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EARLY PLEISTOCENE DISTAL PYROCLASTIC-FALLOUT MATERIAL IN CONTINENTAL AND MARINE DEPOSITS OF WESTERN UMBRIA (ITALY): CHEMICAL COMPOSITION, PROVENANCE AND CORRELATION POTENTIAL

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ABSTRACT: Bizzarri R. *et al*., *Early Pleistocene distal pyroclastic-fallout material in continental and marine deposits of western Umbria (Italy): chemical composition, provenance and correlation potential.* (IT ISSN 0394-3356, 2010).
Distal pyroclastic fallout material has been recently documented in the Orvieto area (Umbria, central Italy), within Early Pleistocene continental and marine deposits. Due to the age constrains, the association with Middle Pleistocene "Paleobolsena" Volcanic events can be excluded. In order to individuate a possible provenance, the Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) analytical procedure has been carried out. The procedure has been tested on pumice lapilli (2-5 mm) and glass inclusions contained in idiomorphic clinopyroxene crystals, both coming from the Early Pleistocene conglomerate of the Il Caio section. The study is still in progress: some preliminary results are here proposed. Data on melt inclusions seem to be more reliable than data on pumice fragments for the purpose of recognising pristine magmatic compositions of pyroclastic material and to achieve information on the provenance of volcanic clasts. Nevertheless, both data suggest the affinity with the Roman Comagmatic Provence. Since crystal fragments with melt inclusions are common in many distal fallout deposits, the LA-ICP-MS protocol presented here can be of general application to tephrochronology and volcanological studies. Together with the biostratigraphic record, indeed, the procedure looks promising as a tool for stratigraphic correlations and geodynamic reconstructions.

RIASSUNTO: Bizzarri R. et al., *Depositi piroclastici da caduta nei depositi marini e continentali del Pleistocene inferiore in Umbria occidentale (Italia): composizione chimica, provenienza e potenzialità di correlazione. (IT ISSN 0394-3356, 2010).*
Depositi piroclastici da caduta sono stati recentemente segnalati nell'area orvietana (Umbria, Italia Centrale), in depositi sia marini che continentali datati al Pleistocene inferiore. Su base biostratigrafica sembra da escludere la correlazione con gli eventi esplosivi del Pleistocene medio riferibili al "Paleobolsena". Per individuarne la provenienza, è stata impostata la procedura analitica LA-ICP-MS, testata in via preliminare sia su lapilli pomicei che su inclusioni vetrose, contenute all'interno di cristalli idiomorfi di clinopirosseno, provenienti dai conglomerati del Pleistocene inferiore della sezione de Il Caio. Lo studio è ancora in corso; proponiamo qui alcuni risultati preliminari. I dati delle inclusioni vetrose sembrano più attendibili rispetto alle pomici ai fini della ricostruzione della composizione primaria del magma e della provenienza dei clasti vulcanici. Nonostante ciò, entrambi i dati suggeriscono un'affinità dei materiali analizzati con le rocce della Provincia Comagmatica Romana. Poiché cristalli con inclusioni vetrose sono comuni in molti depositi da caduta, l'analisi LA-ICP-MS può essere di applicazione generale negli studi tefrocronologici e vulcanologici. Associata all'analisi biostratigrafica, la procedura appare uno strumento promettente per le correlazioni stratigrafiche e le ricostruzioni geodinamiche.

Keywords: Pyroclastic deposits, LA-ICP-MS, Melt inclusions, Tephrochronology, Early Pleistocene, Central Italy.

Parole chiave: Depositi piroclastici, LA-ICP-MS, Inclusioni fluide, Tefrocronologia, Pleistocene inferiore, Italia Centrale.

1. AIMS AND METHODS

Rapid, precise and reliable major and trace element composition of distal pyroclastic material is critical in tephrochronological and volcanological studies. Investigation on ashes and pumice fragments is generally used for these purposes. Distal pyroclastic fallout material has been recently documented in the Orvieto area (Umbria, central Italy: (Fig. 1A)), in both continental and marine deposits, biostratigraphically referred to the Early Pleistocene (Bizzarri *et al.*, 2003; Bizzarri, 2006; Famiani, 2010). These deposits bearing distal pyroclastic fallout material crop out on a 10-20 km wide area around the Orvieto town. Particularly, five sections are here considered: *Il Caio* section, *Camorena* section, *Padella* section, *Sugano* well and the small outcrop of *F.so Aiuole*. Most of the volcanic material is represented by leucite-bearing pumice clasts and idiomorphic pyroxene crystals (Fig. 1B); although volcanic materials are included in sedimentary deposits, they lack clear reworking evidences. The idiomorphic pyroxene crystals range among 0.5 and 10 mm, show a preserved *habitus*, and can be related to a local source, probably represented by a small, still unknown volcanic vent in 10 to 20 km radium, whose activity, presumably intermittent, covered a time span of at least 300 ky (MNN 19 b-d Nannofossil zones). The age constrains permit us to exclude a correlation to Middle Pleistocene "*Paleobolsena*" Volcanic events. In order to determine magma composition (major and trace elements) of distal pyroclastic material, and to individuate its possible provenance, the Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) analytical protocol has been carried out, by coupled investigation of pumice clasts and glass inclusions trapped in minerals. The procedure has been tested on pumice lapilli (2-5 mm in diameter) and microscopic glass inclusions contained in single idiomorphic clinopyroxene crystals (2-10 mm), both coming from the *Il Caio* section (Figs. 1B, 2). LA-ICP-MS analysis on pumice clasts has been carried out on glass beads obtained by the melting of small amounts of rock powder. A few mg of pumice is sufficient for a complete major and trace element analysis, which allows us to study extremely small samples, typical of distal fallout deposits. LA-ICP-MS analysis of glass inclusions is carried out *in situ*; an inclusion of at least 50 μm is sufficient to determine a complete set of major and trace elements. The capability of the LA-ICP-MS instrumentation to perform spatially resolved and whole rock trace element analysis is largely assessed in the literature (e.g. LONGERICH *et al*., 1996; GÜNTHER *et al*., 1997, 1999; NORMAN *et al*. 1998; DURRANT 1999; EGGINS, 2003; PETRELLI *et al*., 2007, 2008).

2. GEOLOGICAL SETTING AND BIOSTRATIGRAPHIC CONSTRAINS

The five study sections (Figs. 1A, 1C) belong to the *Paglia Valley*, a NW-SE oriented half-graben, which accommodated a coastal marine environment from Early Pliocene to Early Pleistocene (AMBROSETTI *et al*., 1987; BIZZARRI *et al*., 2003; MANCINI *et al*., 2004; BIZZARRI, 2006). The *Camorena* and *Sugano* well sections document a clayey, marine offshore sedimentation, whereas the *Aiuole* and *Padella* sections mainly represent a sandy lower shoreface marine environment (Figs. 1A, 1C). Nannofossil assemblages allow to recognize four biostratigraphic events (bm*G*, t*Cm*, bl*G*, tl*G*, *sensu* Raffi, 2002: Fig. 1C) and to assign to deposits a time range comprised between ~1.9 and ~1.1 Ma (MNN 19a to e Nannofossil Subzones). Three horizons, enriched in volcanoclastic materials (mainly pumice fragments and idiomorphic pyroxene crystals), have been documented (Fig. 1C). On the other hand, the *Il Caio* section (Fig. 1C)

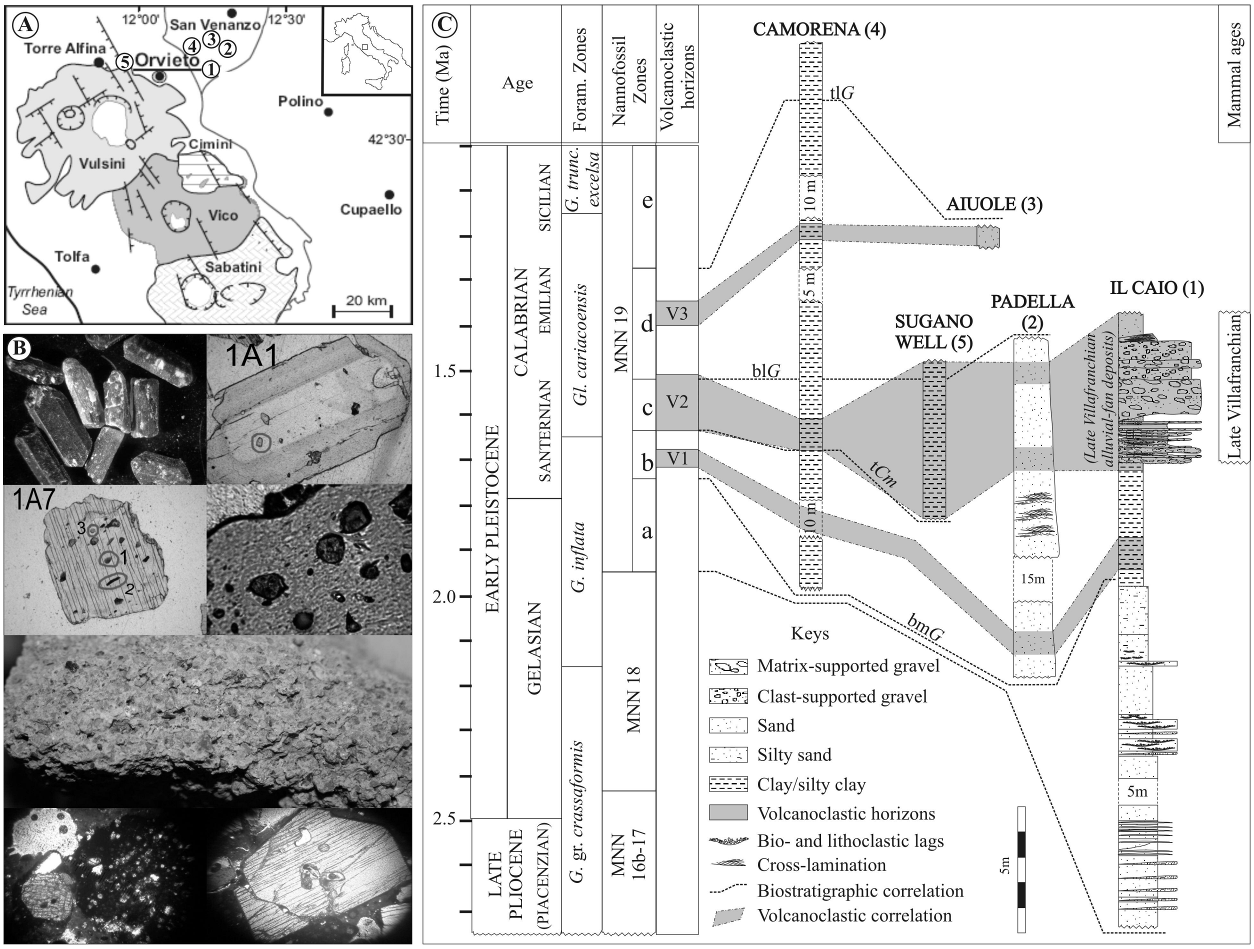

Figure 1 - A) Schematic sketch of the area and location of studied sections: 1=Il Caio, 2=Padella, 3=Aiuole, 4=Camorena, 5=Sugano well. Extension of main volcanic districts products (Vulsini, Cimini, Vico and Sabatini Mountains) is also reported. B) Remote fallout analyzed materials: melt inclusions-bearing pyroxenes and leucite-rich pumices. C) Biostratigraphic correlation of studied sections and volcanic events: bmG=medium Gephyrocapsa FO, tCm= C. macintyrei LO, blG large Gephyrocapsa FO, tlG= large Gephyrocapsa LO.

A) Schema semplificato dell'area e ubicazione delle sezioni studiate: 1=Il Caio, 2=Padella, 3=Aiuole, 4=Camorena, 5=Sugano well. Viene riportata anche l'estensione dei prodotti correlati ai principali distretti vulcanici (Vulsini, Cimini, Vico e Sabatini) presenti nell'area. B) Aspetto dei depositi piroclastici analizzati (pirosseni con inclusioni vetrose e pomici a leucite). C) Correlazione biostratigrafica delle sezioni studiate e degli eventi vulcanici: bmG=medium Gephyrocapsa FO, tCm= C. macintyrei LO, blG large Gephyrocapsa FO, tlG= large Gephyrocapsa LO.

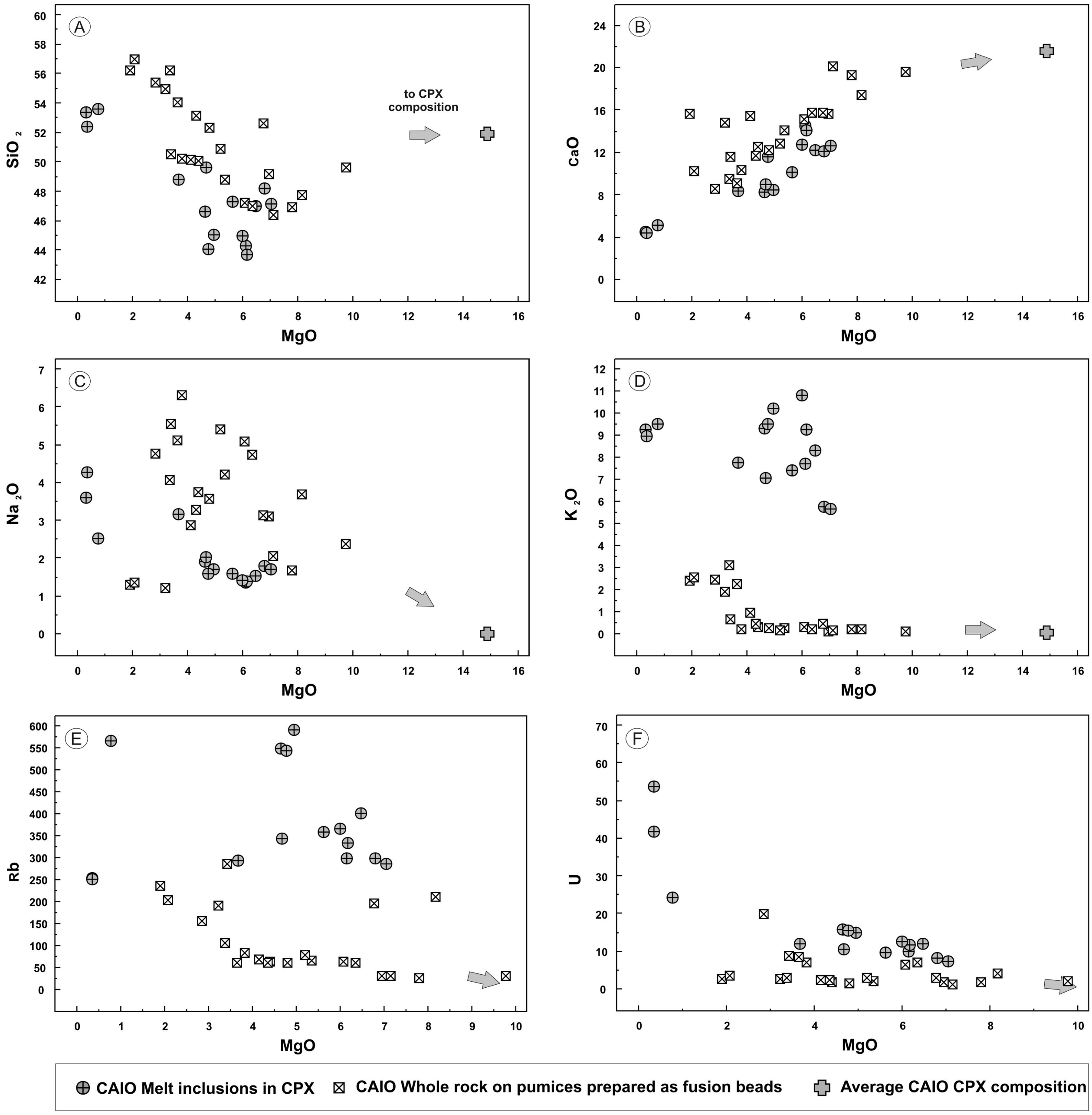

Figure 2 - Variation diagrams of representative major and trace elements against MgO for melt inclusions hosted in pyroxene phases and pumice samples prepared as fusion beads.

Diagrammi di variazione dei più rappresentativi elementi maggiori e in tracce vs MgO, per le inclusioni fluide nei pirosseni e i campioni di pomici (perle di fusione).

consists in a lower portion (~23m) of shallow marine deposits and an upper part (~6m) characterized by continental alluvial fan deposits (BIZZARRI *et al*., 2003). The alluvial-fan deposits contain, dispersed within sedimentary clasts, small fragments of pyroclastic materials including pumices and clinopyroxenes. Nevertheless, an idiomorphic pyroxenes-rich horizon has also been documented inside the marine deposits (Fig. 1C). Calcareous nannoplankton assemblages with *Gephyrocapsa oceanica s.l*. (3.5-4 μm), *Calcidiscus macintyrei, Helicosphaera sellii, Coccolithus pelagicus*, referable to Early Pleistocene (MNN 19a and 19b sub-zones: RAFFI, 2002) fix the lower limit of the section to ~1.90 Ma, and the top of marine deposits to ~1.62 Ma. The bm*G* event (*sensu* RAFFI, 2002), dating ~1.75 Ma has also been documented. In addition, Late Villafranchian freshwater mollusc assemblage (BIZZARRI *et al*., 2003), collected in alluvial-fan deposits, point to an age not higher than 1.4 Ma for the section's top. As a consequence, the age of V2 and V1 horizons (Fig. 1C) is comprised between 1.4 Ma and 1.62 Ma, and between 1.75 and 1.62 Ma, respectively. Analogous age constrains characterize the other four outcrops (Fig. 1C). Distal fallout deposits, documented in the five sections, cover a time span of about 300 ky, from ~1.75 to ~1.4 Ma (MNN 19 b-d Nannofossil zones), and biostratigraphic constrains confirm the occurrence of three successive steps in volcanic activity (V1, V2, V3 volcanoclastic horizons: Fig. 1C). The V1 horizon is documented in marine deposits on the *Il Caio* and *Padella* sections and occurs in the MNN 19b zone (~1.75 to 1.62 Ma). The main volcanoclastic horizon (V2) is recognizable in the *Il Caio*, *Padella* and *Camorena* sections, in the *Sugano* well, and dates to 1.62-1.5 Ma (MNN 19c zone). The V3 horizon (*Camorena* section, *F.so Aiuole* outcrop) is biostratigraphically constrained at ~1.50 Ma (MNN 19d zone).

3. ANALYSES ON IL CAIO VOLCANOCLASTIC DEPOSITS

The volcanic fragments coming from alluvial-fan deposits in the uppermost part of the *Il Caio* section has been selected as a reference to test the described analytic protocol, due to their abundance and the grade of preservation, in spite of the high-energy sedimentary environment, as well as for their major dimensions in respect to fragments collected in the other sites. On the other hand, this section has been formerly described both on its sedimentary, stratigraphic and geochemical-petrologic features (Bizzarri *et al.*, 2003). Data obtained on melt inclusions, glass beads of pumices are shown as variation diagrams of major and trace elements against MgO (Fig. 2), as spider diagrams (Fig. 3), and as incompatible trace element ratios (Fig. 4). Analyses of pumice samples are shifted to higher CaO and SiO_2 than data on melt inclusions (Fig. 2) and there is an overall higher concentration of K_2O, Rb, Pb, U, in the melt inclusions than in the pumice samples (Fig. 2). Na_2O is much higher and more scattered in the pumice samples than in the melt inclusions. Differences for SiO_2 and CaO between pumice samples and melt inclusions are likely related to the presence of cpx phenocryst in the pumice clasts. Cpx compositions reported on the Harker diagrams show, in fact, continuity with compositions of pumice samples, suggesting some effect of mineral composition on pumice major elements (see arrows in Fig. 2). It must be reminded that pumice clasts have a small size and also a single cpx phenocryst may have strong effects on major element chemistry, shifting pumice compositions toward those of the mineral phase. This can also be responsible for narrower ranges of incompatible elements in pumice samples, since the presence of volumetrically significant cpx may passively decrease abundances of elements that are not hosted by cpx. Low concentrations of K_2O and Rb in pumices, along with the large scattering and high concentrations of Na_2O likely reflect secondary alteration processes. In particular leucite is completely transformed into analcite. Lower Pb and U contents of pumices than glass inclusions are also likely due to secondary alteration processes of the groundmass, since these two elements are mobile during deuteric processes. Note that those elements that are poorly mobile during secondary processes (e.g., REE, Nb, Ta, Zr, Th etc.; Fig. 3) show similar ranges of abundances and ratios (Fig. 4 A) in both pumices

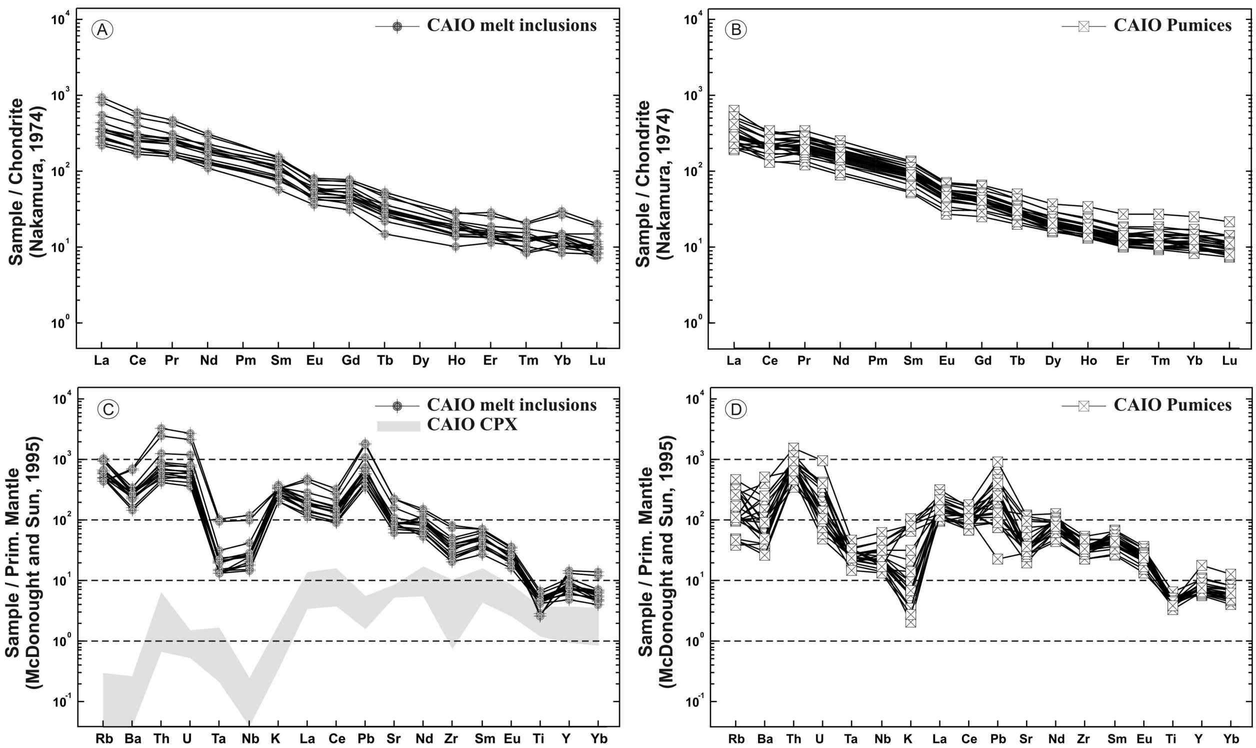

Figure 3 - (A, B) REE patterns of melt inclusions hosted in pyroxene phases (A) and pumice samples (B); (C, D) Incompatible element patterns normalized to primordial mantle composition for melt inclusions and cpx (C) and pumice samples (D).

(A, B) diagrammi REE delle inclusioni fluide all'interno dei pirosseni (A) e delle pomici (B); (C, D) Andamento degli elementi incompatibili normalizzati alla composizione del mantello primordiale per le inclusioni fluide (C) e le pomici (D).

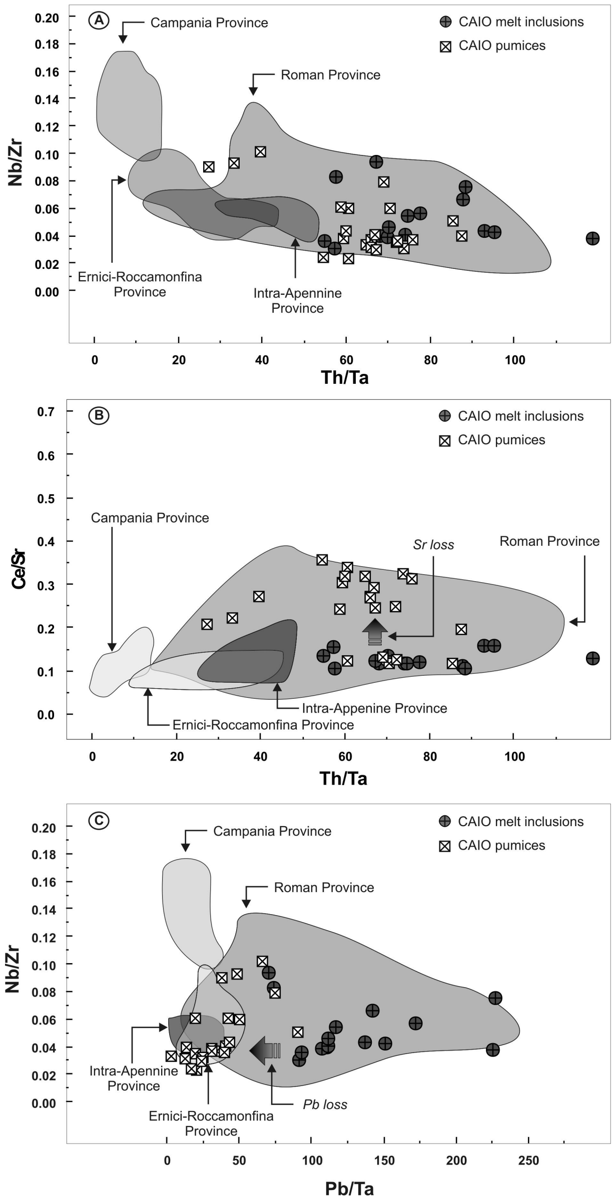

Figure 4 - Variation of trace element ratios in the Plio-Quaternary rocks (MgO>4 wt.%) from the Central Italy area (from PECCERILLO, 2005) compared with CAIO melt-inclusions and pumice samples: (A) Nb/Zr Vs Th/Ta; (B) Ce/Sr Vs Th/Ta; (C) Nb/Zr Vs Pb/Ta. See text for details.

Variazione degli elementi in tracce nelle rocce plio-quaternarie (MgO>4 wt.%) del centro Italia comparata con le inclusioni fluide e le pomici del Caio (da PECCERILLO, 2005): (A) Nb/Zr vs Th/Ta (B) Ce/Sr vs Th/Ta; (C) Nb/Zr vs Pb/Ta. Ulteriori dettagli nel testo.

and melt inclusions. Overall, the data suggest a strong role of secondary processes in modifying pumice compositions. In contrast, melt inclusions do not appear to be affected by secondary processes. Elements that are immobile during secondary processes (e.g. REE, Nb, Ta, Zr, Th, etc.) show similar range of compositions and element ratios in pumice and melt inclusions (Figs. 3, 4). The ultrapotassic affinity of the investigated pumice samples and melt inclusion is obvious. Their affinity with magmas of the Roman province is suggested by both the petrography of the pumice clasts and by major and trace element geochemistry of pumice and melt inclusions (PECCERILLO, 2005). All samples are silica undersatured, REE patterns for both melt inclusions and pumice are fractionated with LREE progressively enriched with respect to HREE (Figs. 3A, 3B). Most samples display a small negative Eu anomaly. REE patterns do not evidence any difference between pumice samples and melt inclusion supporting the idea that REE were relatively immobile during alteration processes. Similar REE patterns are observed in the ultrapotassic rocks of central Italy (PECCERILLO, 2005). However, small negative Ce anomalies are common in the pumice samples, but not in the melt inclusions and the Roman magmas. Data on pumice samples reveal high concentrations of incompatible elements, especially some Large Ion Lithophile Elements (LILE: Ba, Th, U, LREE, Pb), and relatively low concentrations of High Field Strength Elements (HFSE: Ta, Nb, Hf, Zr, Ti) resembling ultrapotassic rocks (i.e. tephrite to phonolite) from the Roman volcanoes. However, some elements such as Rb, Pb and K are depleted in pumice samples whereas others (e.g. Na_2O) are enriched, likely due to secondary processes (Figs. 3C, 3D). Data on melt inclusions entrapped in clinopyroxene crystals reveal a narrower range of compositions than pumice samples for several major and trace elements. Trace element distribution reveals high enrichments for all LILE, including K, Rb and Pb, and low HFSE, matching more closely Roman ultrapotassic magmas. Ratios of immobile trace elements (e.g. Nb/Zr, Th/Ta, etc.) are similar in pumice clasts and the glass inclusions, and both fall in the field of Roman volcanic rocks (Fig. 4A). Other ratios involving mobile elements (e.g. Ce/Sr, Pb/Ta, Ce/Pb, Th/U, K/Na) are very different in the pumice samples with respect to melt inclusions, the latter falling within the field of Roman volcanics (Figs. 4B, 4C).

4. CONCLUDING REMARKS

The study is still in progress. Since crystal fragments with melt inclusions are common in many distal fallout deposits, the proposed LA-ICP-MS protocol on melt inclusions can be of general application to tephrochronology and volcanological studies. The application to the fall out material included in the *Il Caio* Early Pleistocene section clearly shows that pumice fragments are affected by secondary processes but not melt inclusions. Therefore data on melt inclusions seem to be more reliable than data on pumices for the purpose of recognising pristine magmatic compositions of pyroclastic material and to achieve information on the provenance of volcanic clasts. Elements that are immobile during secondary processes (e.g. REE, Nb, Ta, Zr, Th etc.) show a similar range of compositions and element ratios in pumices and melt inclusions. All geochemical data, such as the ultrapotassic character, the silica undersatured signature, the progressive enrichment of LREE with respect to HREE, the high LILE enrichments and high LILE/HFSE patterns, clearly define a strict affinity of *Il Caio* pyroclastic materials with magmas of the Roman magmatic province (PECCERILLO, 2005). The next step will be to apply this procedure to idiomorphic clinopyroxene crystals and/or pumice clasts collected in other sites, to test the real Roman affinity for the *Camorena, Sugano* well, *Padella* and *F.so Aiuole* fallout deposits, in order to confirm their inferred biostratigraphic correlation. This first application of melt inclusion geochemical data in the study of pyroclastic fall out materials deposited in a sedimentary basin opens new perspectives in several fields: it could be useful to (a) better constrain the age (sedimentary section are generally well time constrained), (b) define the areal distribution of eruptions and, more in general, (c) reconstruct the evolution of the volcanism within the Mediterranean area. Together with the biostratigraphic record, indeed, the procedure looks promising as a tool for stratigraphic correlation and geodynamic reconstructions.

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