei-like" Neapolitan volcanic source. During the same time interval, another distinctive cluster appears, characterized by a wide compositional variability ranging from phonolite to phonotephrite. In fact, the two main markers emplaced during this period, the San Giovanni del Palco eruption and the Taurano Ignimbrite, both share a quite similar, heterogeneous composition. Although the two trachytic compositions correspond well to those recorded in the recent activity of Campi Flegrei and Ischia, the geochemical variability from phonolite to phonotephrite that characterizes the Taurano Ignimbrite and the San Giovanni del Palco eruption seems quite typical of this eruptive period.
- The Sr-Nd isotopic composition of tephra layers proved to be a crucial tool to assess a correct correlation, as shown by its application to the SGdP and the Taurano Ignimbrite, whose major element glass chemical compositions almost completely overlap. In fact, a highly variable composition of proximal deposits, in distal settings could correspond to a more homogeneous tephra, due to the dynamics of the ash dispersal and its possible variation in direction. Furthermore, especially in the case of ancient eruptive events the lack

of complete successions may lead to miscorrelations due to the partial or complete missing of some geochemical component. Therefore, it seems very appropriate to use all available means, including the isotopic composition of radiogenic elements, to correctly correlate the tephra layers.

- The contribution of this work to the definition of the tephra lattice for the Late Pleistocene is represented by further findings of the main Mediterranean markers (C-22, X-5), which provide new data to refine their distribution. However, we underpin the field finding in intermediate-distal areas of still unknown eruptive events occurred especially in the period immediately preceding the Campanian Ignimbrite eruption and in the 90-120 ka period, interbedded with the main markers.
- The effectiveness of integrating drilled and outcrop successions is demonstrated here; as a matter of fact, without the reinvestigation of the San Marco Evangelista and Camaldoli della Torre tephra layers and the new analyses of the Sarno San Vito tephra layers, our reconstruction would have been much more incomplete, since some important markers such as X-5 and TM24-b were found only in borehole sequences. In particular, the Camaldoli della Torre borehole provided a very well-preserved archive for the last 107 ka.
- The Sarno San Vito borehole sequence, although influenced by the presence of huge thicknesses of alluvial fan deposits, was studied in detail and evidenced the presence of primary volcanic levels. In addition, we also recognized reworked levels that represent a *post quem* reference for the deposition of tephra markers (i.e. C-22 marker in SAT30/32 levels). Our investigation postulates the suitability of the alluvial sequences for tephrostratigraphic studies, provided that the presence of sedimentary hiatuses and erosional phases is taken into account.

From a more general point of view, the detailed study of previous contributions to the Campanian pre-CI volcanic events database, has made us aware of the high risk of miscorrelation that we run especially for ancient eruptions. Indeed, as already pointed out, there are clusters of geochemically homogeneous tephra layers of different ages over the period considered here. In the absence of other distinguishing features (e.g. distribution of lithological components, morphological features of the glass fragments, mineral chemistry) or a precise age constrain it is very dangerous to venture a correlation. For this reason, it would be a good practice to always check previous correlations to avoid inheriting any errors. Instead of proposing uncertain correlations, it would be preferable to report the occurrence of new tephra layers even if it is impossible to correlate them with already known volcanic events, which would be a very useful starting point for subsequent investigations.

Notwithstanding the progress made as a result of the present study, it would be interesting to carry out further research on some of the less well known eruptions. In particular, it might be useful to try and find some distinguishing features to better resolve the period immediately preceding the emplacement of the Campanian Ignimbrite (40-42 ka), for which the recurrence of widespread fallout deposits has been highlighted here. A petrological study of the products of the San Giovanni del Palco eruption would also be of utmost interest, given their extreme geochemical variability.

Appendix 1: Complete $^{40}Ar/^{39}Ar$ laser single crystal fusion results

Appendix 2: Semi-quantitative lithological component analysis

Appendix 3: Individual point chemical data

Appendix 4: Average chemical analyses of investigated tephra and respective main correlatives

Appendix 5: Backscattered electron images of selected samples

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