

Article

The Lower Pleistocene Tephra Layers in the Croton Marine Sequence of Southern Italy: Tracing Their Volcanic Source Area

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Abstract: At least three tephra layers, with ages around 2 Ma, crop out in the Pleistocene marine sequence of the Croton basin, in southern Italy. We present the petrography and the mineral and glass chemistry of these layers, in order to correlate them with other Pleistocene sequences and, possibly, to identify the volcanic source(s). The oldest layer (a1) contains glass shards with homogeneous rhyolitic composition, together with crystals of ortho- and clinopyroxene, plagioclase and amphibole. The age, petrography and major elements’ glass composition allow for correlation with coeval tephra layers cropping out in the southern Apennines, near the town of Craco, in Valle Ricca, near Rome, and in the Periadriatic basin, in central Italy. Two other younger tephra layers (a3 and a4) can be distinguished by the absence of hydrous phases in a3 and the occurrence of biotite in a4. They show a higher variability in glass composition, which may be related to multiple volcanic sources. A fourth tephra of unknown position, but probably intermediate between a1 and a3, was also recognized. The volcanic source of the tephra layers was identified in a submerged paleo-arc in the central Tyrrhenian Sea, possibly corresponding to the Ventotene ridge. The paper also provides a dataset of glass trace elements’ composition for future correlations.



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Keywords: Vrica section; LA-ICP-MS microanalyses; tephrostratigraphy

1. Introduction

Volcanic particles erupted during violent explosive eruptions can be injected into the atmosphere, transported by the winds for very long distances and deposited, covering very wide areas. While the tephra layers settling in continental or marine high-energy environments are easily eroded, and are therefore hardly preserved, those settling in calm, deep lakes or sea basins are more easily preserved, forming undisturbed or poorly disturbed layers intercalated between the sea sediments. For this reason, the study of marine and lacustrine cores, or deep marine depositional sequences cropping out on land, is of paramount importance for tephrostratigraphic reconstruction. This is particularly true for the Quaternary studies of the Mediterranean area, where the high number of active volcanoes producing tephra layers with distinctive compositional features has allowed for the synchronization of distal marine and terrestrial archives (e.g., [1–3]). Moreover, attributing distal tephra layers to known volcanic sources has provided important information on the eruptive history of volcanoes, often incomplete with the investigation of the proximal deposits alone.

However, the tephrostratigraphy is relatively well detailed only for the Holocene sequences, and particularly for the last 10 ka. “Young” layers have been detected in many archives, thus representing tephra markers, allowing for a correlation at the scale of the Mediterranean area. Moreover, they are often related to well-known major eruptions of well-preserved or active volcanoes. On the contrary, the investigation of ancient tephra layers poses several problems: (1) their old age often implies incipient or advanced weathering (post-emplacement cementation, precipitation, devitrification, argillification, etc.), which makes geochemical characterization difficult; (2) they often occur at great depths within sedimentary or volcanic sequences, and thus they are difficult to reach during drilling campaigns; their finding is therefore rarer and few correlations are possible; and (3) they could be related to submerged, eroded or not presently visible volcanoes. For these reasons, only a few studies focused on tephra layers older than 500 ka in the Mediterranean area are currently available in the literature (e.g., Pleistocene volcanic layers in the basins of south-western Calabria, [4]; ash in the Mercure basin, 514 ka, [5]; Middle Pleistocene volcanic layers in the Montalbano Jonico basin, [2]; Serravallian volcanoclastic succession in the Amantea basin, [6]; late Messinian layers in central Apennines, [7]; Upper Miocene volcanic ash layers in central Italy [8]).

In this paper, we show the petrographic features and geochemical composition of three tephra layers intercalated within the Pleistocene deep sea sedimentary sequence of the Crotone basin (central-eastern Calabria, southern Italy). The section is well known because it contains the Global Boundary Stratotype Section and Point (GSSP) of the base of the Calabrian stage [9], and the occurrence of three to four tephra layers is highlighted in several papers (e.g., [10–13]). However, a systematic analytical study has never been conducted on these layers, and their glass composition, up to now, has been undetermined. The aim of this study is to fill this knowledge gap by providing a petrographic and compositional characterization of the tephra layers in order to tentatively correlate them with other tephra layers in the Mediterranean area and/or to known volcanic provinces, contributing to a better knowledge of volcanic activity in a period of time recorded in few complete terrestrial stratigraphic sections.

2. Geological Setting

2.1. The Crotone Basin

The tephra layers studied in this paper are included in the Pleistocene marine deposits of the Crotone series in the homonymous basin, situated in the central-eastern sector of Calabria region, between the Sila Massif and the Ionian Sea. The Crotone basin is a graben-like structure locked between two shear zones: the Rossano–San Nicola Shear Zone to the north and the Petilia-Sosti Shear Zone to the south [14–21]. The formation of the basin is related to the migration of the Calabrian–Peloritan arc towards the south-east since the Serravallian/Tortonian and to the subduction of the Ionian oceanic plate [22–28].

The sedimentary sequences filling the basin have ages spanning from the Serravallian (13.82 Ma, [21]) to the Middle Pleistocene (0.7 Ma, [29]) and range from deep marine to continental settings, following changes in the tectonic regime and the sea-level ([21,30] and references therein). In particular, during the Late Gelasian, a phase of rapid tectonic subsidence and basin collapse, related to the opening of the Marsili sub-basin in the Tyrrhenian Sea at 2.3–2.1 Ma, occurred [21,31,32]. This is reflected by the deposition of the marine Cutro clays Formation [30], forming the Crotone series. The succession is capped by the Pleistocene arenitic deposits of the San Mauro Formation, representing the infilling of submarine canyons formed as a consequence of the uplift of the basin [29]. This phase finally led to the emergence of large portions of the basin and the formation of marine terraces [33,34].

2.2. The Croton Series

The Croton series comprises three sections, Semaforo, Vrica and Santa Lucia (Figure 1), and is formed by the Cutro clays, which were deposited during the time interval 2.47–1.21 Ma. An accurate reconstruction of the stratigraphy, biostratigraphy and magnetostratigraphy of the series is reported in [12]. In total, 30 complete glacial–interglacial cycles, from Marine Isotope Stage (MIS) 97 to MIS 37 are included in the succession [12]. The deposit consists of gray- to blue-colored, marly to silty marine clays alternating with 31 brownish, organic-rich sapropel layers, moderately to strongly laminated [10–12,35,36] and with volcanic ash beds.

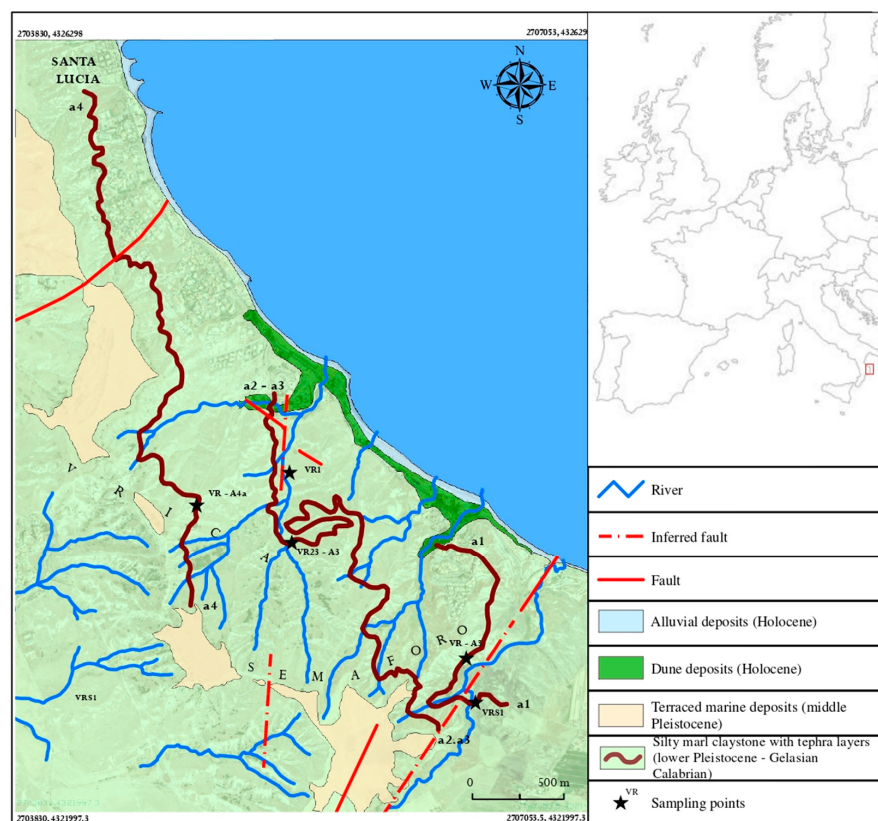


Figure 1. Location and geological map of the study area showing the outcrops of the investigated tephra layers (from [12]) and the sampling points.

The Vrica section became internationally known as Global Stratotype Section and Point (GSSP) when the Plio–Pleistocene boundary at that time was recognized directly above the sapropel “e” [37–39]. On the basis of sapropel calibration, an astronomical age of 1.806 Ma was assigned to this layer, corresponding with the transition between MIS 65 and 64 [11,40,41].

In more recent times, the base of the Pleistocene was re-assigned and lowered to 2.58 Ma following the re-definition of the Quaternary period [42–45] and the point was designated to mark the base of the Calabrian stage [9]. According to this new definition, the whole Croton series is therefore included within the Pleistocene. In particular, the Semaforo section is entirely Gelasian (2.58–1.8 Ma), the Vrica section contains the transition Gelasian–Calabrian (1.8 Ma), and the Santa Lucia section is entirely Calabrian (1.8–0.77 Ma).

2.3. The Tephra Layers

The occurrence of volcanic ash layer(s) interbedded in the Croton series is already mentioned in [46], where the authors recognize a tephra, named marker bed “m”, very close to the old Plio–Pleistocene boundary. Later, [47] recognized and dated two tephras:

one containing biotite and coincident with the “m” marker and an older one, hornblende-bearing and with a K-Ar age on hornblende of 2.22 ± 0.03 Ma (error as 1σ). The same authors obtained a K/Ar age of 1.99 ± 0.08 Ma on the biotites of the “m” marker. However, as it lies immediately above the base of the present Calabrian stage, the tephra layer “m” must be slightly younger than 1.806 Ma. More recently, [12] recognized four outcropping layers, named a1, a2, a3 and a4, the last corresponding to the “m” marker bed (Figure 1). Layer a2 was also recognized in a borehole cored at the base of the Vrica section. For the oldest a1 layer, an age of 2.31 ± 0.34 Ma (error as 1σ) was obtained by the isothermal plateau fission track (ITPFT) method on glass shards. Hereafter, we will refer to the different tephra layers using the [12] names.

3. Materials and Methods

3.1. Sampling

Five samples were picked from different ash layers and used for successive petrographic and compositional analyses. The sample positions are indicated in Figure 1 and in the stratigraphic column of Figure 2.

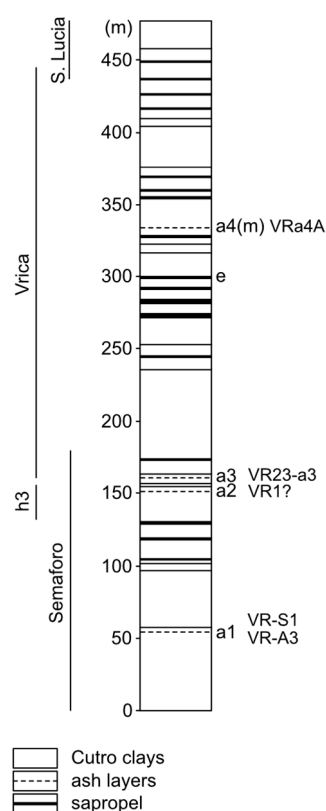


Figure 2. Schematic composite stratigraphic column of the studied succession showing the position of the tephra layers, the sapropel “e” and the collected samples within the different sections. h3: hole 3 of [12]. Modified after [12].

Two samples (VR-S1 and VR-A3) come from the lowermost a1 tephra layer outcropping in the “Semaforo” section (Figure 3a). The ash layer here is whitish, 4–5 cm-thick and easily recognizable in the field because it is slightly more coherent than the clays in which it is interbedded. The grain size varies from fine to medium ash. Layer a3 was sampled in the Vrica area (sample VR23-a3, Figure 3b). The layer is few centimeters thick, with a grain size in the range of fine ash, and appears reddish, due to pervasive weathering. Layer a4 was sampled above the sapropel “e” marking the Calabrian–Gelasian limit (Sample VRa4A, Figure 3c,d). It is whitish and is the thinnest (1–2 cm) and finest of the sampled layers, with

grain sizes ranging from very fine to fine ash. Finally, we picked a small sample (VR-1) of an ash layer, not in its place, but between the position of sample VR23-a3 and the position of the hole h3 of [12], where the authors recognized layer a2. The layer is weathered and the apparent grain size ranges from fine to very fine ash.

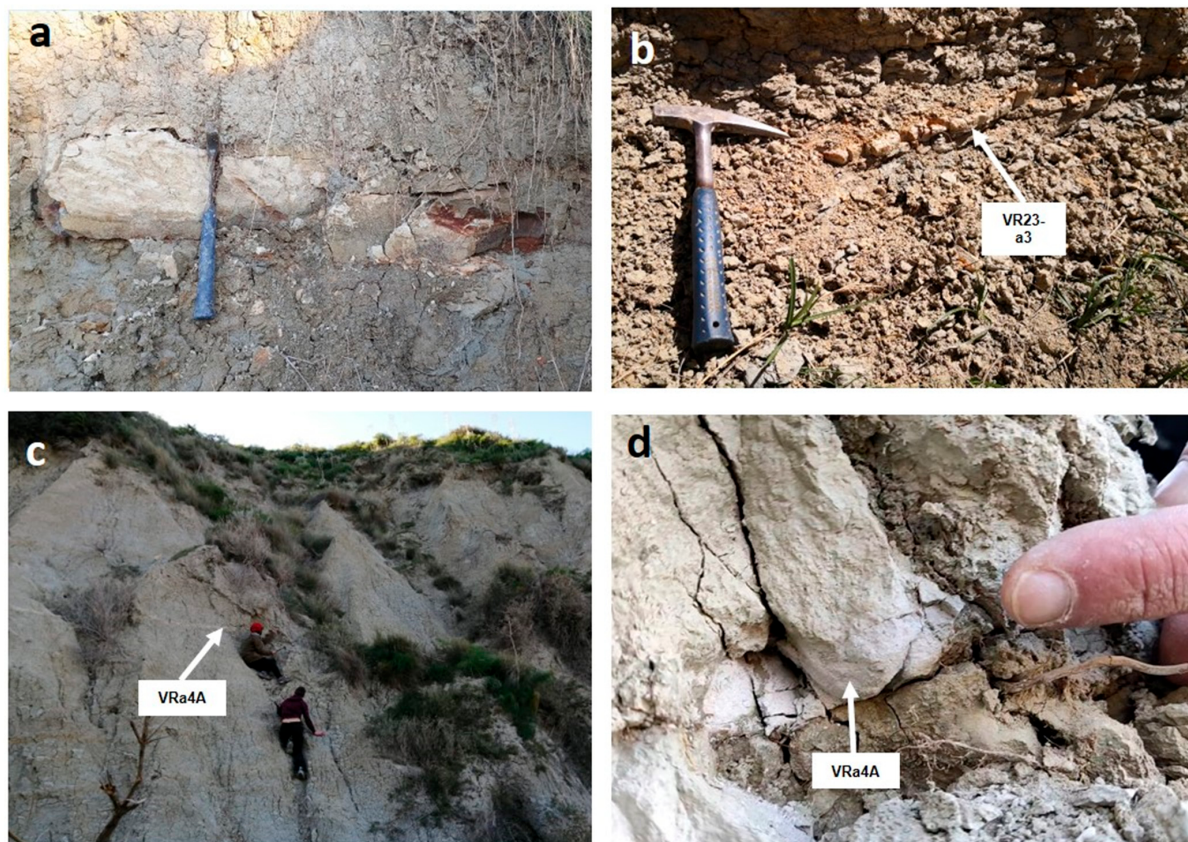


Figure 3. Outcrops of tephra layers. (a) Semaforo section, sample VRS1 (tephra layer a1); (b) Vrica section, outcrop of tephra layer a3; (c) Vrica section, outcrop of tephra layer a4; (d) detail of tephra layer a4.

3.2. Analytical Methods

A petrographic study on a bulk material thin section was conducted on the five samples under a polarizing optical microscope and scanning electron microscope (SEM) at the CM2 Laboratory of the Department of Biology, Ecology and Earth Science of Calabria University (Rende, Italy). The instrument used was a Zeiss Crossbeam 350 (Zeiss, Oberkochen, Germany) equipped with an EDS (energy dispersive spectroscopy) microanalytical system, EDAX Octane Elite.

Mineral phases and glass shards were analyzed by electron probe micro-analyzer (EPMA) JEOL-JXA 8230 (JEOL, Tokyo, Japan) at the same laboratory. The instrument was equipped with a W source and 5 WDS spectrometers with LDE, TAP, PETJ and LiF crystals and a Si/Li crystal detector model JEOL EX-94310FaL1Q ((JEOL, Tokyo, Japan)—of the silicon drift type. The detector constants and work conditions for major element determination on crystals were as follows: tilt angle 0, voltage 15 kV, beam diameter of 1 μm and a beam current of 10 nA. Acquisition times were 30 s for Fe, Cl, Mn, Ti, Mg and P and 10 s for F, Si, Al, K, Ca and Na. The conditions for the glass analyses were tilt angle 0, voltage 15 kV, a 2 μm defocused beam and a beam current of 6 nA. In order to minimize Na loss, the acquisition time for this element was 10 s, while for the other elements, an acquisition time of 30 s was used. The analytical precision was 0.5% for concentrations higher than 15 wt.%, 1% for about 5 wt.%, 5% for abundances of 1 wt.% and less than 20%

for concentrations near the detection limit, never below 1000 ppm. Analyses with a total oxide sum lower than 93 wt.% were discarded. The total of the chemical elemental analysis, for glass and minerals, was normalized to 100 wt.% in all plots and tables. The standard materials used for the glass and mineral analyses are listed in Table S1. The whole sets of glass and mineral analyses are shown in Tables S2–S6.

Trace element analyses of matrix glasses were performed at the Department of Earth Sciences “A. Desio” of the University of Milan (Milan, Italy) using an Analyte excite 193 nm ArF excimer laser (Teledyne CETAC Technologies, Omaha, NE, USA) coupled with a Thermo Fisher Scientific iCAP-RQ mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The operating conditions were as follows: 4 J/cm² fluence, 40 µm spot size and 8 Hz repetition rate. The acquisition time was 30 s on the sample and 30 s on the background. Data reduction was carried out with the software package GLITTER 4.5 [48] using SiO₂ wt.% concentrations from microprobe analyses as internal standard. The international reference material NIST612 [49] was used as a calibration standard, and a set of reference glasses (ARM-3, [50]; BCR-2G, GSD-2G and ATHO-G, [51]) was used to monitor accuracy. The reproducibility was less than 20% for most elements. The analyses of standards are shown in Table S7; the whole set of glass analyses is shown in Table S8.

4. Results

4.1. Petrography

Samples from layer a1 from the Semaforo section (VR-S1 and VR-A3) are almost entirely made up of pyroclastic fragments, mainly represented by glass shards with elongated or cuspidate shapes and rare pumices, set in a clayey matrix (Figure 4a,b). The average grain size of the glass shards ranges from a few tens to hundreds of microns. Volcanic minerals, both felsic and mafic, also occur. The most abundant phase is plagioclase, followed by ortho- and clinopyroxene and amphibole. Fe-Ti oxides and rare apatite also occur. The mineral phases generally occur as single crystals, often rimmed by a glass film (Figure 4c,d). The non-volcanic fraction is almost absent. A few crystals of quartz, probably of metamorphic origin, have been observed. The two samples show moderate weathering, slightly higher in sample VR-A3.

Sample VR23-a3 from the a3 layer of [12] appears highly weathered, with glass fragments and crystals set in a clay matrix. The volcanic glass occurs in the form of poorly vesiculated shards, with few small, round vesicles and often including microphenocrysts of plagioclase, pyroxene and Fe-Ti oxides (Figure 4e).

A different population of non-vesiculated, almost completely microcrystalline fragments, sometimes including phenocrysts of plagioclase, also occurs, probably representing lava lithics. Fragments showing the two typologies of more or less vesiculated and crystalline glasses have sometimes been observed (Figure 4f). Volcanic crystals, occurring as loose crystals and microphenocrysts in the glass fragments, are represented by plagioclase, ortho- and clinopyroxene and rare oxides. No hydrous phase has been detected.

Sample VRa4A from the uppermost a4 layer, at the Calabrian–Gelasian limit, is almost entirely composed of volcanic glass fragments, occurring both as highly vesiculated pumices, up to 100 microns in size, and as cuspidate or elongated shards, with these last fragments probably deriving from the fragmentation of the former (Figure 4g,h). A different, very subordinate population of partly crystalline, poorly to highly vesiculated fragments also occurs (Figure 4i). The mineral phases are mainly represented by plagioclase, followed by biotite, ortho- and clinopyroxene. Apatite and Fe-Ti oxides are rare. The minerals often show remnants of volcanic glass at the rim (Figure 4j). Some highly crystalline unvesiculated fragments (lava lithics) also occur.

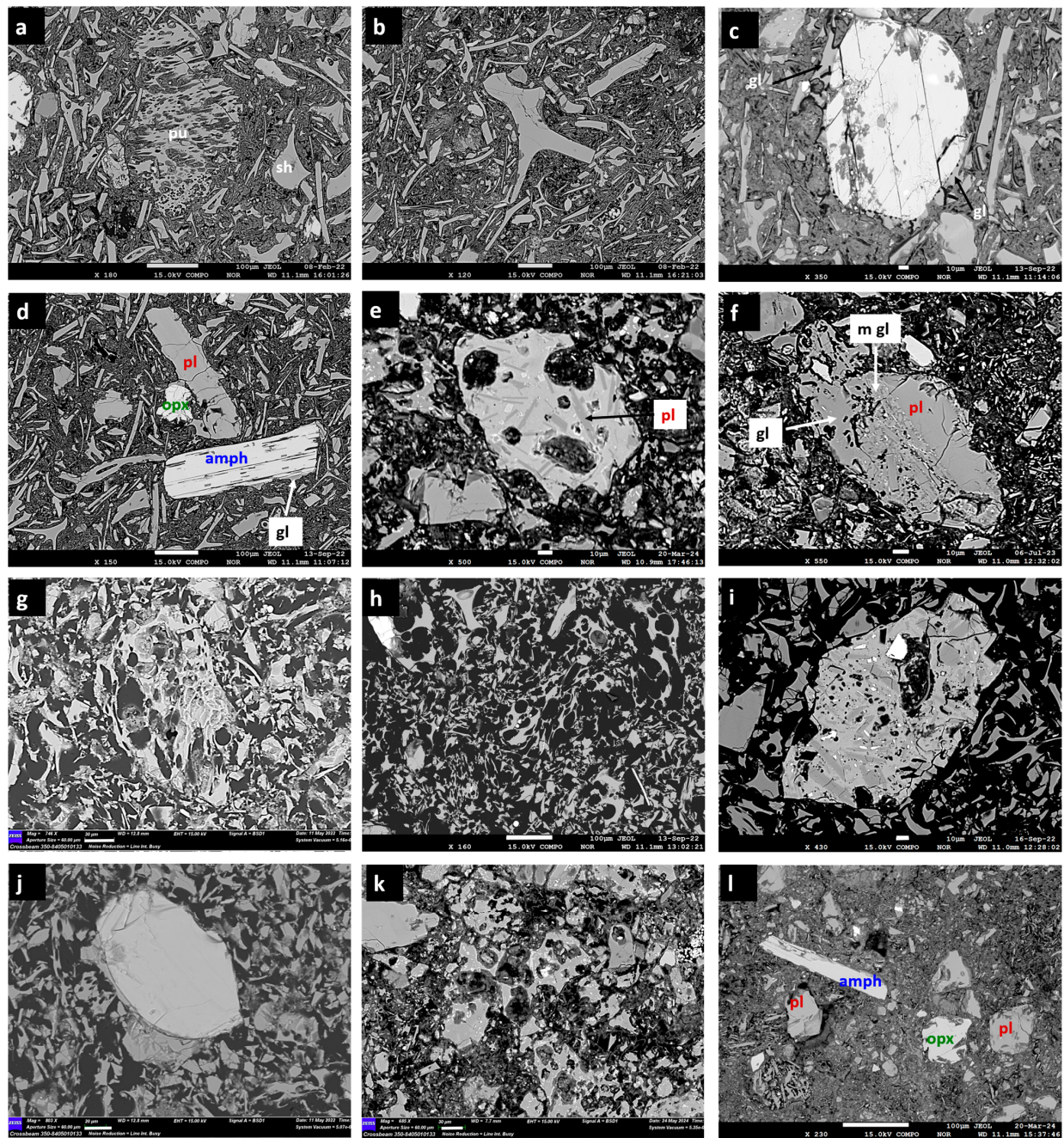


Figure 4. Microphotographs of glass shards and minerals of the studied samples. All the images were obtained by SEM or EPMA in back-scattered electrons function. (a–d) layer a1: (a) pumice clast (pu) and glass shards (sh) (scale bar: 100 μ m); (b) cuspidate glass shard and smaller shards of different shapes (scale bar: 100 μ m); (c) amphibole crystal surrounded by a glass film (gl) (scale bar: 10 μ m) and (d) plagioclase (pl), orthopyroxene (opx) and amphibole (amph) with glass film. Several glass shards are also visible (scale bar: 100 μ m). (e,f) layer a3: (e) juvenile fragment with few rounded vesicles and plagioclase microcrysts (scale bar: 10 μ m) and (f) composite fragment formed of vesiculated glass (v gl) and microcrystalline glass (m gl) with a plagioclase phenocryst (scale bar: 10 μ m). (g–j) layer a4: (g) pumice fragment and glass shards (scale bar: 30 μ m); (h) glass shards (scale bar: 100 μ m); (i) partially crystalline fragment with plagioclases and oxides microcrysts (scale bar: 10 μ m) and (j) biotite crystal surrounded by glass (scale bar: 20 μ m). (k,l) sample VR—1-unknown stratigraphic position. (k) glass fragments with plagioclase microcrysts set in an argillified matrix (scale bar: 30 μ m) and (l) minerals and glass shards in an argillified matrix (scale bar: 10 μ m).

Finally, sample VR1, of uncertain provenance, is highly weathered. The few recognizable glass fragments, set in a completely argillified matrix, are small and contain many elongated plagioclase crystals (Figure 4k). Loose crystals are represented by plagioclase, orthopyroxene, amphibole, biotite and subordinate clinopyroxene (Figure 4l).

4.2. Mineral Chemistry

Plagioclase in the samples from the a1 layer ranges in composition from bytownite to andesine (An_{38-82}), but most of the crystals have an $An_{50}Ab_{50}$ composition. Some crystals show a normal zoning (Figure 5a). Plagioclase occurring as loose crystals or in highly crystalline fragments in layer a3 reaches anorthitic compositions (up to An_{93}). In contrast, that in almost aphiric fragments is smaller and andesinic in composition (An_{31-47}) (Figure 5b). The crystals of the uppermost layer a4 show a composition variable from bytownite to andesine (Figure 5c). In this sample, only plagioclases occurring as loose phenocrysts have been analyzed.

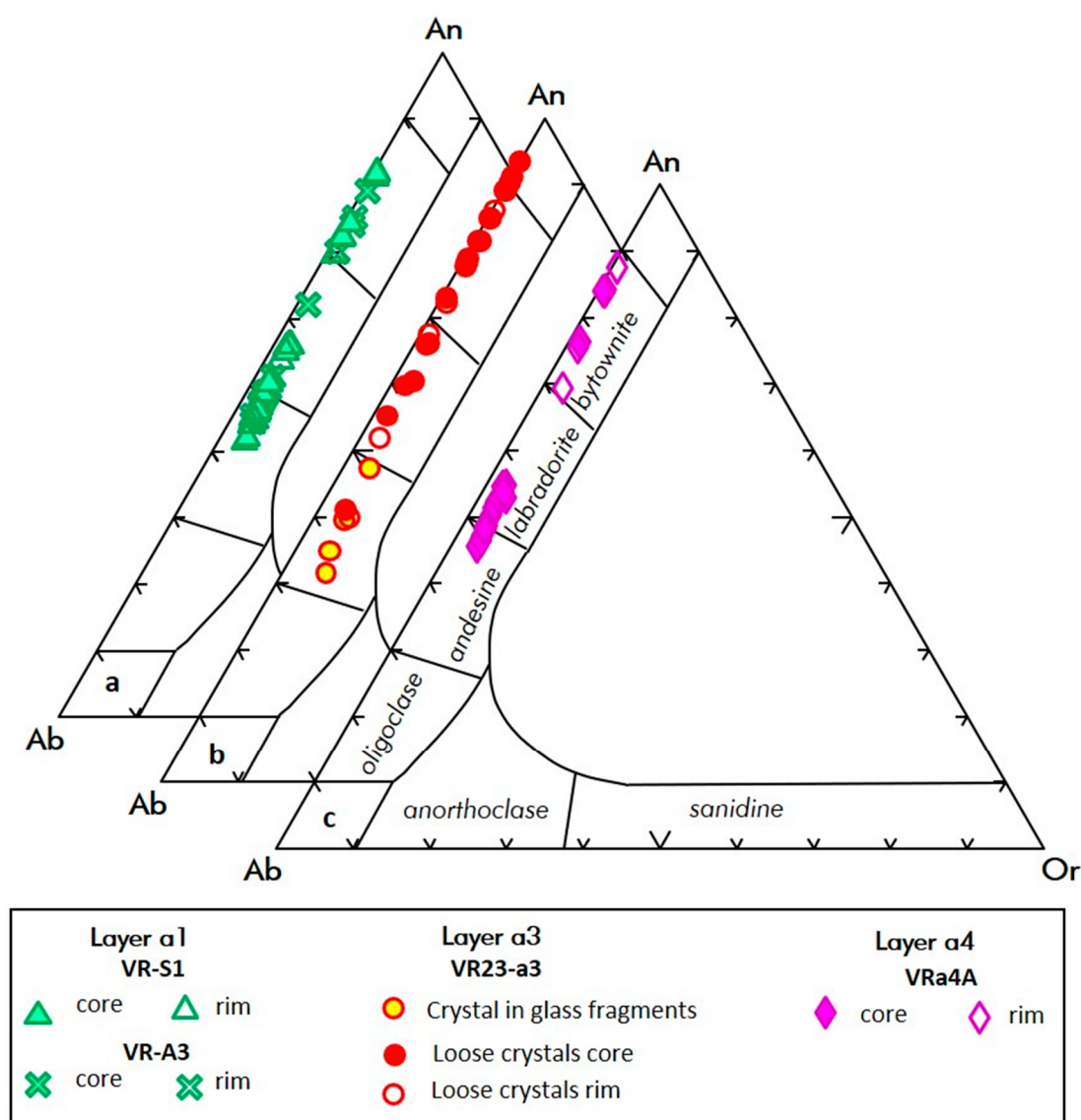


Figure 5. Plagioclase composition of the studied tephtras. (a) Layer a1; (b) layer a3; (c) layer a4.

The composition of pyroxene of a1 and a4 layers is similar and rather homogeneous, with clinopyroxene falling in the augite field and orthopyroxene with an enstatitic composition ($En_{59-70}Fe_{26-38}Wo_{2-5}$) (Figure 6a). Some crystals of clinopyroxene in the sample

from the a3 layer show more Ca-rich compositions ($Wo_{>45}$), falling in the diopside field. The orthopyroxene of the same layer has poorly variable composition ($En_{65-69}Fe_{28-32}Wo_3$).

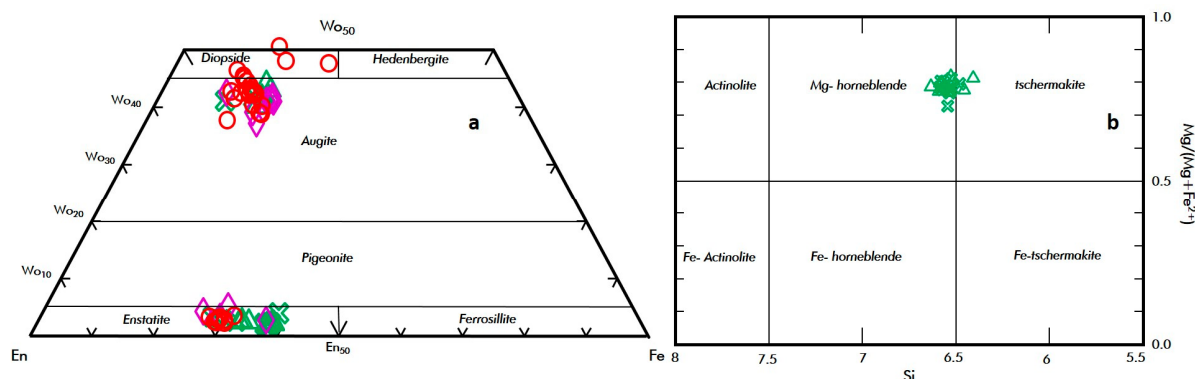


Figure 6. (a) Pyroxene composition of the three studied layers. (b) Composition of amphiboles of samples from layer a1. Symbols as in Figure 5.

Amphibole in the samples of the a1 layer belongs to the calcic group and can be classified as Mg-hornblende and tschermakite according to the classification of [52] (Figure 6b). Biotite of the uppermost a4 layer has a Mg# of 0.61.

4.3. Glass Chemistry

Major element composition was determined on glass shards of all the sampled layers. However, the very high degree of weathering of sample VR1 (possibly a2 layer of [12]) made it difficult to obtain acceptable results, and only a few analyses are available. For the same reason, trace element compositions of glass shards from sample VR1 were not determined. In Table 1, the average composition of each sample is shown.

Table 1. Mean compositions of glass shards of the four analyzed tephra (normalized data).

	a1		a2?		a3		a4		a4		a4		a4	
	VRS1 * (15)	s.d.	VRA3 (26)	s.d.	VR1 (8)	s.d.	Vr23-a3 pop 1 (23)	s.d.	Vr23-a3 pop 2 (7)	s.d.	VRa4A (27)	s.d.	VRa4A cg (18)	s.d.
SiO ₂	75.28	0.24	75.53	0.31	78.31	1.13	76.99	1.12	71.99	1.44	69.40	0.72	58.67	2.18
TiO ₂	0.25	0.10	0.23	0.07	0.53	0.07	0.51	0.11	0.57	0.16	0.44	0.10	1.27	0.15
Al ₂ O ₃	13.14	0.12	13.18	0.11	13.23	0.29	12.82	0.45	14.7	0.82	16.02	0.75	15.17	1.11
FeO	1.55	0.08	1.46	0.10	1.84	0.62	1.71	0.48	2.89	0.88	2.77	0.13	9.37	1.59
MnO	0.06	0.03	0.04	0.03	0.04	0.03	0.05	0.04	0.06	0.04	0.10	0.04	0.18	0.04
MgO	0.25	0.02	0.25	0.03	0.12	0.08	0.12	0.14	0.44	0.24	0.55	0.03	3.19	1.05
CaO	0.94	0.05	0.93	0.07	0.53	0.25	0.37	0.21	1.39	0.67	1.54	0.07	5.76	1.58
Na ₂ O	3.05	0.22	2.91	0.21	1.71	0.31	2.4	0.27	2.91	0.45	3.39	0.18	2.57	0.69
K ₂ O	5.08	0.11	5.07	0.16	3.34	0.22	4.76	0.55	4.67	0.9	5.51	0.12	3.51	1.58
P ₂ O ₅	0.03	0.03	0.03	0.03	0.08	0.03	0.06	0.03	0.11	0.07	0.08	0.03	0.16	0.03
S ₂ O ₃	0.00	0.00	0.00	0.00	0.02	0.02	0.02	0.02	0.01	0.02	0.00	0.00	0.00	0.00
Cl	0.37	0.04	0.36	0.04	0.26	0.07	0.21	0.05	0.25	0.07	0.22	0.03	0.14	0.04
sum	100	0	100	0	100	0	100	0	100	0	100	0	100	0

*: a: The number in brackets is the number of analyses; b: Total iron expressed as FeO. pop: Population; cg: Crystalline glass.

In Figure 7a, the TAS diagram [53] for the analyzed glass fragments is shown. Most of the samples fall in the field of rhyolite. However, some differences can be observed between the glass from the different layers, and some intra-sample variability is also shown.

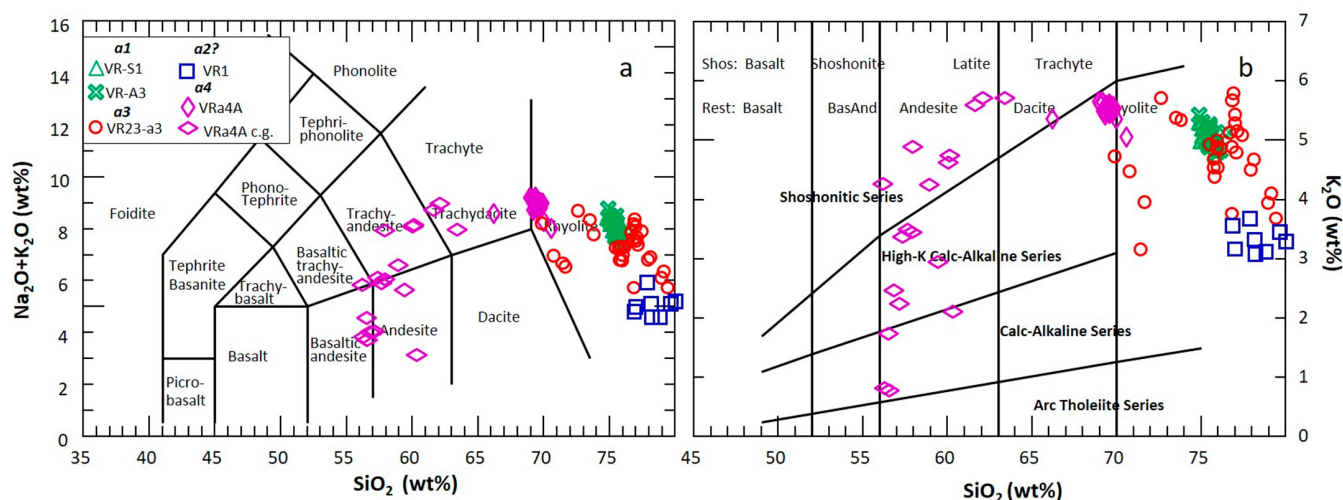


Figure 7. (a) TAS diagram [53] and (b) K_2O –silica diagram [54] for the glass shard analyses of the tephra layers. Data presented on an anhydrous basis.

The glasses of the two samples from the a1 layer have a very homogeneous composition with an average silica content of 75 wt.% and alkalis ranging from 7 to 9 wt%. The glass of sample VR1, possibly related to the a2 layer, shows the highest silica and the lowest alkali content; however, it cannot be excluded that this last feature is related to the weathering of the sample, causing alkali loss.

In the sample from the a3 layer, a wider compositional variability is observed. Most of the glass fragments have a silica content higher than 75 wt.%; however, a subordinate population of glass with a lower silica content and variable alkalies also occurs (population 2 in Table 1).

Finally, the glass of the uppermost a4 layer is less SiO_2 -rich with respect to the others but shows a slightly higher alkali content. As previously stated, a different population of glass occurs in this sample, showing a lower vesicularity and higher crystallinity (cg in Table 1). The glass analyses of these fragments are highly dispersed but, as a whole, show a lower silica and alkali content. In the K_2O vs. silica diagram (Figure 7b), most of the analyses fall in the field of high potassium calc-alkaline magmas, except for VR-1, whose potassium content is slightly lower. The Harker diagrams (Figure 8) confirm the high variability in a4 glass composition, with the microcrystalline glass fragments showing higher MgO , FeO and CaO contents. The three lowermost layers have similar concentrations in the three elements. The chlorine content clearly distinguishes the glass of the a1 layer ($\text{Cl} > 0.3$ wt.%) from that of a4 (average Cl about 0.2 wt.%). The glass of the two intermediate layers has rather variable chlorine contents, with average values around 0.22–0.26 wt.%.

The trace element contents are rather constant for the glass fragments of the a1 layer and show a wider variability for a3 and a4 glass (Table S8). The spider diagram of glass trace elements (Figure 9a) shows troughs at Nb-Ta and Ti for all of the samples, a typical feature of magmas from convergent geodynamic settings. Negative peaks are also shown by Ba and Sr. Chondrite-normalized REE patterns (Figure 9b) reveal LREE enrichment over the HREE (average La/Yb between 10 and 20) and show a visible Eu anomaly (average Eu/Eu^* between 0.5 and 0.7). The glass of the a1 samples shows lower contents in all of the rare earth elements with respect to the a3 and a4 samples and much lower variability. The glasses of the uppermost layer have higher HFSE contents (Nb, Zr), while the glass of the a3 layer has a lower Rb content with respect to the other two (Figure 9c–e).

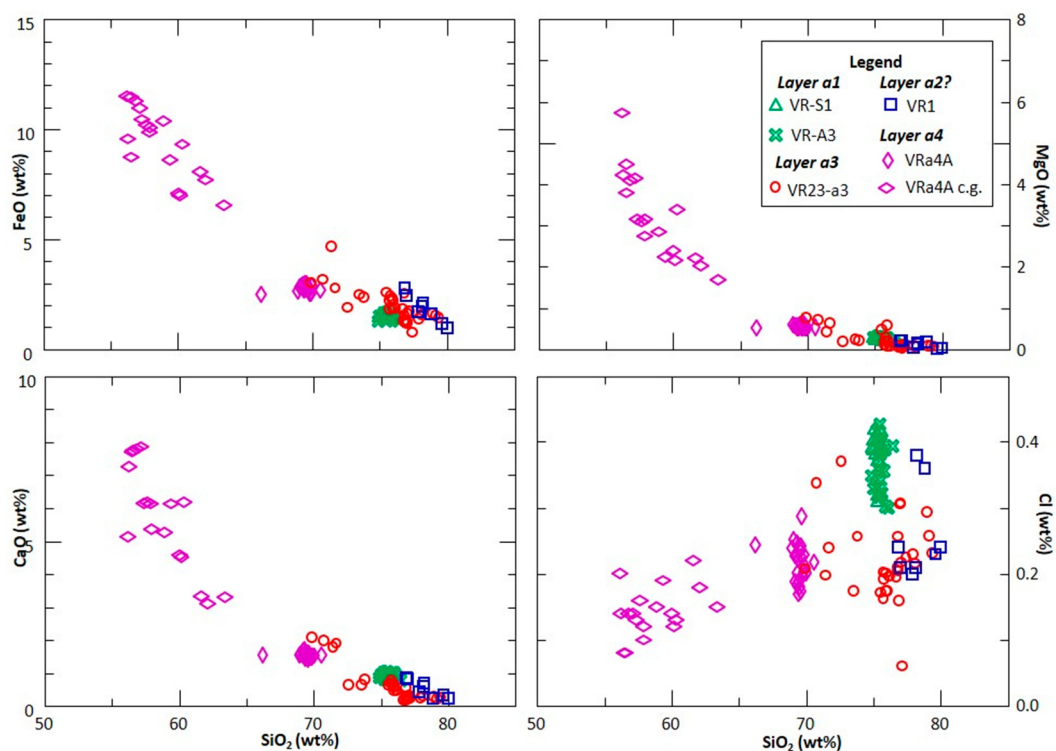


Figure 8. Harker diagrams for the glass of the four tephra layers.

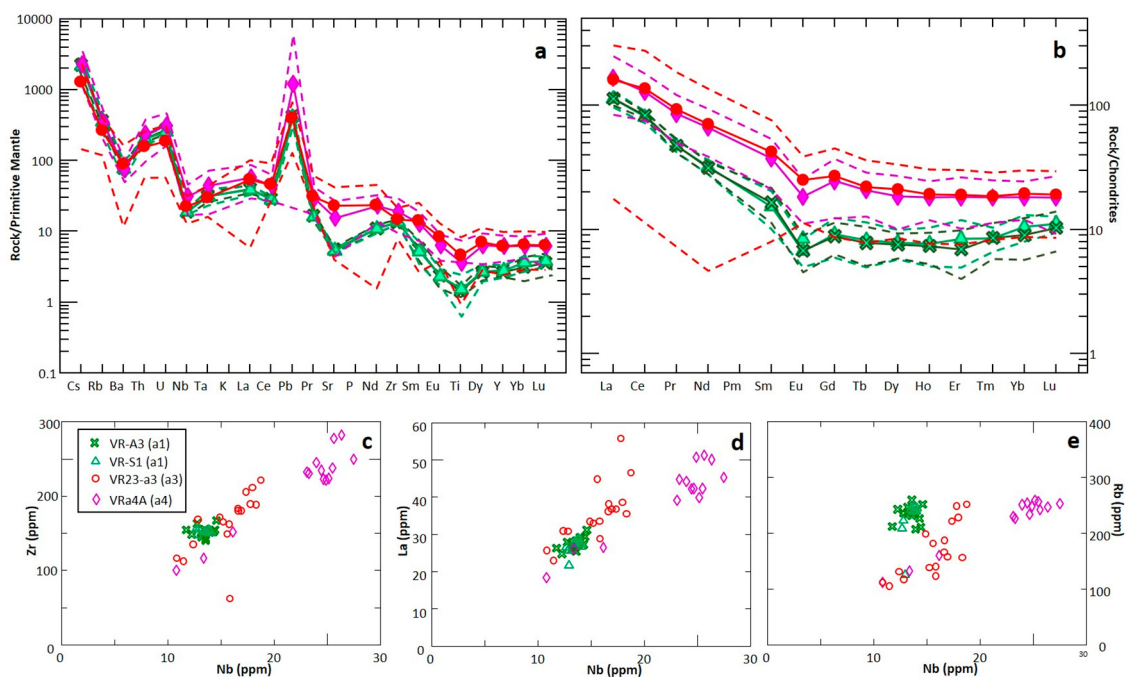


Figure 9. (a) Spider diagram of incompatible elements (normalization to primitive mantle after [55]; (b) spider diagram of rare earth elements (normalization to chondrites after [55]). In (a,b), the solid line with symbols represents the average value for each sample, while the dashed lines of the same color encompass the compositional variability. As a comparison, the glass composition of samples from subduction zones has been plotted and is represented by the black asterisk (average Upper Pilato compositions, Lipari, Aeolian Islands, Italy; data from [56]). (c–e) Variation diagrams of incompatible elements as a function of Nb content.

5. Discussion

5.1. Single vs. Multiple Volcanic Sources

As shown in the previous section, many differences in petrography, mineral composition and glass chemistry occur between the samples of the different layers, and in some samples, a strong intra-sample variability is also observed. On the basis of pyroxene and amphibole composition, [12] suggests different volcanic sources for the same volcanic ash layer, at least for a2, a3 and a4 tephtras.

The analyses carried out in this work show a high homogeneity in mineral and glass composition for the a1 layer, for which there is no evidence of multiple volcanic sources nor heterogeneous eruptions.

In layer a3, a certain variability in the glass composition, in terms of major and trace elements, has been observed. This variability could be explained by slight differences in the weathering degree or the variable crystallinity of the glass. However, it cannot be excluded that they are due to the simultaneous deposition of tephtras from different volcanoes. This could also be confirmed by the occurrence of clinopyroxene crystals with different compositions (diopside and augite).

The uppermost layer clearly shows the occurrence of two distinct populations of glasses with different shapes, textures and compositions. Such differences can be explained with the contribution, in different proportions, of at least two eruptions to this tephra layer. Alternatively, this layer could be the result of sedimentation from a single eruption from a chemically zoned magma chamber, where the poorly vesiculated, microcrystalline and silica-poor fragments represent the less differentiated magma crystallized at the bottom or along the walls of the magma chamber, while the main population of almost aphyric, highly vesiculated, rhyolitic glass is formed by the more evolved, volatile-rich magma at the top of the reservoir. Tapping of different magma chambers or syn-eruptive mixing or mingling could also produce chemically heterogeneous glass shards [57].

5.2. Correlation with Other Pleistocene Tephtras in the Mediterranean Area

Several distal tephra deposits have been recognized as interbedded in the stratigraphic sequences of the Apennines (for a review, see [58]). However, for most of them, no precise age or compositional data are available, and thus establishing a possible correlation with the Croton basin tephtras is impossible.

In central Italy, near the towns of Mosciano S. Angelo and Bellante (Abruzzo region, see the position in Figure 10), a tephra layer was found interbedded in the middle Pliocene–Lower Pleistocene marine sequences of the Periadriatic basin and was analyzed and dated by fission tracks on glass and apatite by [59]. Age determinations for this layer range from 2.08 ± 0.19 to 2.12 ± 0.19 Ma (errors as 1σ). The same authors correlate this tephra to that cropping out in different quarries in Valle Ricca, near Rome, on the Tyrrhenian coast and whose age is 2.03 ± 0.26 Ma [60,61] and, tentatively, to the oldest layer of this study. Considering the uncertainties associated with the determined ages, these layers can correspond to each of the tephtras of the Croton basin. However, the mineralogy of the Valle Ricca volcanic ash layer, including plagioclase, sanidine, Mg-hornblende and clinopyroxene, does not perfectly match the mineral assemblages of any of the analyzed samples in the Croton basin. The main differences are represented by the occurrence of orthopyroxene and the absence of sanidine in these last samples. A comparison of the geochemical composition of glass fragments demonstrates how the Croton a1 tephra is very similar to the tephra layers of central Italy layers, and particularly to the Periadriatic tephtras, in terms of major element contents (Figure 11a–c). A correlation between a1 and Periadriatic tephra layers is therefore possible. The wide dispersion of a3 compositions

and the lack of radiometric age determination on this layer make it difficult to confirm or exclude a correlation with the central Italy tephra.

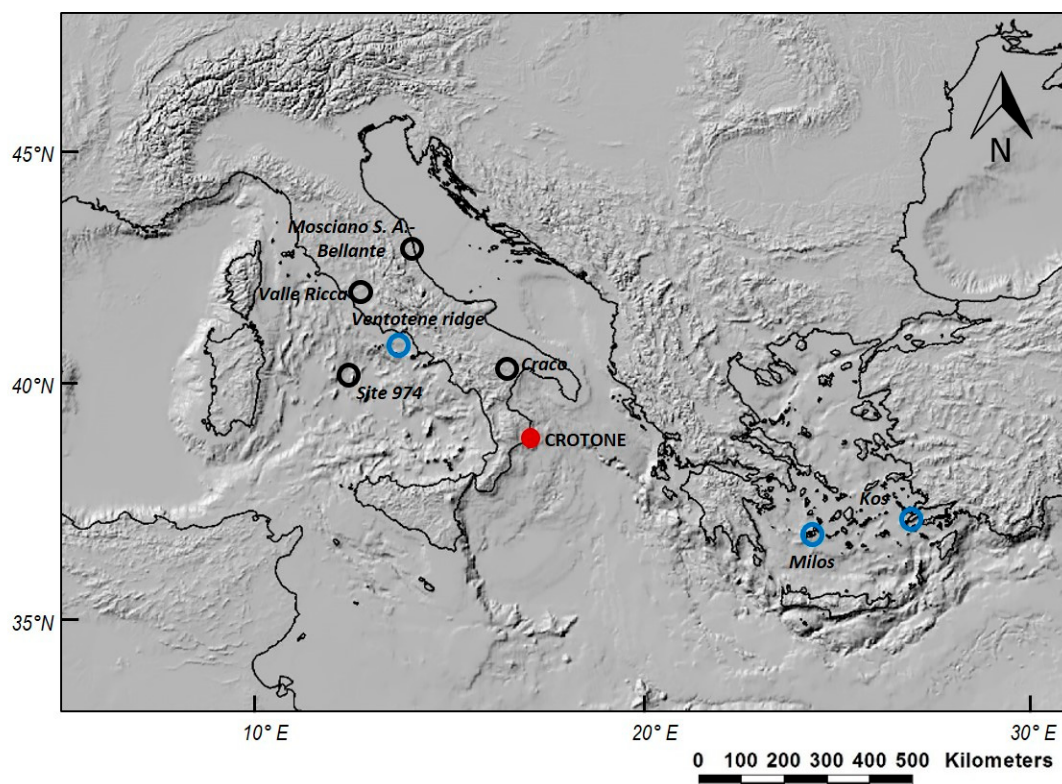


Figure 10. Location of areas where Lower Pleistocene tephra layers have been recognized (black circles). Possible sources discussed in the text are also shown (blue circles).

Ref. [62] analyzed and dated two volcanoclastic turbiditic successions in the southern Apennines, specifically in the area of Craco (Basilicata, south Italy, Figure 10), about 150 km NNW of Crotona. The deposit, whose $^{39}\text{Ar}/^{40}\text{Ar}$ age is 2.24 ± 0.06 Ma, contains glass shards and crystals of plagioclase, ortho- and clinopyroxene, hornblende and rare biotite. The age and petrography of these deposits are, therefore, very similar to those of the a1 layer in the Crotona area. A correlation between the two layers is confirmed by the geochemistry of the glass major elements: in addition to being superimposed with the a1 samples in the TAS diagram (Figure 11a) and in the Al_2O_3 and FeO vs. SiO_2 diagrams (Figure 11b,c), the glass of Craco ash also shows the same distinctively high chlorine content and the same alkali ratios (Figure 11d).

Plio–Pleistocene tephra layers have also been recognized in the cores of ODP Leg 161 in the central Tyrrhenian basin, site 974 [63] (Figure 10). Among the analyzed tephra layers, the sample vt7538–7539 has an estimated age of 1.8 Ma and is thus comparable with that of the Vrica a4 layer. A possible correlation between the two tephras was suggested by [64]. However, the petrography of the 7538–7539 sample, including quartz, plagioclase, K-feldspar, clinopyroxene and amphibole, does not match that of the a4 layer. A comparison of the glass composition (Figure 11a–d) shows higher silica contents and lower $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios for the glasses of the central Tyrrhenian core, and seems, therefore, to exclude a correlation between the two tephras. Analogously, an older tephra in the same core, vt7502 (2.4 Ma), cannot be correlated with the sub-coeval a1 layer of the Crotona basin, having a highly potassium alkaline character (Figure 11a–d).

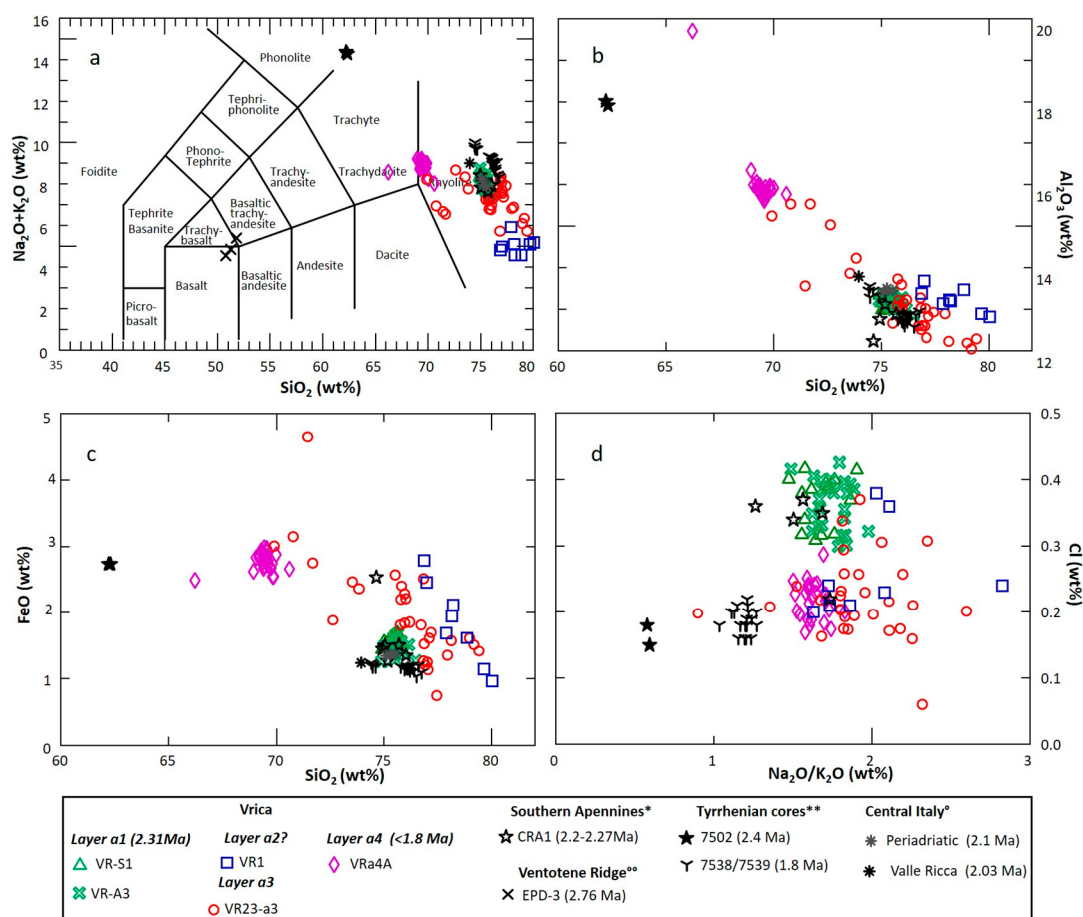


Figure 11. Comparison, on the basis of glass major elements, between the tephras of the Crotona basin and other Lower Pleistocene tephras recognized in Italy. The composition of the Ventotene ridge lavas is also shown for comparison. (a) TAS diagram; (b) Al_2O_3 vs. silica; (c) FeO vs. silica; (d) chlorine vs. alkalis ratio. Note the similarity in composition between the glass of a1 Crotona tephra (green symbols) and those of Southern Apennines (empty black star) and Central Italy (black and gray asterisk) with similar ages. Conversely, the composition of glass from the cores in the Tyrrhenian Sea of 1.8 Ma (solid black star) does not match that of coeval a4 tephra (purple diamond). Data sources; *: [62]; **: [63]; °: [59]; °°: [65].

5.3. Source Area(s)

The geodynamic setting of the source area(s) of the tephra layers can be inferred by the immobile trace elements using the diagrams of Figure 12 for high silica rocks [66]. An origin from volcanic arc and/or syn-collisional geodynamic setting seems probable for all the samples. A possible exception is represented by the glass of the a4 layer, showing a weak within-plate affinity. However, even in this layer, the occurrence of ortho- and clinopyroxene in the mineralogical assemblage, together with the calc-alkaline character of the glass and the negative spikes in Ti and Nb in the spider diagrams, points to an origin related to convergence tectonic settings.

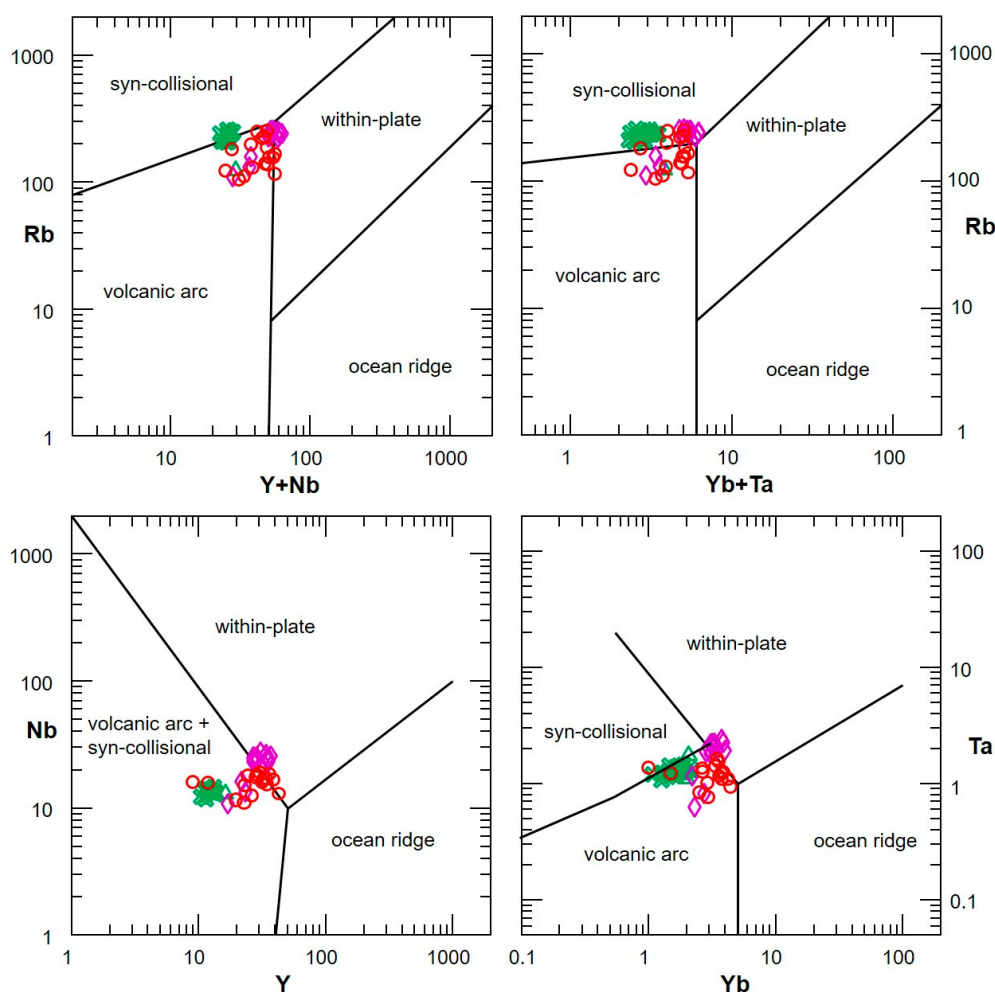


Figure 12. Diagrams of immobile elements for the identification of tectonic setting (after [65]). All elements are in ppm. Symbols as in the previous figures.

Many volcanic arcs were active in the Mediterranean basin and surrounding areas during the Plio–Pleistocene. In particular, in the time-span of interest (2.4–1.8 Ma), many volcanic islands were active in the Aegean Sea (for a review, see [67]). However, it has been demonstrated that during explosive eruptions in the Mediterranean area the dispersion of the eruptive column by the dominant winds is preferentially from west towards east, and only rarely in the opposite direction. In a recent paper [68], it was calculated that, for an eruptive column of 30 km in height, the probability of having ash dispersion towards the west is only 1% at a distance from the source ranging between 570 and 860 km, roughly corresponding to the present distance between the Croton basin and the islands of the Aegean Sea (see, as an example, the position of the Milos and Kos islands in Figure 10). It seems, therefore, highly probable that the source area is to be found towards the west, in the Tyrrhenian Sea or along the Tyrrhenian peninsular margin.

A compositional similarity with the rhyolites of Ponza was evidenced for the Southern Apennines tephra cropping out in the area of Craco, and probably correlated with the a1 layer [62]. However, the detailed reconstruction of the volcanic history of the Pontine islands made by [69] clearly shows a gap in the volcanic activity on the island of Ponza between 2.9 and 1 Ma, while the island of Palmarola entirely formed between 1.64 and 1.52 Ma. It is, therefore, more plausible that the source area of the a1 layer is to be found in the submerged volcanoes in the central Tyrrhenian Sea. According to [70], a volcanic arc formed between 5 and 2 Ma between the Vavilov and Marsili basins. The volcanic arc includes the seamounts Anchise and Glauco, together with the Ventotene south seamount

and the rhyolites of Ponza. Recently, volcanic rocks from the Ventotene volcanic ridge, located in the eastern Pontine islands (Figure 10), were dredged and dated by [65]. The dredged samples are trachibasaltic lavas (Figure 11a) with an age of 2.76 ± 0.039 Ma; therefore, they are older than the lowermost a1 layer of the Crotona basin. However, the calc-alkaline affinity and the orogenic geochemical signatures of the Ventotene ridge samples suggest that this paleo-arc can be the source area of the Lower Pleistocene volcanoclastic deposits interbedded in the marine deposits of the Crotona basin, Southern Apennines and Periadriatic basin.

6. Conclusions

The main conclusions of this work can be summarized as follows:

- 1- At least three tephra layers are interbedded in the Lower Pleistocene sequence of the Crotona basin. Though no specific sedimentological analysis was possible, due to the cohesion of the tephras, the lack of visible traction structures, the rather homogeneous grain size of each layer and the absence of non-volcanic components point to a primary origin of these tephras, deriving from the ash transported by the wind in the umbrella region of a Plinian column(s), deposited and poorly reworked in a deep marine environment. The occurrence in the mineralogical assemblage of the three tephras of ortho- and clinopyroxene, together with the composition of the trace elements of the glass shards, allows us to infer that they are related to subduction-related volcanism. According to the prevalent dispersion towards the east of the eruptive columns in the Mediterranean area, the source could be identified in a paleo-arc located in the Central Tyrrhenian Sea, possibly identifiable with the Ventotene volcanic ridge.
- 2- The lowermost layer (a1, 2.31 ± 0.34 Ma) is made up of compositionally highly homogeneous rhyolitic glass shards and crystals of plagioclase, ortho- and clinopyroxene and amphibole. The age, petrography and composition of the glass allow us to correlate this layer to the tephra layers that crop out in Basilicata and central Italy. It therefore represents evidence of a highly explosive activity occurring in the paleo-arc during the Lower Pleistocene, whose products were dispersed over a wide area.
- 3- Due to its uncertain position and its high weathering degree, no correlation was possible for sample A1, possibly representative of layer a2 of [12]. The mineralogical assemblage is given by plagioclase, orthopyroxene, amphibole, biotite and subordinate clinopyroxene. The few analyzed glass shards have a rhyolitic composition and a lower alkali content with respect to the other layers.
- 4- The age of the a3 layer is unknown, but, due to its stratigraphic position, it must be comprised between that of a1 and 1.8 Ma (i.e., the age of the Gelasian–Calabrian limit). Its mineralogical assemblage is represented by plagioclase, ortho- and clinopyroxene and rare oxides. The composition of the glass shards is rhyolitic, and at least two populations of glass shards have been identified. No correlation with known tephra layers in the Mediterranean area was possible for this layer.
- 5- Layer a4 lies above the Gelasian–Calabrian limit, which allows us to infer an age younger than 1.8 Ma. The mineralogical assemblage is given by plagioclase, biotite, ortho- and clinopyroxene; apatite and Fe-Ti oxides are accessory phases. Most of the glass shards and pumices of which it is composed are aphyric and highly vesiculated, with a silica content of about 69 wt.%. The occurrence of a second population of highly crystalline, less vesiculated, and less silica-rich glass shards could indicate the contribution of multiple sources or an origin related to a chemically heterogeneous magma. Also, for this layer, no possible correlation was found.
- 6- The detailed petrographic and geochemical characterization of the tephra layers interbedded in the Crotona marine sequence, besides adding further knowledge to the

best-studied early Pleistocene succession in the world, is of great importance for future identification and correlation of Gelasian–Calabrian sequences in the Mediterranean area. In the Crotona sequence, the GSSP of the base of the Calabrian stage occurs between two of the studied tephra layers, namely a3 and a4. As they are easily recognizable in the field, while the sapropel “e” is not always easily identified [9], their finding and identification are of great importance in stratigraphic studies as intra-basinal marker beds. In this work, we could not recognize these two tephras in other sedimentary basins. However, future studies could reveal their occurrence in other lower Pleistocene sequences, such as those in which the lowermost a1 layer has been recognized. The correlation on a petrographic and compositional basis with those of Vrica will be fundamental for stratigraphic correlations of Lower Pleistocene sequences at a regional scale.

As a final consideration, we remark that all the correlations found in this work are mainly based on petrography and the major elements content of the glass, as analyses of the trace elements of tephra layers have only recently become routine practice. In recent decades, many authors have underlined the importance of trace elements in tephrostratigraphic studies, as they enable better discrimination of the source and, in many cases, are less affected by weathering processes (e.g., [3,71] and references therein). The glass trace elements obtained for the tephras of the Crotona basin will, therefore, be a useful tool for future studies aimed at correlating Lower Pleistocene sequences in the Mediterranean area and, possibly, at identifying the old volcanic sources in the Tyrrhenian Sea.

In conclusion, the findings of this work highlight the importance of studying distal volcanoclastic deposits, which often represent the only witness of old eruptions from volcanic edifices that are no longer exposed and for which it is very hard to obtain volcanological and geochemical information. Moreover, the correlation of tephra layers occurring at high distances from one another is essential to synchronize sedimentary sequences in distant basins.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min15020156/s1>. Table S1: Standard materials used for EMPA glass and mineral analysis; Table S2: Major elements’ glass composition determined by EPMA; Table S3: Pyroxene composition determined by EPMA; Table S4: Plagioclase composition determined by EPMA; Table S5: Amphibole composition determined by EPMA; Table S6: Biotite composition determined by EPMA; Table S7: Analyses of standards used for LA-ICP-MS microanalysis; Table S8: Trace elements’ glass analyses by LA-ICP-MS.

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