Geochemical fingerprints of volcanic materials: Identification of a pumice trade route from Pompeii to Rome

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ABSTRACT

Geochemical investigations on samples of pumice and lava extracted from the mortars and concretes of the Forum of Caesar and the Forum and Markets of Trajan are presented and integrated with previous analyses of lava samples from Rome and Pompeii, and of pumices from the Colosseum and the Dioclethian's Bath, with the aim to identify the lithological provenance of these materials. Discrimination diagrams based on ratios of selected trace elements (i.e., Zr/Y, Nb/Y, Th/Ta, Nb/Zr) allow us to recognize the geochemical signature of the different volcanic regions of central Italy. These diagrams indicate that in the mortars of the Forum of Caesar and Forum of Trajan, the Roman builders integrated the scanty pumices from deposits of the Monti Sabatini Volcanic District near Rome with others coming from the Vesuvius and Phlegrean Fields. Some of the pumices employed in the vaulted ceilings of these monuments display a peculiar geochemistry that has a unique correspondence with a pyroclastic deposit recovered in a borehole drilled on the southern flanks of Vesuvius. Similarly, lava flows from this borehole display a different trace-element signature with respect to that of other coeval lava flows of the northern flanks of Vesuvius, and it has a closer correspondence to that of the archaeological lava samples. These observations, integrated with historical and archaeological data, indicate that the Roman builders had a profound empirical knowledge of the physical properties of the volcanic rocks from different regions, and suggest that a systematic cultivation of lightweight volcanic material occurred in the area of Pompeii for exportation to Rome and, likely, to other regions of the Mediterranean.

INTRODUCTION

Recent work has discovered the presence of millimeter-sized, white to yellowish pumice clasts in the mortar of the vaulted ceilings of the Forum of Caesar (46–44 BCE; Jackson et al., 2009a) and Forum of Trajan (96–115 CE; Bianchi et al., 2009; Jackson et al., 2009b), along with decimeter-sized vesicular lavas constituting the coarse aggregate of the concrete (Amici, 1991). The Forum of Caesar (46–44 BCE) is the earliest monument in Rome in which the use of this particular lightweight lava, imported from the Vesuvius area (Lancaster et al., 2011), has been documented, so far. Subsequently, the employment of this material, apparently with the purpose of reducing the weight of the vaulted ceilings, became more common, as it is observed in several monuments of Imperial age (e.g., Basilica Julia, Basilica Ulpia, Baths of Trajan, Pantheon and Baths of Caracalla; De Angelis d'Ossat, 1930; Lugli, 1957; de Laine, 1997; Lancaster, 2005). Besides the first appearance of the vesicular lava, the Forum of Caesar is also the first monument in Rome to record the introduction of pumice in the fine aggregate of the mortars, as known so far, suggesting also that the pumice may have been imported from Campania, along with the lava. However, while during the Imperial age, the use of pumice was coupled to that of the vesicular lava only in the concretes of the vaulted ceiling (Jackson et al., 2010), in the Forum of Caesar it was mixed with volcanic ash (pozzolan) also in the mortar of the walls (Jackson et al., 2009a), evidencing an innovative approach by the Roman constructors and suggesting an attempt to experiment with new mixing of aggregates in the mortars. Establishing the provenance of the pumice and the criteria of its selection is therefore of great importance to understanding the evolution of technical expertise of Roman engineers and their empirical knowledge about the physical properties of the volcanic materials, and it provides insights on the exploitation of the natural resources, and the commercial exchanges and the trade routes of the Roman world at the beginning of the Imperial age.

Petrographic studies and geochemical analyses on major elements are not diagnostic to ascertain the lithological provenance of the pumices employed in the Forum of Caesar and Forum of Trajan (Jackson et al., 2009a, 2009b). Indeed, the presence of K-feldspar phenocrysts (sanidine) in the pumices indicates a general provenance from the highly potassic magmas of the greater Roman Comagmatic Region, including the Latial and the Campanian Volcanic Districts (Washington, 1906) (Fig. 1). Moreover, the small size and high porosity of the pumice clasts favor rapid alteration, which may induce significant changes in the original chemical composition, so hindering the use of the common classification diagrams (e.g., total alkali-silica [TAS] diagram; Le Bas et al., 1986). To overcome these difficulties, in this work, we performed trace-element analyses on seven pumice and three vesicular lava specimens extracted from the mortars of different structures of the Forum of Caesar and the Forum and Markets of Trajan, and we rely on the relative abundance of immobile elements, which are supposed to be less sensitive to weathering processes (Cann, 1970; Floyd and Winchester, 1975; Pearce, 1996; Duzgoren-Aydin et al., 2002). Following the approach outlined in Marra et al. (2011), who showed that the ratios of Zr, Nb, Y, Th, and

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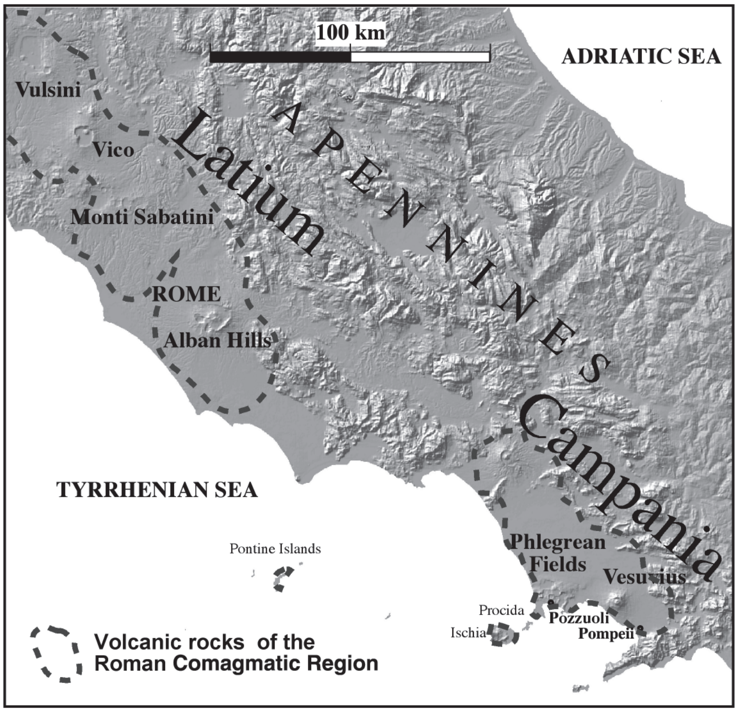


Figure 1. Digital elevation map (DEM) of central Italy showing the location of the volcanic districts of the Roman region.

Ta represent reliable geochemical signatures of specific volcanic areas of central Italy and, sometimes, of single eruption units, we review the scientific literature and propose several classification diagrams with the aim to compare the geochemical compositions of the archaeological samples (integrated with seven samples from Rome and Pompeii analyzed by Lancaster et al., 2011) with the primary deposits of the diverse volcanic regions of Italy.

Finally, a review of ancient literary sources gives indications for quarry locations, methods of transportation, and possible storage areas of the various volcanic materials from late Republican era through the Imperial era, as well as on builders' criteria for selecting different kinds of pumice as aggregate in the mortars of the Forum of Caesar and the Forum and Markets of Trajan.

POSSIBLE SOURCE AREA FOR THE PUMICE

The volcanic rocks that constitute the geologic substrate of Rome (Figs. 1 and 2) were broadly employed in concrete masonry and to produce dimension stone of the ancient city (Lugli, 1957; Fornaseri et al., 1963; Heiken et al., 2005; Jackson and Marra, 2006). These rocks were erupted by the potassic volcanic districts of Alban Hills and Monti Sabatini, between 561 ka and 36 ka (Karner et al., 2001; Marra et al., 2004, 2009; Freda et al., 2006). The Alban Hills volcano (De Rita et al., 1988, 1995; Giordano et al., 2006), despite a highly explosive eruptive behavior, never produced significant pumice deposits, due to its peculiar magma composition and evolution (Freda et al., 1997; Gaeta et al., 2006). By contrast, relatively large pumice deposits are associated with several explosive eruptions occurring at the Monti Sabatini (Mattias and Ventriglia, 1970; De Rita et al., 1993; Sottili et al., 2004, 2010). Twenty- to 50-cm-thick layers of the distal fraction of these pumice deposits are occasionally exposed within the City of Rome and its close surroundings, whereas they crop out in up to 1-m-thick beds along and nearby the Via Tiberina and Via Flaminia, 20–35 km to the north (Fig. 2; Karner et al., 2001).

Exploitation of these outcrops and transportation of the pumice to Rome may not have been much profitable, especially if compared with that from other quarrying sectors. Indeed, a more appealing source for the pumice used as aggregate in the Roman concretes may have been the large deposits emplaced by the activity of the Phlegrean Fields and Vesuvius, occurring in the Bay of Naples (Santacroce, 1987; Rosi and Sbrana, 1987). Exportation of the Campanian pyroclastics used in the formulation of harbor concretes occurred along the central Italian coast (Oleson et al., 2004; Brandon et al., 2008). The pumice employed in the mortars of the monumental concretes may have followed the same route as the Vesuvian vesicular lava used in the construction of the Forum of Caesar (46–44 BCE) and during the whole Imperial age (Lancaster et al., 2011).

Other possible source areas for the pumice might have been the Vico (Perini et al., 2004, and references therein) and Vulsini (Palladino et al., 2010, and references therein) Volcanic Districts, although the longer distance from Rome with respect to Monti Sabatini makes this hypothesis less probable.

Finally, a provenance from the Pontine Islands, off the coast of Latium, or even from the Aeolian Islands, where large pumice deposits occur (Peccerillo, 2005, and references therein), is excluded based on the very different chemical composition of these volcanic deposits, which have higher SiO_2 contents (up to 72%).

DATA

Zr/Y-Nb/Y and Th/Ta-Nb/Zr Diagrams

Zr/Y, Nb/Y, Nb/Zr, and Th/Ta have been computed for all the pyroclastic products and lava flows of the Roman Comagmatic Region (including the volcanic districts of Latium and Campania, commonly reported as the Roman and the Campanian provinces, respectively; Peccerillo, 2005) for which absolute trace-element concentrations were published in the literature through 2011, and are reported in the diagrams of Figures 3, 4, and 5. Remarkably, in the Zr/Y versus Nb/Y plot, the lava flows of Vesuvius and the Phlegrean Fields (here defined as the restricted Campanian province: CA) are separated by a straight line (oblique dashed line in Fig. 3A) from those of Latium, including Vulsini (VU), Vico (VI), Monti Sabatini (MS), Alban Hills (AH), and those of the Roccamonfina (RM) district. The latter is commonly attributed to the Campanian Province (e.g., Peccerillo, 2005); however, based on data from the diagrams of Figure 3 and 4, we prefer to include it into an enlarged Roman Province and consider a restricted Campanian Province, including only Phlegrean Fields (with Procida and Ischia) and Vesuvius. Moreover, the Campanian lavas define a horizontally elongated and vertically narrow compositional field in the Th/Ta versus Nb/Zr diagram (Fig. 3B), with Th/Ta values between 4 and 12, whereas those of the enlarged Roman Province display Th/Ta >12, with the exception of one analyses of a Roccamonfina sample.

Similarly, there is substantially no overlapping among the Zr/Y versus Nb/Y compositional fields of the pyroclastic products

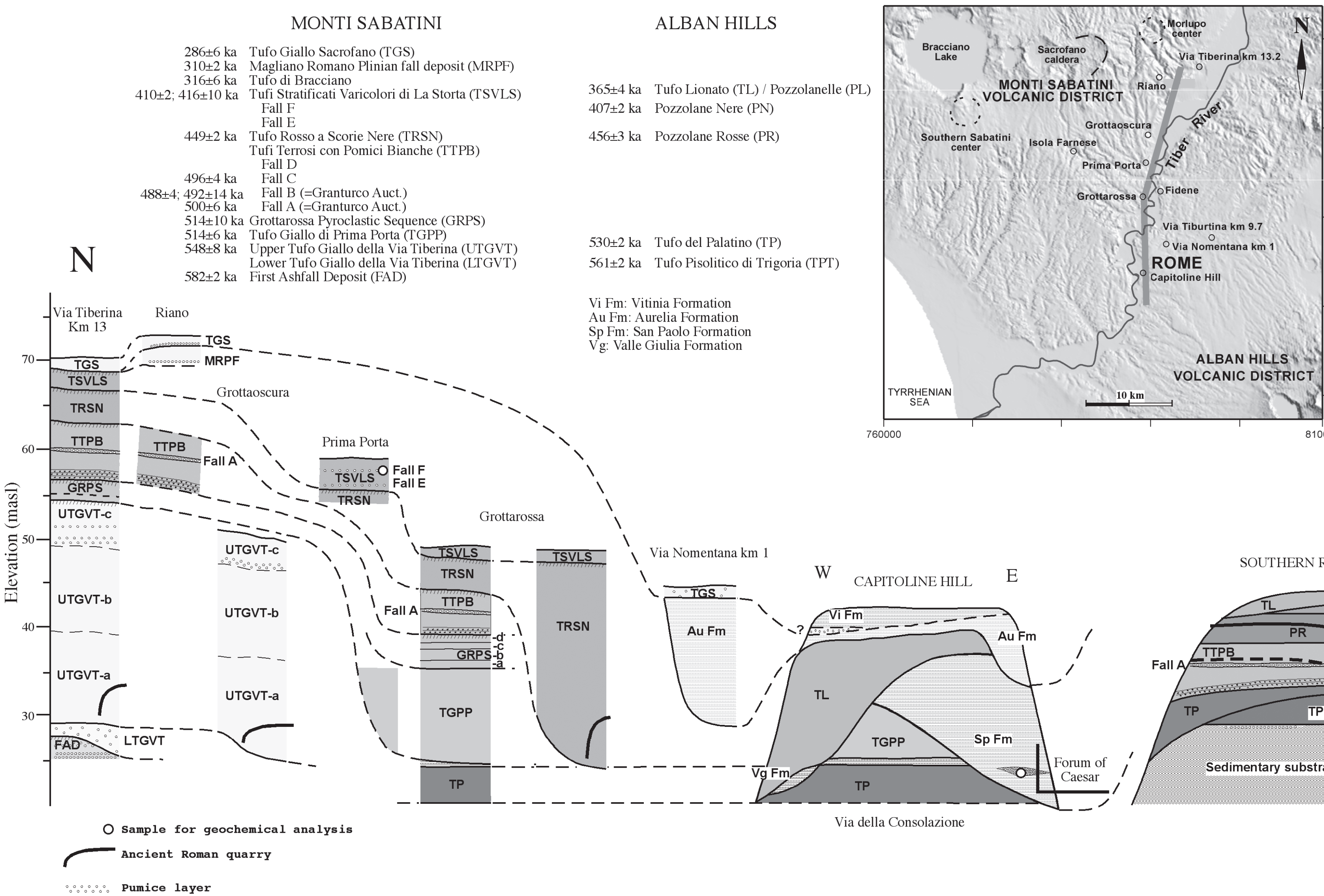


Figure 2. Schematic cross section showing the stratigraphy of the volcanic deposits of Monti Sabatini and their interfingering with those of the Alban Hills and with the volcaniclastic successions in the surroundings of Rome. Chronostratigraphy is after Karner and Renne (1998), Karner et al. (2001), Sottili et al. (2010), and Marra et al. (2009).

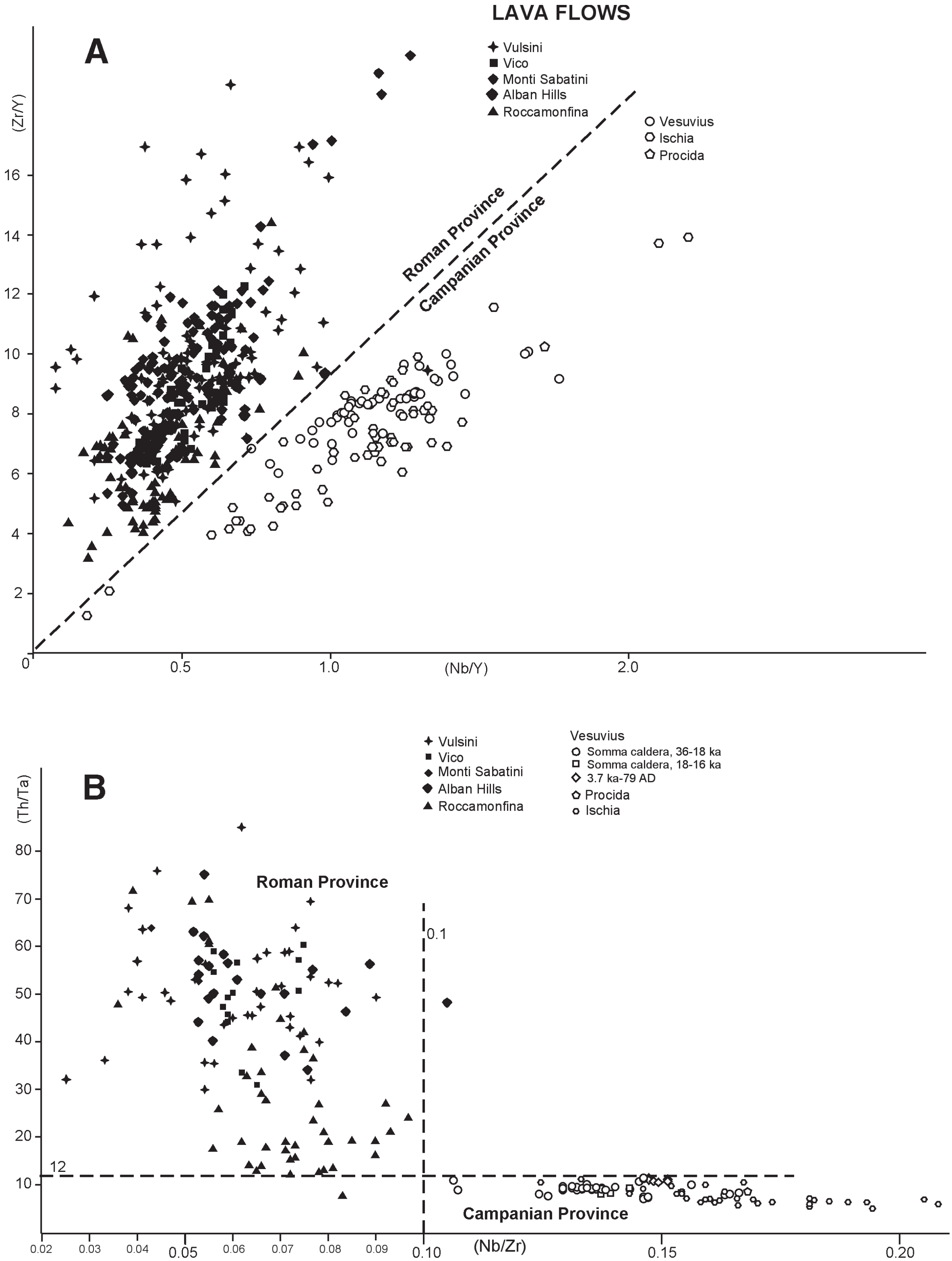


Figure 3. Zr/Y versus Nb/Y (A) and Th/Ta versus Nb/Zr (B) compositions of lava flows of the Roman Comagmatic Region (data from Lustrino et al., 2010). Volcanic districts of Vesuvius, Phlegrean Fields, Ischia, and Procida (here defined as the restricted Campanian province) are separated by a straight line (oblique dashed line in part A) from those of Latium, consisting of Vulsini, Vico, Monti Sabatini, and the Alban Hills, plus Roccamonfina. The angular coefficient of the parting line between the fields for lava flows of these two volcanic regions corresponds to a Nb/Zr ratio of ~0.10, which represents a lower limit for the lava flows of the Campanian province, and an upper limit for those of the Roman province (dashed vertical line in part B). Similarly, a Th/Ta ratio around 12 (horizontal dashed line in part B) is a boundary for the fields of the Campania and Latium (plus Roccamonfina) lavas.

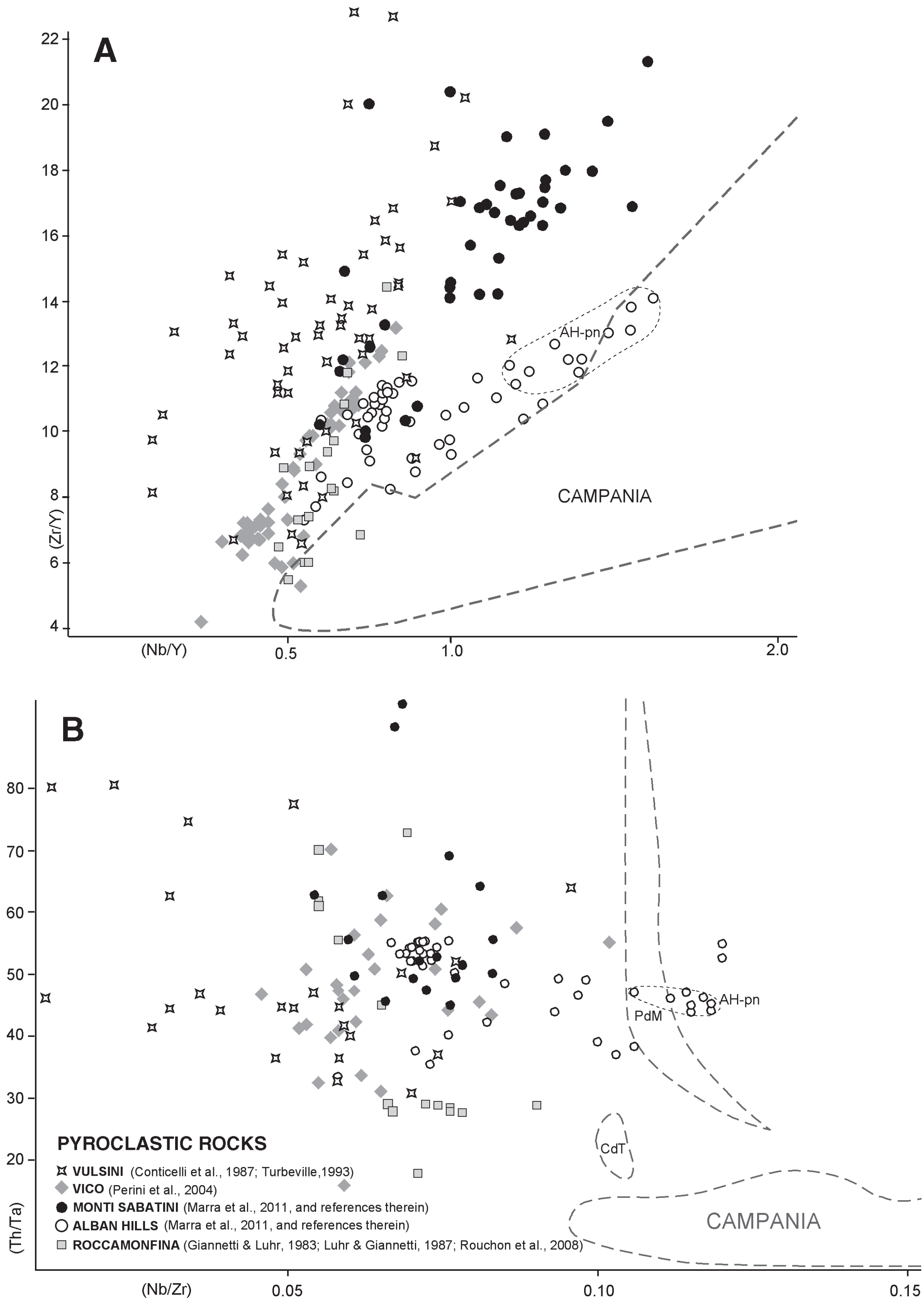


Figure 4. Zr/Y versus Nb/Y (A) and Th/Ta versus Nb/Zr (B) compositions of pyroclastic rocks of Latium and Roccamonfina Volcanic Districts compared to the compositional fields (dashed lines) of the Campanian products (see Fig. 5). A very limited overlapping occurs between the two volcanic regions, limited to the peculiar compositions of the Pozzolane Nere (pn) and the Pomici di Marcato (PdM) eruptions from the Alban Hills and Vesuvius, respectively.

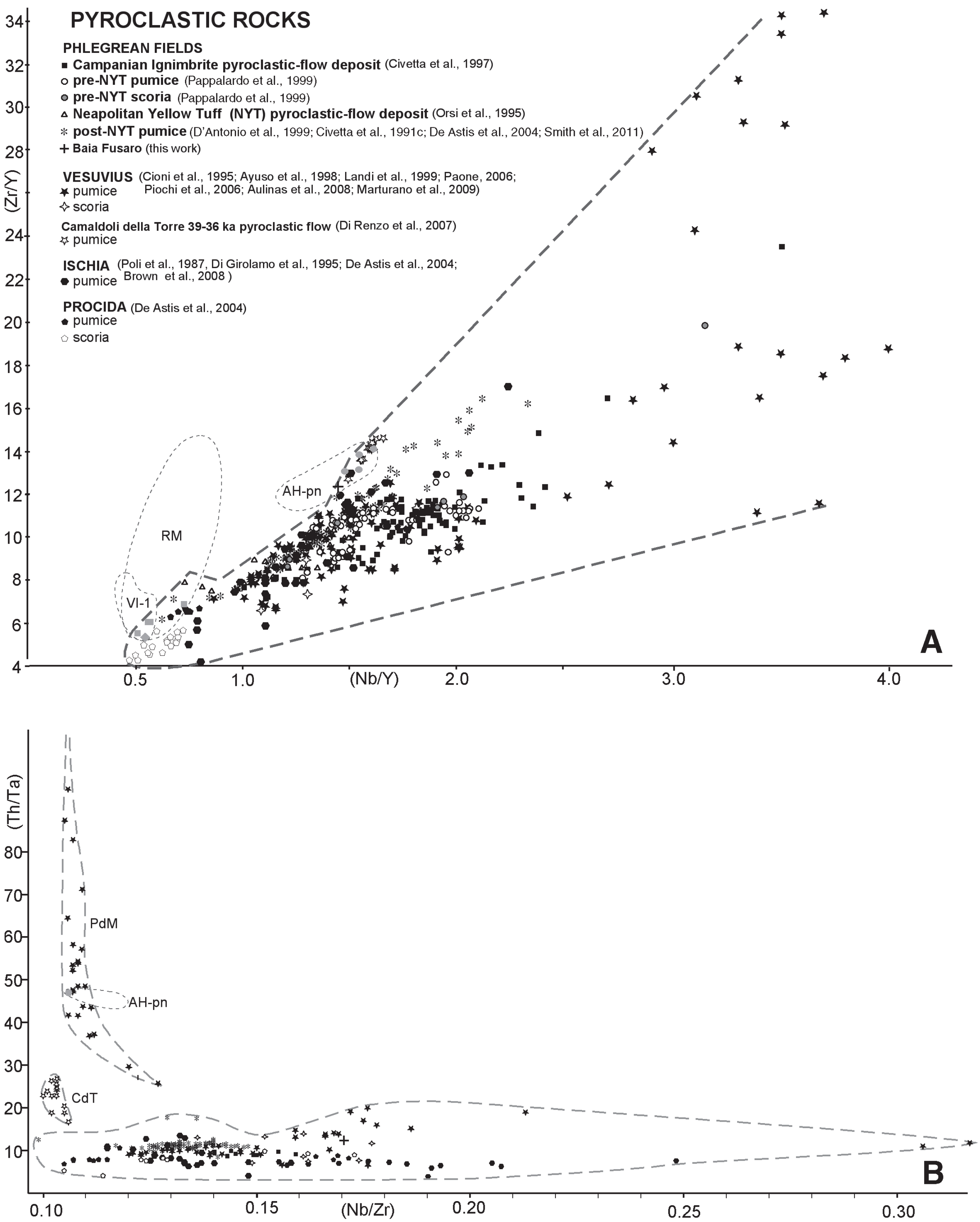


Figure 5. Zr/Y versus Nb/Y (A) and Th/Ta versus Nb/Zr (B) compositions of pyroclastic rocks of Campania. The compositions of the products from Latium and Roccamonfina partially overlapping with the compositional fields of the Campanian products (see Fig. 4) are also shown.

of Campania (bordered by the dashed line in Figs. 4A and 5A) and those of Latium and Roccamonfina, with the exception of a limited numbers of analyses. A definite separation also occurs when Th/Ta and Nb/Zr are considered (Figs. 4B and 5B). With the exception of the Pozzolane Nere Eruption Unit (AHpn, Fig. 4), which, in turn, overlaps the outlier compositions of the "Pomici di Mercato" eruption (PdM), the pyroclastic products of Vulsini, Vico, Monti Sabatini, Alban Hills, and Roccamonfina display clearly distinguished fields with respect to the Campanian ones.

In order to establish the lithologic provenance of the pumices employed in the mortars of the Forum of Caesar and Forum of Trajan, we selected Zr/Y, Nb/Y, Nb/Zr, and Th/Ta for the pumice deposits of Latium and Campania, and we built the diagrams of Figure 6 to compare the archaeological samples. The compositional fields of the Vesuvius lavas are also reported in Figure 6 (dashed line) in order to compare the samples of vesicular lava used by the Roman builders.

Each volcanic district is characterized by a compositional field displaying an elongated shape on the Nb/Y versus Zr/Y diagram of Figure 6A, which should be considered a geochemical signature of the magma feeding the volcanic districts (Marra et al., 2011). Indeed, with the exception of the Roccamonfina district, a clockwise rotation of the main axes of Zr/Y Nb/Y distribution follows the regional location of each field, from north to south (VU, VI, MS, AH; Figs. 4A and 6A). Although a discussion of the causes of these trends is beyond the scope of the present research, this feature represents a useful tool for identifying the provenance of archaeological materials such as the pumices employed in the ancient Roman mortars. Based on this feature, the attribution of three pumice samples (FC-p2, BU-p1, and GA-p2) to the products erupted by the Monti Sabatini Volcanic District is straightforward, whereas all the other pumices display an evident "Campanian" signature (Fig. 6A). Similarly, all the vesicular lava samples have Zr/Y and Nb/Y values univocally evidencing their Campanian origin, and, in particular, all but one (BU1) match the composition of one particular subfield (see further discussion) of the Vesuvius lava flows (Fig. 6A). An indubitably different regional provenance for the three pumice samples with a Monti Sabatini Zr/Y and Nb/Y composition is evidenced also in the Th/Ta versus Nb/Zr diagram of Figure 6B, where these samples plot within the field of the Latium volcanoes and are clearly distinguished from the other pumice and lava samples with a tight Campanian Th/Ta versus Nb/Zr values.

However, Figure 4B shows that Th/Ta and Nb/Zr values do not represent as good a means of discrimination among the volcanic districts of the Roman province. A wider range of variability characterizes Th/Ta for most products of the Roman province, a feature that is not balanced by distinct Nb/Zr values in the case of Vulsini and Monti Sabatini, hindering the possibility to make discriminations based on this geochemical feature alone. Moreover, a possible decrease of Th/Ta as a consequence of strong weathering has been inferred from the study of the pedogenized Monti Sabatini deposits (Marra et al., 2011), accounting for the fact that the mortar pumices (which are strongly altered) with Monti Sabatini compositions lap the lower margin of the Th/Ta-Nb/Zr field of this volcanic district in Figure 6B.

For all the aforementioned reasons, in this study, we will rely mainly on the Zr/Y versus Nb/Y diagrams, which appear to be able to distinguish among the specific eruptive units within each volcanic region. Aimed at this scope, in the following section, we describe the petrographic and geochemical features of the primary volcanic products that originated widespread pumice deposits and represent the best candidates for exploitation, and we will compare their trace-element composition with that of the archaeological samples.

STRATIGRAPHIC, PETROGRAPHIC, AND GEOCHEMICAL DATA FOR THE PRIMARY PUMICE DEPOSITS

Monti Sabatini Pumice Deposits

The general stratigraphy of the southern sector of Monti Sabatini Volcanic District is shown in the cross sections of Figure 2, which extend along the western side of the Tiber River valley from km 13.5 of Via Tiberina, through Riano, Grottaoscura, and Grottarossa, where the main ancient Roman quarries were located (Lugli, 1957; Jackson and Marra, 2006), to the center of Rome at Capitoline Hill. The only exploitable white pumice layers throughout this sector appear to be First Ashfall Deposits and Fall A and Fall B layers within the Tufi Terrosi con Pomici Bianche.

(1) First Ashfall deposits, 582 ± 2–548 ± 5 ka (Karner et al., 2001): This unit crops out at the base of the volcanic succession at km 13.5 of Via Tiberina (Fig. 2). Within the City of Rome, First Ashfall deposits are 10–20 cm thick; they are buried by younger volcanic rocks and have been found only in boreholes (Karner et al., 2001).

The pumice has phonolitic composition and a subaphyric texture characterized by a vitrophyric groundmass and low vesicularity; scarce clinopyroxene, sanidine, plagioclase, and oxide phenocrysts are present (Masotta et al., 2010).

(2) Fall A and Fall B layers within the Tufi Terrosi con Pomici Bianche (500 ± 6–488 ± 2 ka (Karner and Renne, 1998; Karner et al., 2001): Among the four fallout deposits of the Tufi Terrosi con Pomici Bianche (Fall A–D; Sottili et al., 2004), Fall A and Fall B have a general southeastern dispersion axis, accounting for a widespread distribution, although with thickness never exceeding few decimeters in the area of Rome (Pomici Bianche layers within the Tufi Terrosi—Karner et al., 2001; "Granturco"—Fornaseri et al., 1963). Fall A is more continuous and underlies the Tufo Rosso a Scorie Nere pyroclastic-flow deposit along the western side of the Tiber River valley between Grottarossa and Prima Porta (Fig. 2). In Rome, the same pumice fall is intercalated within an up to 6-m-thick pack of altered ash, ubiquitously present below the Pozzolane Rosse pyroclastic-flow deposit (Fig. 2). Two samples collected in Grottarossa and at km 9.7 of Via Tiburtina were analyzed in Marra et al. (2011). The comparison of trace-element signatures of these samples to those of Fall A and Fall B provided in Sottili et al. (2004) and Lancaster et al. (2011) allowed us to revise their previous attribution to Fall B and correlate them to Fall A (Fig. 7).

Fall A pumice has a trachytic composition (Sottili et al., 2004) and shows a subaphyric texture with moderate-to-high iso-oriented vesicles; it contains very scarce sanidine, biotite, clinopyroxene, and accessory plagioclase, leucite, and oxide phenocrysts (Plate 1a, GSA Data Repository material[1]).

Several other pumice deposits are associated with the activity at Monti Sabatini Volcanic District, but none of these is exposed with significant thickness along the Tiber Valley north of Rome, or within the city. The Zr/Y and Nb/Y compositions of all these deposits are plotted in the diagram of Figure 7 for comparison with those of the pumice mortar samples. Remarkably, Zr/Y and Nb/Y values for two samples of Fall A collected in Grottarossa and at km 9.7 of Via Tiburtina are consistent with those of three mortar pumice samples (Fig. 7). This is verified also for the ash-flow deposit of the Lower Tufo Giallo della Via Tiberina, and, to a lesser extent, for the Tufo Giallo di Sacrofano, although extraction of pumice from these semilithified tuffs

[1]GSA Data Repository item 2013072, Appendix with description of methods; two tables with geochemical data (Table DR1) and analytical standards and errors (Table DR2); two plates with photomicrographs, is available at http://www.geosociety.org/pubs/ft2013.htm or by request to editing@geosociety.org.

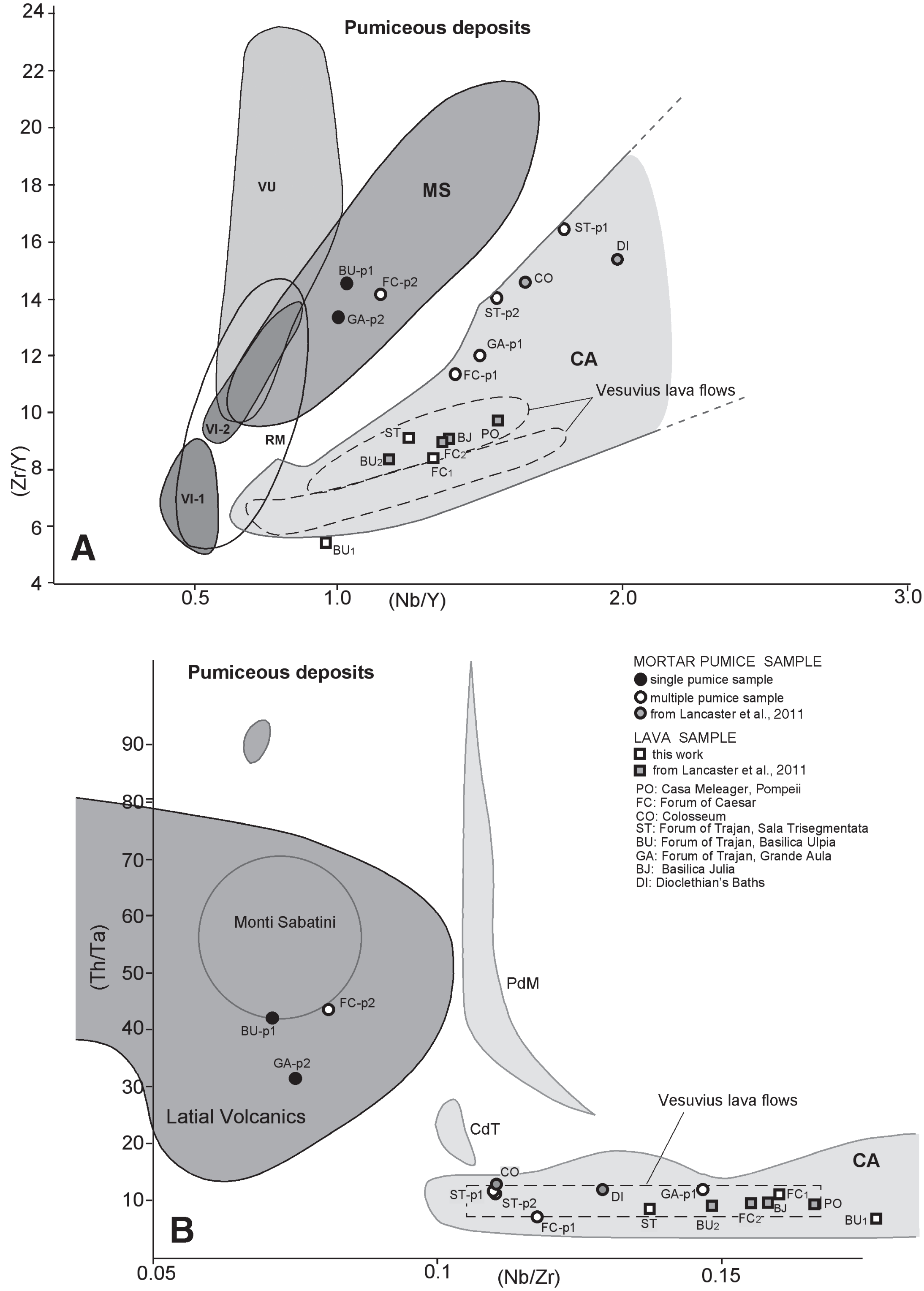


Figure 6. Compositional fields based on Zr/Y versus Nb/Y (A) and Th/Ta versus Nb/Zr (B) for the major pumice deposits erupted by the volcanoes of the Roman region, for which trace-element analyses are available in the literature. These include: (1) the pumiceous products of Latera, Canino, Farnese, and Montefiascone units of the Vulsini Volcanic District (VU) (Turbeville, 1992; Conticelli et al., 1987; Brocchini et al., 2000); (2) the pumiceous products of the two major eruptive periods of the Vico Volcanic District (VI-1, VI-2) (Perini et al., 2004); (3) the pumiceous deposits of the Monti Sabatini (MS) Volcanic District (Marra et al., 2011, and references therein); (4) the Brown Leucitic Tuff and the White Trachytic Tuff pumices (RM) (Luhr and Giannetti, 1987; Giannetti and Luhr, 1983); and (5) the average compositions for the Campanian volcanic products (CA), including lava flow (dashed lines, see Fig. 12), pyroclastic-flow, and pumice-fall deposits (data from Peccerillo, 2005; Lustrino et al., 2010, and references therein). Zr/Y-Nb/Y ratios of the mortar pumice and of the vesicular lava samples are also shown.

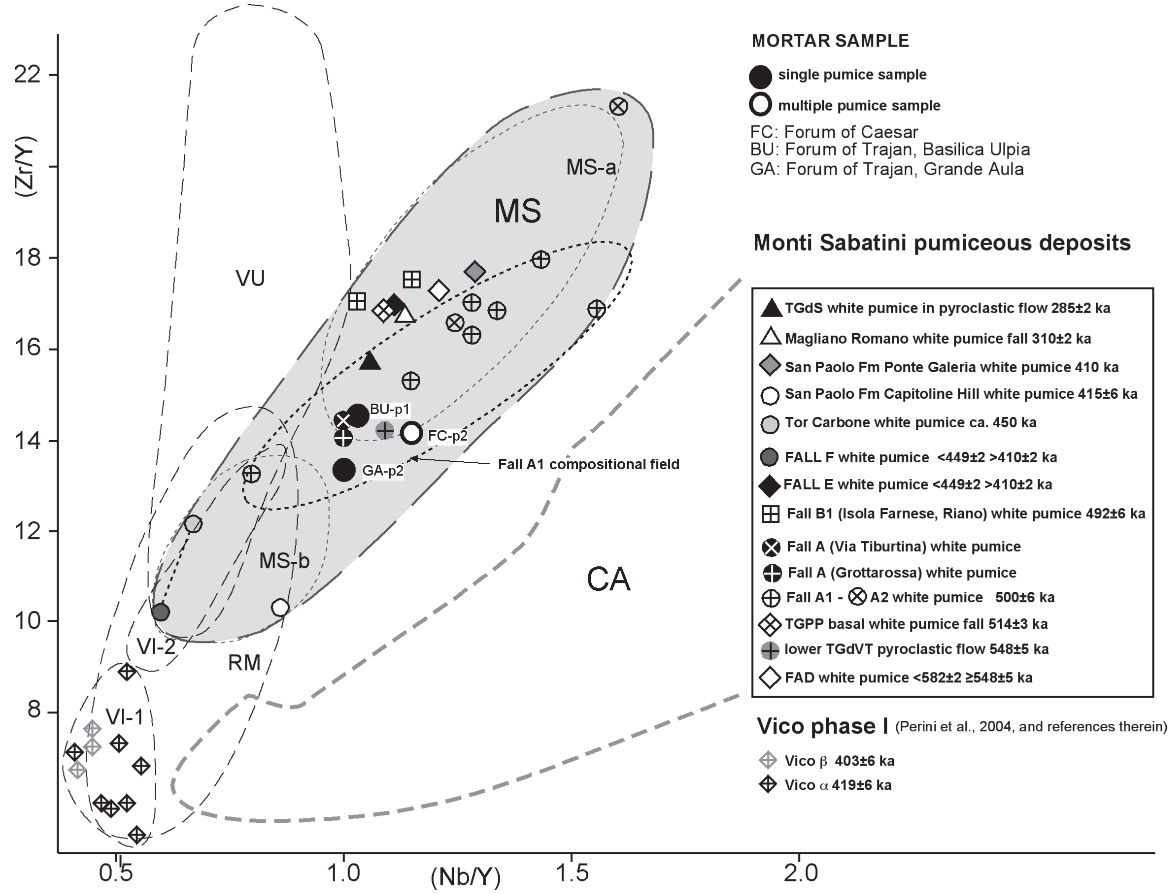


Figure 7. Zr/Y-Nb/Y diagram for the principal pumiceous deposits of Monti Sabatini Volcanic District (geochemical data from Marra et al., 2011; Sottili et al., 2004; Lancaster et al., 2011), to compare with the mortar pumice samples analyzed in this work. VU—Vulsini; VI—Vico; MS—Monti Sabatini; RM—Roccamonfina; CA—Campania. Abbreviations of volcanic products as in Figure 2.

seems to be a difficult and unprofitable task. For these reasons, we exclude the possibility that the pumice employed in the mortars may derive from these units.

San Paolo Formation and Fall F Pumice

The San Paolo Formation is a fluvial deposit that filled the incision of the Tiber River and its tributaries between 437 and 407 ka (Karner and Marra, 1998). This deposit crops out on the flanks of the Capitoline Hill (Fig. 2), where it is composed of yellow clay and sand with frequent intercalations of volcaniclastic horizons and centimeter-sized yellowish pumice (Corazza et al., 2004). The pumice is generally aphyric or contains very small sanidine, clinopyroxene, and biotite crystals (Plate 1b, GSA Data Repository material [see footnote 1]).

It presents well-developed pedogenic iron oxyhydrate surface coatings and traces of zeolitic alteration. The $^{40}Ar/^{39}Ar$ dating on this pumice yielded consistent ages of 416 ± 10 ka and 415 ± 6 ka (Karner et al., 2001; Marra et al., 2011). Previous petrographic studies of the mortars of the Forum of Caesar (Jackson et al., 2009a) hypothesized that the Roman builders mixed the volcaniclastic sand of the San Paolo Formation with granular ash of the Pozzolane Rosse pyroclastic flow (Jackson et al., 2010) in the fine aggregate, and that the pumice derived from this sedimentary deposit.

One sample of pumice extracted from the sedimentary deposit (SP FC-p, Table DR1 in GSA Data Repository material [see footnote 1]) yielded Zr/Y and Nb/Y that diverge from the usual compositions of Monti Sabatini pumiceous deposits (field MS-a in Fig. 7). Instead, it plots within the secondary field (MS-b, Fig. 7), which includes several lithified, highly zeolitized Monti Sabatini pyroclastic-flow deposits (Marra et al., 2011). When the composition of another coeval pumice layer (Karner and Marra, 1998; Karner et al., 2001), interbedded within the sedimentary deposits of the San Paolo Formation in Ponte Galeria southwest of Rome, is considered (Fig. 7), the possibility that the anomalous composition of the pumice from the Capitoline Hill outcrop may be a consequence of strong weathering (Marra et al., 2011) cannot be excluded. In any case, this peculiar Zr/Y versus Nb/Y composition makes the pumice of the San Paolo Formation cropping out at the Capitoline Hill clearly distinguishable from all the other Monti Sabatini pumices, and it is also different from that of the pumice samples extracted from the mortar of the vaults of the Forum of Caesar, allowing us to exclude the possibility that it was employed in its formulation.

Fall F was previously thought to correlate to the San Paolo Formation pumice layer (Marra et al., 2011), and we analyzed one sample collected in Prima Porta north of Rome to verify this hypothesis. Also in this case, the strong weathering of the analyzed sample (loss on ignition[LOI] = 18.3%; Table DR1) suggests that its deep alteration may be the cause of its location plotting within the MS-b secondary field, but far from sample SP FC-p (Fig. 7). Combined with recent radiometric dating of Fall F yielding an age of

447 ± 7 ka (work in progress), compared to the 415–410 ka age of the San Paolo Formation pumice, these facts exclude their correlation. In contrast, the Zr/Y versus Nb/Y compositions of Fall F and those of the partially reworked Tor Carbone pumice analyzed in Marra et al. (2011) define a trend (dashed line in Fig. 7) parallel to that of the Monti Sabatini compositional field, which should be regarded as indicative of the same magma composition (Marra et al., 2011). The stratigraphic position of the Tor Carbone pumice, indicating an age of ca. 450 ka (Marra et al., 2011), is also consistent with that of Fall F, suggesting a correlation of these deposits.

Vico and Vulsini Districts

Vico volcano is composed of a central volcanic edifice characterized by mainly explosive activity developed in three main cycles spanning the time span 419–95 ka (Perini et al., 2004, and references therein). In particular, Vico Period I (419–403 ka) emplaced widespread pyroclastic-fall deposits (Vico α, 419 ± 6 ka; and Vico β, 403 ± 6 ka—Laurenzi and Villa, 1987; Rio Ferriera Formation—Perini et al., 1997). Zr, Nb, and Y data from Perini et al. (2004) for the pumiceous deposits associated with this period of activity define a well-clustered field (VI-I) in Figures 6 and 7. Despite the fact that the radiometric ages of the San Paolo Formation and Vico α pumices are indistinguishable, the latter has lower Zr/Y and Nb/Y values, suggesting they are not correlated, unless the shifted position of the San Paolo Formation pumice is a consequence of its strong alteration (Fig. 7).

Period II (305–138 ka) emplaced relatively minor fallout deposits. The Zr, Nb, and Y abundances for the pumice deposits of this period (Perini et al., 2004) define a distinct field in Figures 6 and 7 (VI-2) with respect to the Vico I deposits, partially overlapping the compositional fields for the Vulsini Monti Sabatini and Roccamonfina products.

No significant pumice deposits were erupted during the Period III of activity at Vico.

Explosive volcanic activity occurred at the Vulsini district in the time span 600–130 ka from five major source areas: paleo-Vulsini, Bolsena-Orvieto, Southern Vulsini, Latera, and Montefiascone (Vezzoli et al., 1987; Palladino et al., 2010). This activity was characterized by five major sub-Plinian to Plinian fall deposits mostly occurring in the eastern sector of the district (Nappi et al., 1994), and subordinately in the western sector (Palladino and Agosta, 1997). Trace-element compositions for the Vulsini activity pumiceous deposits, comprising the Latera (Turbeville, 1992), Canino and Farnese (Conticelli et al., 1987), and the Montefiascone (Brocchini et al., 2000) units, define the compositional field in Figures 6 and 7, evidencing that none of the archaeological pumice samples has Zr/Y versus Nb/Y composition compatible with those of the Vulsini and Vico districts.

Campanian Province

Vesuvius

Although buried lava flows have been dated back to 400 ka, the present Somma-Vesuvius volcano formed largely in the last 39 k.y. (Santacroce, 1987; Santacroce et al., 2005). Early volcanism (36–18 ka) includes the Mount Somma stratovolcano, the main activity of which was dominated by lava flows and low-energy explosive eruptions. Eruptive activity at Mount Vesuvius (18 ka to 1944 CE) followed the Mount Somma phase and included several large Plinian and sub-Plinian eruptions that emplaced widespread pumice deposits (see legend in Fig. 8).

The Zr/Y versus Nb/Y diagram for pumice samples of the major Plinian to sub-Plinian eruptions occurring at Vesuvius, plus pyroclastic-flow deposits recovered in a borehole in Camaldoli della Torre and attributed to a peripheral vent located on the southern flanks of Vesuvius (Di Renzo et al., 2007), is shown in Figure 8. Because the purpose of this study is to identify the deposits of archaeological importance, we have omitted data for Vesuvian products younger than the 472 CE explosive eruption. In this diagram, the values of each eruptive unit plot within narrowly elongated, distinct fields, displaying a subrectilinear trend (gray areas in Fig. 8). As already discussed in Marra et al. (2011), the subrectilinear trends imply roughly constant Zr/Nb values. Each field is characterized by its own elongation and distance from the origin of the axes. All these features result from the combination of the geochemical composition of the original magma and its degree of differentiation within the magma chamber.

Independently from the petrologic implications of such trends, which will be treated in a separate work and are out the scope of the present work, the diagram of Figure 8 for Vesuvius shows the potentiality of selected trace-element ratios to classify the pyroclastic rocks and to compare the composition of the pumice extracted from the mortars of the Forum of Caesar and Forum of Trajan.

In particular, the pumice of the Camaldoli della Torre (CdT) 39–36 ka deposit has distinctive, closely grouped Th/Ta, Nb/Zr, Zr/Y, and Nb/Y values (Figs. 6 and 8). Notably, the Zr/Y and Nb/Y values are rather close to the composition of the pumice of the Sala Trisegmentata of the Forum of Trajan (ST-p1, ST-p2) analyzed here, and the pumice in the mortar of the concrete vaults of the Colosseum (CO) (Lancaster et al., 2011). Consistently, these archaeological pumice samples have Th/Ta and Nb/Zr values closest to those of the Camaldoli della Torre pumice (Fig. 6).

The pumices from the Forum of Caesar (FC-p1) and from the Grande Aula of Trajan's Markets (GA-p1) instead display compositions similar to that of the Sarno Eruption unit of Vesuvius, which comprises the widespread pumice deposit also known as Pomici di Base (Landi et al., 1999).

Phlegrean Fields

Volcanism at the Phlegrean Fields (Campi Flegrei) district began at ca. 60 ka (Orsi et al., 1996), and was dominated by two very large eruptions: at 39 ka, the Campanian Ignimbrite (Civetta et al., 1997), and at 12 ka, the Neapolitan Yellow Tuff (Orsi et al., 1995). Large pumice-fall deposits were emplaced at the onset of these eruptions, as well as during the entire span of Campi Flegrei activity. In particular, intense, explosive volcanism, with phreatomagmatic phases, followed the Neapolitan Yellow Tuff eruption. The pumiceous deposits associated with this phase, spanning from 12 ka to 1538 CE, were erupted from a number of vents scattered through the Campi Flegrei caldera (D'Antonio et al., 1999; Civetta et al., 1991b) and represent the most likely source of pozzolan exploited in Roman times in this area. We analyzed a pumice sample (BAIA-p) collected from a block-and-ash-flow deposit of this late activity, in an outcrop in Fusaro, at the Parco Palazzine di Baia, in the vicinity of the ancient port of Baiae. Consistently, the BAIA-p sample plot within the compositional field as this late phase of activity in the Zr/Y versus Nb/Y diagram of Figure 9. The Baia pumice contains sanidine and clinopyroxene crystals (Plate 1c, 1d, GSA Data Repository material [see footnote 1]), and colorless glass with interpenetrations of yellowish brown glass.

The Zr/Y versus Nb/Y compositions of the products of the Phlegrean Fields activity are plotted in the diagram of Figure 9A. Notably, samples of distinct eruptive phases plot within elongated, rectilinear compositional fields (rectangular boxes in Fig. 9A), similar to that observed for the Vesuvius volcanics. With respect to these compositions, the mortar samples can be subdivided in two groups of three: a first group (ST-p1, ST-p2, and CO) that has no correspondence to the products of the Phlegrean Fields but, as previously shown, only to the peculiar composition of the Camaldoli della Torre 39–36 ka products; and a second group (FC-p1, GA-p1, and DI) that matches the compositions of the

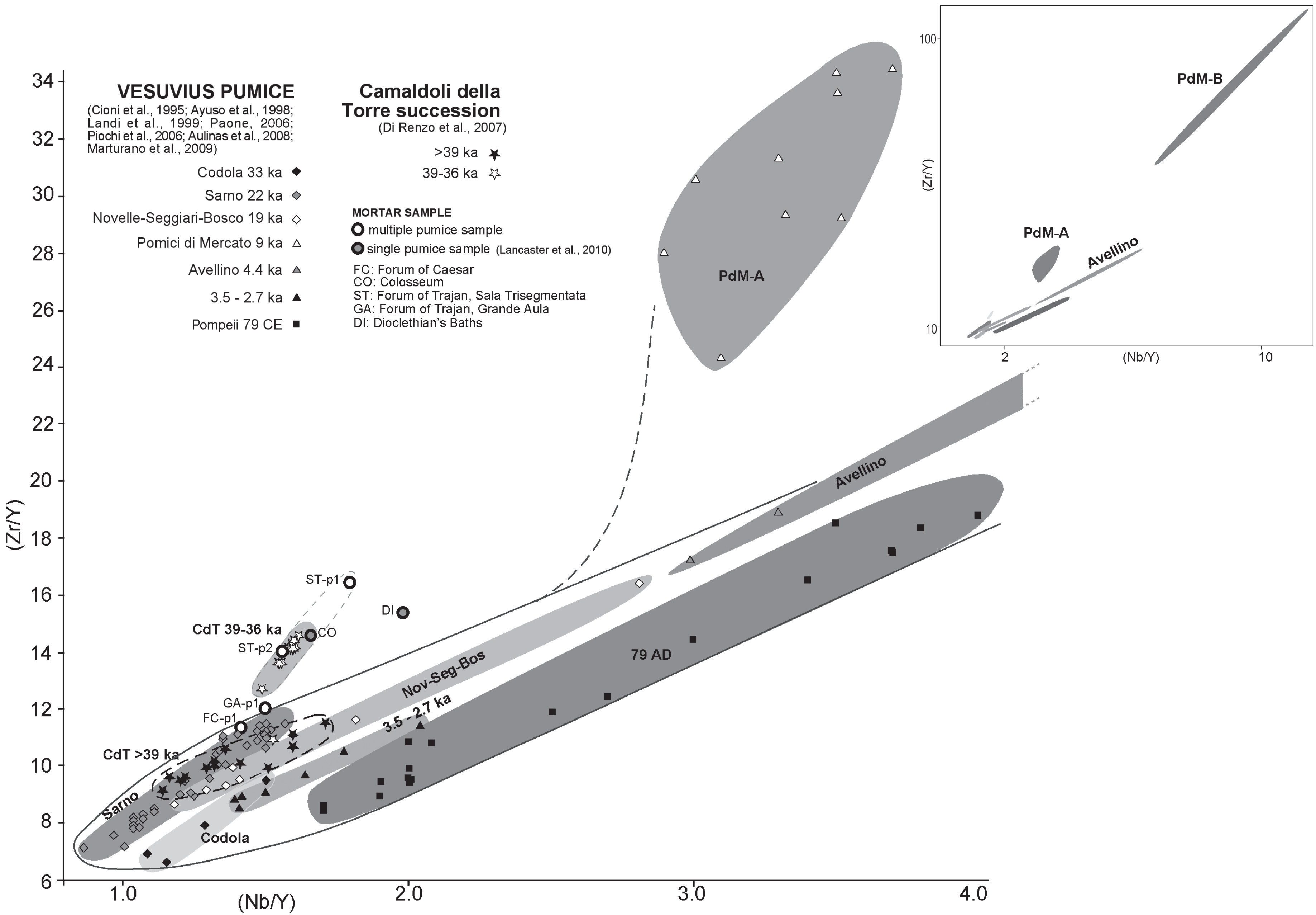


Figure 8. Zr/Y versus Nb/Y diagram for the pumice deposits of Vesuvius (products younger than 79 CE are omitted) compared to the mortar pumice compositions (see text for discussion). As discussed in the text, data for each eruption unit tend to cluster within a compositional field of its own (gray shaded areas), characterized by a subrectilinear trend. The out-of-scale compositional field for the Pomici di Marcato (PdM) eruption is shown in the inset. Nomenclature and chronology are from Santacroce et al. (2008).

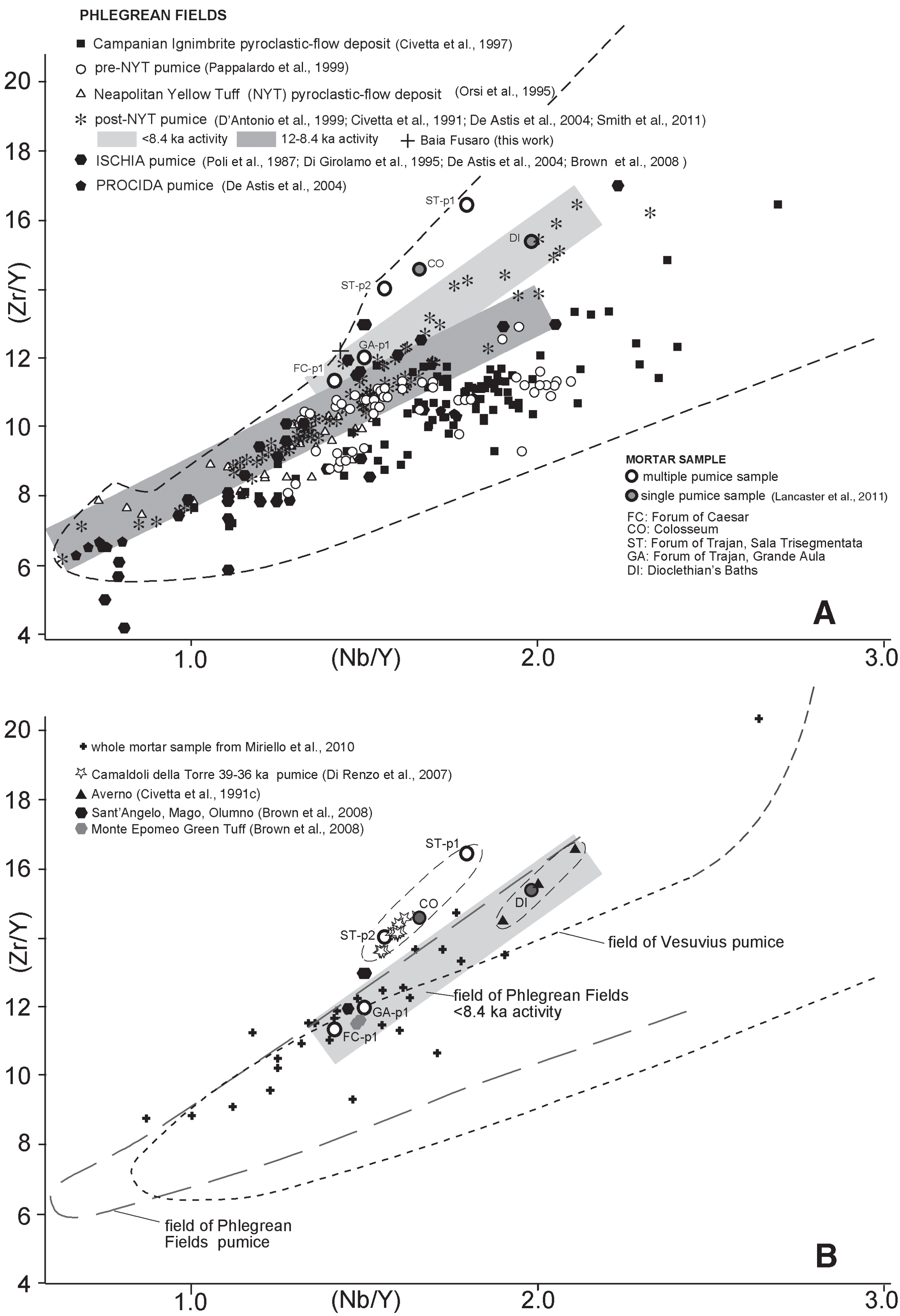


Figure 9. (A) Zr/Y versus Nb/Y diagram for the pumice deposits of the Phlegrean Fields (including Procida and Ischia) compared to the mortar pumice compositions. (B) Compositional fields for particular volcanic units are shown in order to compare the mortar pumice compositions provided in this work and those of mortar samples from Pompeii analyzed in Miriello et al. (2010) (see text for discussion).

latest phase of activity at the Phlegrean Field (<8.4 ka). In particular, the pumices from the Forum of Caesar and Grande Aula, beside correlating well the Vesuvian pumice of the Sarno eruption, have compositions very similar to that of the reference sample for the late Phlegrean activity collected in Baia (Fig. 9A). When also the compatible compositions of some products from Ischia (see next paragraph and Fig. 9B) are considered, the attribution of these two mortar samples to one specific volcanic district of Campania cannot be established based on the Zr/Y versus Nb/Y alone.

Ischia and Procida

The activity of Ischia spanned the interval ≥150 ka to 1302 CE (Brown et al., 2008; Civetta et al., 1991a; Poli et al., 1987). During the 75–50 ka time interval (phase III pro parte, Poli et al., 1987), explosive eruptions emplaced large pumice deposits (i.e., Mago, Olumno, Tisichiello, and Porticello tephras; Brown et al., 2008). Other significant pumice deposits are also associated with this phase of activity (e.g., Sant'Angelo, Monte Epomeo, La Roia, Capo Grosso, Chiumanno, Schiappone tephras; Brown et al., 2008), as well as with the later activity (phases IV–V [Poli et al., 1987]; including, among others, the Formiche di Vivara-I pumice fall [De Astis et al., 2004]).

On Procida Island, five monogenic volcanoes—Vivara, Terra Murata, Pozzo Vecchio, Fiumicello, and Solchiaro—were active in the 80–12 ka time span (Di Girolamo and Stanzione, 1973; Pescatore and Rolandi, 1981; Di Girolamo et al., 1984; Rosi et al., 1988). Significant pumice-fall deposits are associated with the Pozzo Vecchio and Solchiaro units, whereas scoriaceous products prevail in the Vivara, Terra Murata, and Fiumicello units (De Astis et al., 2004).

Apart from few specific deposits (i.e., Sant'Angelo, Mago, Olumno, and Monte Epomeo eruptions; Brown et al., 2008; Fig. 9B), no other product of Ischia and Procida has Zr/Y-Nb/Y compositions compatible to that of the studied archaeological pumice samples.

MORTAR PUMICE GEOCHEMICAL AND PETROGRAPHICAL DATA

Forum of Caesar

Vaulted Ceiling of the Tabernae (FC-V)

Two main populations of pumice were previously recognized in thin section (Jackson et al., 2009a) and sampled for geochemical analyses: rounded, small light yellowish gray, pumice (specimen FC-p1), and larger, sharp-edged, pale yellowish orange pumice (specimen FC-p2).

The study performed for this work also allowed us to recognize two main distinct populations of light-colored pumice.

(1) Smaller pumice, with acicular sanidine, biotite, and plagioclase, corresponding to specimen FC-p1 (Plate 2a, GSA Data Repository material [see footnote 1]): Despite the mineralogic assemblage being similar to that of the Monti Sabatini Fall A, the textural features of this specimen are very different from those of the Sabatini pumices, and the Zr/Y-Nb/Y, as well as the Th/Ta-Nb/Zr compositions (Figs. 6 and 8) allow us to unequivocally attribute it to the Campanian districts, although it may correlate to diverse eruptive units of different districts (i.e., Sarno eruption from Vesuvius, the late Phlegrean Fields activity, or the Ischia activity; Fig. 9B).

(2) Larger, subaphyric pumice, with rare sanidine crystals (Plate 2b, GSA Data Repository material [see footnote 1]), corresponding to specimen FC-p2. The Zr/Y-Nb/Y composition of this pumice falls within the Monti Sabatini field (Fig. 6) and, in particular, matches that of two samples of Fall A collected in Grottarossa and in northeastern Rome (Fig. 7). Noteworthy, the trace-element composition of multiple-pumice sample FC-p2 is close to that yielded by the single-pumice samples extracted from the mortar of the vaults of Basilica Ulpia (BU-p1) and of Grande Aula (GA-p2) at the Forum of Trajan (Figs. 6 and 7), supporting the reliability of the result and the identification of this type of pumice also in the case of the multiple-pumice analysis.

Also, the petrographic features are similar to those of the Fall A1 pumice, with subaphyric texture and rare sanidine crystals, although other accessory minerals, including plagioclase and leucite, are missing here. However, the smaller size of the pumice in the mortar may justify the scarcity of phenocrysts and, consequently, the absence of plagioclase and other accessory mineral phases.

Neither of the analyzed samples yielded compositions matching that of the San Paolo Formation outcrop at the Forum of Caesar, which has a peculiar composition that makes it easily distinguishable from most other Monti Sabatini pumice (Fig. 7).

Walls of the Tabernae (FC-W)

Although no geochemical analysis has been performed on pumice samples from the mortar of the walls of the tabernae, optical observation revealed the presence of pumice of likely provenance from Vesuvius. Beside phenocryst-poor pumices very similar to those identified as Fall A in the mortar of the vaults, there are pumices with plagioclase + clinopyroxene + phlogopite association displaying magma mixing textures (Plate 2c, GSA Data Repository material [see footnote 1]) that are typical of the Vesuvius (Civetta et al., 1991c) or, less frequently, of the Phlegrean Fields products (e.g., Arienzo et al., 2010), as observed also in the sample we collected in Baia (BAIA-01; Plate 1c, GSA Data Repository material [see footnote 1]). Indeed, the intermingling of colorless and moderate brown glasses is the evidence of two different magmas feeding the eruption, as has been described for several Vesuvius eruptions (Piochi et al., 2005). Moreover, nepheline phenocrysts are occasionally observed, which are diagnostic of a Vesuvian origin (e.g., the "Avellino" pumice; Barberi et al., 1981). However, magma mixing textures do not occur in the Sarno eruption pumice (Landi et al., 1999), and therefore this particular pumice in the walls of the tabernae is definitely a different one with respect to those of population A from sample FC-p1.

Forum and Markets of Trajan

Grande Aula (GA-1, GA-2)

The mortars of the vaulted ceiling of the Grande Aula contain varying proportions of different pumices. In particular, a large prevalence of pumice with sanidine + plagioclase + clinopyroxene and characteristic mixed-magma textures (Plate 2d, GSA Data Repository material [see footnote 1]), which are presumably of Vesuvian provenance, as well as smaller pumice with acicular sanidine and plagioclase (Plate 2e, GSA Data Repository material [see footnote 1]), similar to those observed in the mortars of the vaults of the Forum of Caesar and correlatable to diverse Campanian pumices, is observed in thin section GA-1, in good agreement with the trace-element composition of multiple-sample GA-p1, plotting within the Campanian field (Figs. 6 and 8). Several larger, crystal-poor pumices are observed in thin section GA-2 (Plate 2f, GSA Data Repository material [see footnote 1]), and are well represented by the Zr/Y versus Nb/Y chemistry of the single pale-yellowish orange pumice (specimen GA-p2) that falls in the Monti Sabatini compositional field (Figs. 6 and 7). Therefore, in analogy with that observed at Forum of Caesar, a mix of Campanian and Monti Sabatini pumice also occurs in the mortars of the Grande Aula at the Markets of Trajan.

Basilica Ulpia (BU-1, BU-2)

A prevalence of subaphyric, yellowish orange pumice with rare sanidine is observed in both thin sections BU-1 and BU-2 from Basilica Ulpia (Plate 2g, GSA Data Repository material [see footnote 1]). Consistently, the Zr/Y-Nb/Y chemistry of the single-pumice specimen

BU-p1 falls within the Monti Sabatini field, close to that of the other subaphyric pumice sample from the Grande Aula (GA-p2), and to the Fall A samples collected near Rome (Figs. 6 and 7). However, the presence of loose crystals characteristic of the Vesuvian products, such as melilite (Plate 2h, GSA Data Repository material [see footnote 1]), is indicative of mixing of pumice from both Monti Sabatini and Vesuvius also in this mortar. In addition, there are occasional subangular fragments of colorless glass with clusters of acicular sanidine and subordinate plagioclase, similar to the pumices described in the vaults of the Forum of Caesar and to those occurring in the mortar of Sala Trisegmentata (Plate 2i, GSA Data Repository material [see footnote 1]), in the Grande Aula (Plate 2e, GSA Data Repository material [see footnote 1]), as well as in the Baia sample (Fig. 8D). Therefore, these pumices should be considered characteristic of the Campanian products, but they do not allow discrimination between Vesuvius and Phlegrean Fields.

Trisegmentata (ST-1)

Two samples were collected from a coarser (ST-p1) and a finer (ST-p2) population of pumices. Two principal types of pumice are recognized in thin section within the mortar of Sala Trisegmentata, but only the second one should be considered representative of both the analyzed samples:

(1) the aforementioned colorless glass with clusters of acicular sanidine (Plate 2i, GSA Data Repository material [see footnote 1]); and

(2) very light-yellow, subaphyric pumice with elongated vesicles and rare phlogopite crystals (Plate 2k, GSA Data Repository material [see footnote 1]).

The two analyzed multiple samples plot at the highest margin of the Campanian field in the Zr/Y versus Nb/Y diagram of Figures 6 and 8. While it is not possible to exclude that this may be the result of sampling a mixed Monti Sabatini and Campanian population, the analyses on a single pumice collected by Lancaster et al. (2011) from the mortar of the vaulted ceiling of Colosseum yielded a very similar composition, suggesting that the data for the mortar pumice of Sala Trisegmentata may be regarded as reliable.

Colosseum

The provenance of the Colosseum pumice sample (CO) was attributed in previous work to the Phlegrean Fields (Lancaster et al., 2011) because of its elevated Zr/Y (>14; Fig. 6). The more representative examination of Campanian trace-element data performed here indicates, instead, that the Zr/Y values for this pumice, as well as those of the two Sala Trisegmentata samples, ST-p1 and ST-p2, plot slightly above the compositional field of the Phlegrean Fields deposits (Fig. 6B). A striking match with the pyroclastic deposit identified so far only in the Camaldoli della Torre (CdT) borehole, which, in turn, displays a distinctive geochemistry among all the Campanian products, is evidenced in Figure 9B.

Dioclethian's Bath

The gray pumiceous scoria (DI) used as coarse aggregate in the concrete of the Baths of Diocletian (298–305 CE) has Zr/Y and Nb/Y values that correlate with several products erupted during the last 8.4 k.y. by local vents in the Phlegrean Fields (Fig. 9B). These deposits crop out along the coast of the Gulf of Pozzuoli. In particular, the composition of this sample (Fig. 6B) correlates well with the Averno Lake deposits (Civetta et al., 1991b).

LAVA COARSE AGGREGATES

Previous Works

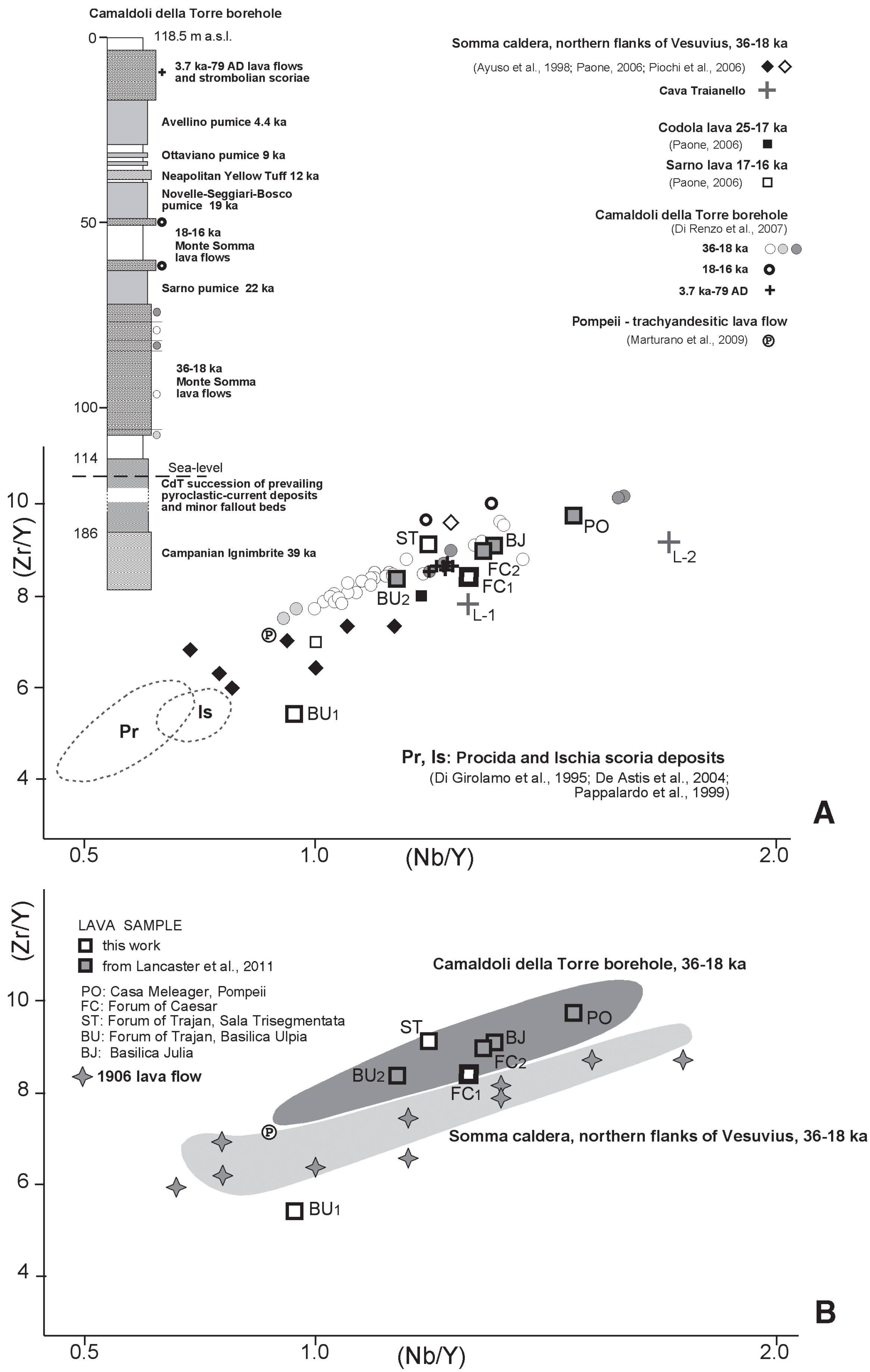
The main effusive activity of Mount Somma stratovolcano spanned the interval 36–18 ka. The products of this early phase of activity crop out mainly on the northern flanks of Vesuvius, but they are also present in isolated outcrops to the SE of the volcano, and were recently found in a drill hole at Camaldoli della Torre (Di Renzo et al., 2007; Fig. 10). Here, the Mount Somma lava flows overlie a 67-m-thick succession of pyroclastic flow and fallout deposits yielding a peculiar Zr/Y versus Nb/Y composition (Camaldoli della Torre 39–36 ka; Fig. 8), which have been attributed to the activity of a local vent (Di Renzo et al., 2007).

Classification of the lava flows from Vesuvius is traditionally based on their total alkali-silica content, expressed on the TAS diagram (Le Bas et al., 1986; Santacroce et al., 2005). Using this classification, Lancaster et al. (2011) attributed the vesicular lava samples from the Forum of Caesar, Basilica Julia, Basilica Ulpia, and from a fallen wall within Pompeii to the 36–18 ka activity of Somma-Vesuvius volcano, which has a shoshonitic, or potassic basaltic-trachyandesitic composition. They have ruled out correlations of the archaeological samples with the lava flows underlying Pompeii, because these were generally attributed to the 18–16 ka Somma-Vesuvius activity (Ippolito, 1938; Bellucci, 1998; Di Vito et al., 1998), or to lavas of the 8 ka to 79 CE activity (Cioni et al., 2008), which have a higher SiO_2 content (see Fig. 11). However, a recent analysis of a lava sample collected from the subsoil of Pompeii (Marturano et al., 2009) yielded composition in the shoshonitic field, quite similar to several archaeological lava samples analyzed in Lancaster et al. (2011) (Fig. 11). Furthermore, Di Girolamo (1968) described a scoriaceous, vesiculated, reddish lava flow with phenocrysts of leucite, augite, and olivine along the scarp that borders the archaeological site of Pompeii to the south (Fig. 12). He classified this as a leucitic tephrite-basanite "foam lava," which overlies the less-vesiculated gray lava flows found in boreholes beneath Pompeii. According to the observations of Di Girolamo, several authors (Cinque, 1991; Di Vito et al., 1997; D'Ambrosio et al., 2001) have attributed the scoriaceous lavas cropping out on the hill of Pompeii to the more recent activity of a local vent (e.g., "Vulcano di Pompei"; Cinque and Irollo, 2004). Unfortunately, no geochemical analysis is available for these lavas to compare compositions of the vesicular lavas employed locally as rubble stone in the walls, and as coarse aggregate in the vaults in Rome.

Geochemical Data

We compared a homogeneous data set of lava samples older than 472 CE (age of the Pollena eruption), for which major- as well as trace-element analyses are available in the literature, to the set of the investigated archaeological samples, and we have plotted their Zr/Y-Nb/Y ratios in the diagram of Figure 10 and their total alkali and silica content in the TAS diagram of Figure 11. In this case, and differently from Lancaster et al. (2011), where the archaeological samples were compared to a literature classification diagram built with unreduced data, we reduced (weight normalized to 100%) the whole data set plotted in Figure 11. When the normalized major-element composition is considered, only the two samples from the Forum of Caesar plot within the field defined by most samples of the 36–18 ka lava flows of Monte Somma activity

Figure 10. (A) Zr/Y-Nb/Y diagram for the lava flows of Vesuvius (products younger than 79 CE are omitted) and for the archaeological lava samples. The stratigraphic log of the Camaldoli della Torre (CdT) borehole and the position of the analyzed samples are shown. (B) Compositional fields for the lava flows of the Monte Somma 36–18 ka activity cropping out on the northern flanks of Vesuvius (dark-gray shaded area) and for the 36–18 ka lava flows recovered in the Camaldoli della Torre borehole (light-gray shaded area). See text for comment.


Camaldoli della Torre borehole
118.5 m a.s.l.
3.7 ka-79 AD lava flows and strombolian scoriae
Avellino pumice 4.4 ka
Ottaviano pumice 9 ka
Neapolitan Yellow Tuff 12 ka
Novelle-Seggiari-Bosco pumice 19 ka
18-16 ka Monte Somma lava flows
Sarno pumice 22 ka
36-18 ka Monte Somma lava flows
Sea-level
CdT succession of prevailing pyroclastic-current deposits and minor fallout beds
Campanian Ignimbrite 39 ka
0
50
100
114
186
Somma caldera, northern flanks of Vesuvius, 36-18 ka
(Ayuso et al., 1998; Paone, 2006; Piochi et al., 2006)
Cava Traianello
Codola lava 25-17 ka
(Paone, 2006)
Sarno lava 17-16 ka
(Paone, 2006)
Camaldoli della Torre borehole
(Di Renzo et al., 2007)
36-18 ka
18-16 ka
3.7 ka-79 AD
Pompeii - trachyandesitic lava flow
(Marturano et al., 2009)
(Zr/Y)
(Nb/Y)
ST
BJ
PO
FC2
FC1
BU2
L-1
L-2
BU1
Pr
Is
Pr, Is: Procida and Ischia scoria deposits
(Di Girolamo et al., 1995; De Astis et al., 2004; Pappalardo et al., 1999)
A
4
6
8
10
0.5
1.0
2.0
LAVA SAMPLE
this work
from Lancaster et al., 2011
PO: Casa Meleager, Pompeii
FC: Forum of Caesar
ST: Forum of Trajan, Sala Trisegmentata
BU: Forum of Trajan, Basilica Ulpia
BJ: Basilica Julia
1906 lava flow
Camaldoli della Torre borehole, 36-18 ka
Somma caldera, northern flanks of Vesuvius, 36-18 ka
B

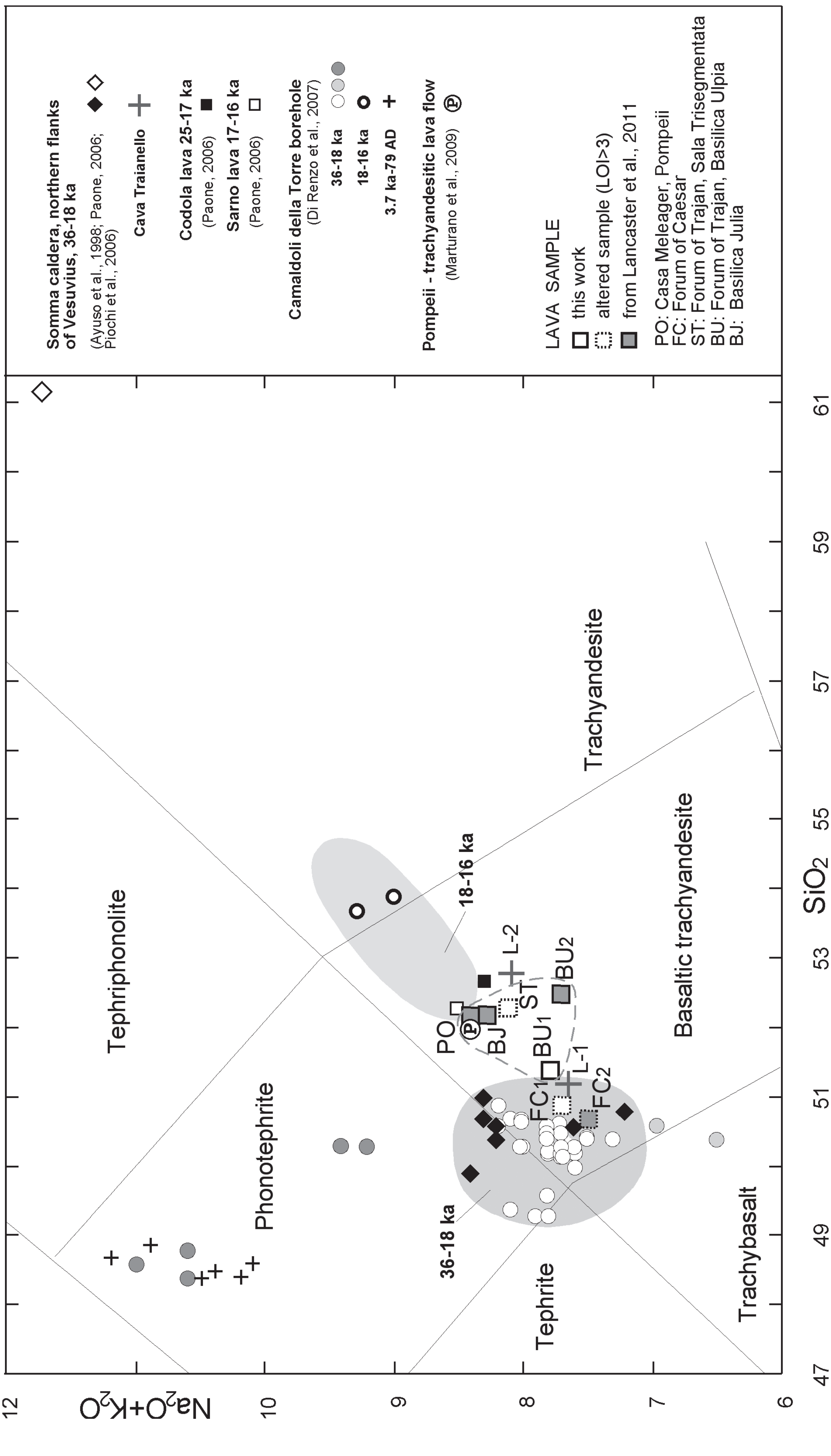


Figure 11. Total alkali-silica (TAS) diagram for the lava flows of Vesuvius and the archaeological lava samples. See text for comments. LOI—loss on ignition.

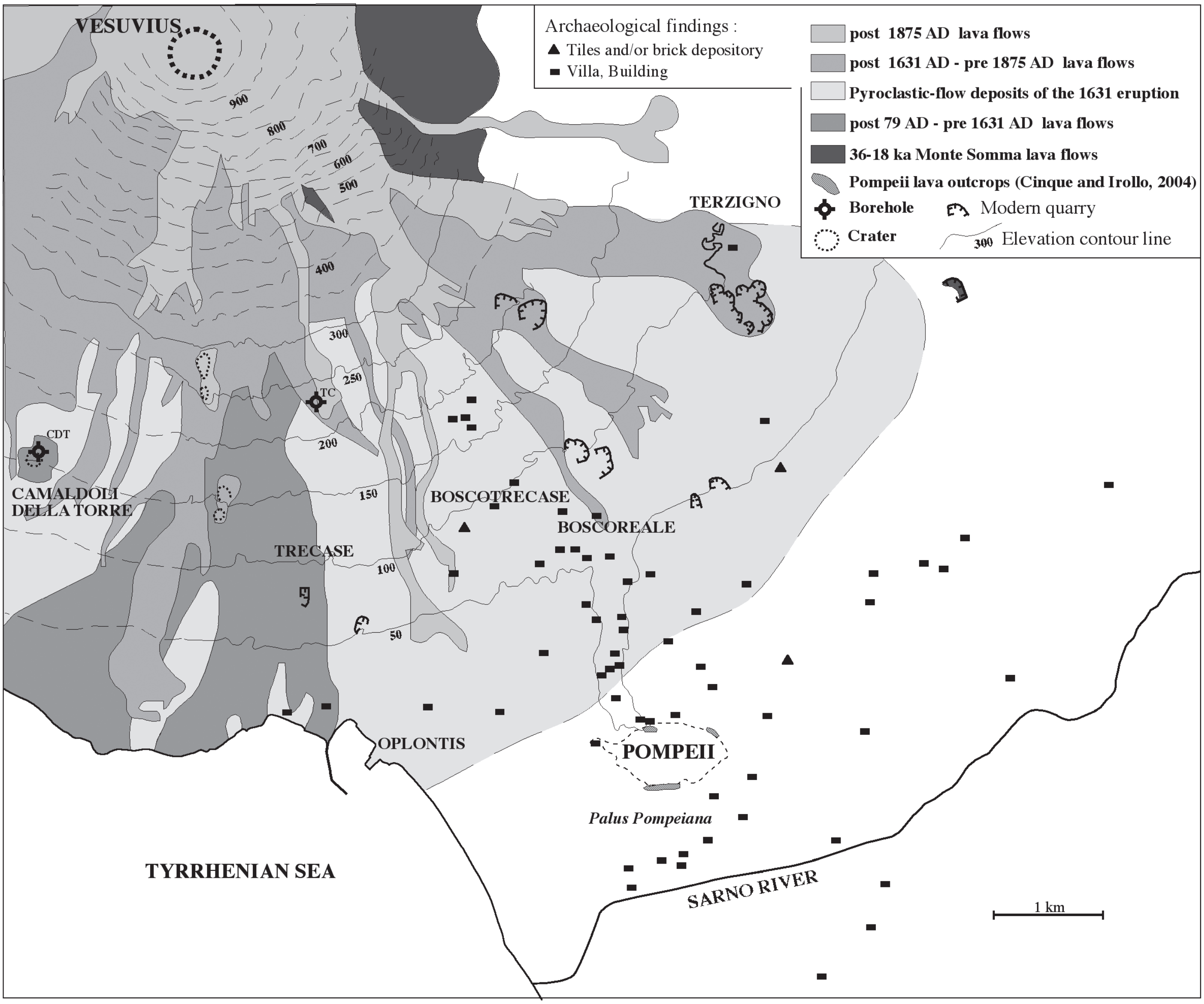


Figure 12. Map showing the outcrops of the Vesuvius lava flows and the inferred extension of the ***Ager Pompeianus*****, based on historical sources and archaeological findings (after Casale and Bianco, 1979; Iorio, 1992).**

(dark-gray shaded area in Fig. 11), those cropping out on the northern flanks of Vesuvius as well as those of the southern flanks recovered in the Camaldoli della Torre borehole. However, these two samples are the most altered ones (LOI = 3.92% and 6.52%, respectively; Table DR1 of this paper; Table 2 *in* Lancaster et al., 2011), and their lower alkali and silica content with respect to the others may be due to alteration rather than to an originally different composition. Indeed, the unaltered (LOI < 2.5%) archaeological samples (dashed contour line in Fig. 11) plot midway between the field of the 36–18 ka lava flows and that of the 18–16 ka lava flows (light-gray shaded area in Fig. 11). Notably, the lava flow from underground Pompeii plots within the field defined by these archaeological samples, in a zone that is adjacent to that proper of the 18–16 ka lava flows, in agreement with the attribution of the lower lavas of Pompeii to this phase of activity (Bellucci, 1998; Di Vito et al., 1998). However, also one sample of the 36–18 ka activity from Cava Traianello (L-2) displays a more differentiated (SiO_2 richer) composition, matching that of the archaeological samples, as previously recognized in Lancaster et al. (2011).

When trace-element composition is considered, the two samples from the Forum of Caesar show Zr/Y and Nb/Y values within the trend defined by the other archaeological samples (Fig. 10A), supporting the notion that Zr, Nb, and Y are insensitive to alteration.

Indeed, all the archaeological samples, similar to the products of a same eruptive unit, plot within a subrectilinear field, parallel to the main field defined by all the Vesuvius lava flows, with the exception of one sample from Basilica Ulpia (BU1 in Fig. 10), which yields an anomalous composition, plotting at the lowest margin of the compositional field for the Vesuvian lavas, and is offset with respect to sample BU2, from the same monument.

Despite the very similar major-element chemistry, a systematic difference in selected trace-element compositions of the lava samples of the southern flanks of Vesuvius collected in the Camaldoli della Torre borehole, with respect to those of the samples coming from the northern flanks, is apparent (Fig. 10B), and two distinct fields can be recognized for the Camaldoli della Torre and for the Monte Somma lava samples, with the Camaldoli della Torre samples displaying a systematically higher Zr/Y as a function of Nb/Y. If not due to a systematic laboratory offset of the measured values for the Camaldoli della Torre samples (which we think unlikely since the oldest pumices from the Camaldoli della Torre borehole [>39 ka], probably erupted by Vesuvius, which were measured in the same laboratory run, display regular Zr/Y and Nb/Y, as shown in Fig. 8), this feature suggests that the lava flows of the Camaldoli della Torre succession were fed by a different magma reservoir, characterized by distinctive trace-element composition, with respect to the central edifice of Vesuvius. Notably, the Zr/Y and Nb/Y composition of the samples of the 1906 CE lava flow erupted by Vesuvius (Santacroce et al., 1993) perfectly overlaps the field of the 36–18 ka lava flows (Fig. 10B). In contrast, all the archaeological samples, with the exception of the anomalous BU1 sample, plot within the upper field: an unlikely coincidence if also due to a laboratory offset, suggesting that their geochemical composition correlates better with that of the 36–18 ka lava flows distributed over the southern slopes of Vesuvius. Instead, Zr/Y-Nb/Y classification of the lava sample from the subsoil of Pompeii is uncertain, since it plots at the lowest margin of the upper field, far from the archaeological samples, as well as from the 18–16 ka lava samples. When major-element composition of the archaeological samples is also considered, which is slightly different with respect to that yielded by most of the Monte Somma lava flows, but also with respect to that of the Camaldoli della Torre 36–18 ka lava flows, the possibility that they come from another peripheral vent closer to Pompeii, which may have been disrupted or covered by later activity, or even from the same Pompeii vent, if the hypothesis by Cinque and Irollo (2004) of a "Pompeii Volcano" is correct, should also be taken into account. Finally, the BU1 sample plots at the margin of both major- and trace-element composition fields of the 36–18 ka lava flows of the northern flanks of Vesuvius, suggesting a different source area with respect to the other sample from Basilica Ulpia.

DISCUSSIONS

Provenance of the Volcanic Products

Results of the geochemical analyses show that builders of the Forum of Caesar (46–44 BCE) and Forum of Trajan (96–115 CE) employed a mixture of pumices from the Monti Sabatini and the Campanian Volcanic Districts in the pozzolanic mortars (Fig. 6). In particular, the Zr/Y and Nb/Y values of three mortar pumice samples from the vaults of the tabernae of Forum of Caesar, Basilica Ulpia, and Grande Aula plot close to two samples of Fall A (Fig. 7), which represents the only Monti Sabatini pumice-fall deposit of significant thickness that crops out in Rome. Two pumice samples from the vaults of the tabernae of the Forum of Caesar and of the Grande Aula of Trajan's Markets have Zr/Y, Nb/Y, Th/Ta, and Nb/Zr indicating unequivocal provenance from the Campanian volcanic province (Fig. 6). Magma-mixing textures and occasional nepheline crystals in some of the pumices in these mortars (Plates 2c and 2e, GSA Data Repository material [see footnote 1]) also suggest a Campanian provenance, in particular, from Vesuvius. The presence of characteristic melanite crystals (Plate 2g, GSA Data Repository material [see footnote 1]), typical of Vesuvius, as well as Monti Sabatini pumice in the cementitious matrix of the Basilica Ulpia sample indicates that aggregates from both districts were used also in this mortar. Finally, pumices from the vault of Sala Trisegmentata have Zr/Y and Nb-Y values not compatible with the compositional field defined by all the analyzed Campanian pumice deposits, except one: the pumices recovered at 120 m below the ground surface in the borehole drilled at Camaldoli della Torre on the southern slope of Vesuvius (Figs. 8 and 10). Sample ST-p2 yielded a geochemical signature quite similar to that of the single pumice extracted from the mortar of the Colosseum's vaults (79 CE) and corresponding to that of the pyroclastic deposit found in the Camaldoli della Torre borehole (Fig. 8 and 9B).

A compilation of Zr/Y and Nb-Y data for the lava flows of Vesuvius, and the comparison of these data with vesicular lava coarse aggregates indicate a different trace-element composition for the 36–18 ka lava flows of the southern flanks of the volcano, as recovered in the Camaldoli della Torre borehole, with respect to lavas from the northern slopes. The archaeological lava samples appear to correlate with the lower part of the Camaldoli della Torre borehole lava succession (Fig. 10). When the high similarity between trace-element composition of the archaeological lava samples and that of the lava samples of the Camaldoli della Torre succession (Fig. 10B) is compared to the high similarity of trace-element composition of the aforementioned mortar pumice samples (ST-p2 and CO) and that of the pumice deposit immediately underlying the 36–18 ka lava flows at Camaldoli della Torre (Figs. 8 and 9B), the hypothesis that this portion of volcanic succession, or its equivalent from other peripheral vents, was exposed locally to the southeast of Vesuvius and that it was exploited in Roman times cannot be ruled out. In particular, the 36–18 ka Monte Somma lava flows crop out and are nowadays still exploited in a quarry located 5 km north of Pompeii and 2 km east of Terzigno (IAVCEI, 1996; Fig. 12). An alternative hypothesis, according to the slightly different major-element composition of the archaeological samples with respect to that of the Camaldoli della Torre lava flows, is the vesicular lava employed by Roman builders, as well as the pumice with the peculiar Zr/Y versus Nb/Y composition, might have been erupted from another peripheral vent located on the southeastern slope of Vesuvius, not excluding a local vent corresponding to the same Pompeii Hill.

The lava and pumice outcrops may have been located in the area between Camaldoli della Torre, Boscotrecase, Terzigno, and Pompeii (Fig. 12), within valley flanks that exposed the lower portion of the volcanic succession. Indeed, a pyroclastic-flow deposit similar to that of Camaldoli della Torre is found in the same stratigraphic position in the Trecase borehole (Brocchini et al., 2001) drilled ~2 km to the east of Camaldoli della Torre (CDT in Fig. 12). This suggests that the pyroclastic-flow and ash-fall deposits may have had a larger distribution, and may have been associated with other eruptive vents that were successively buried by the large volume of lava flows emplaced in historical times, mainly after 1631 CE, on the southern slopes of Vesuvius. If this holds, then also the hypothesized Roman quarries may have been obliterated. The area southeast of Camaldoli della Torre, through Trecase, Boscotrecase, and Terzigno, where several modern quarries are located, is covered by a thick succession of lava flows erupted in medieval times, and between 1631 and 1875 CE (Fig. 12).

A Vesuvian provenance for the pumiceous mortar aggregates of concretes in several buildings in Pompeii, which span the third century BCE to first century CE time period, has been suggested by Miriello et al. (2010) based on their mineral assemblage of nepheline, leucite, and olivine, and major-element compositions. The wide ranging Zr/Y versus Nb/Y values of the Miriello et al. (2010) whole mortar specimens, encompassing both the Vesuvius and Phlegrean Field compositional fields (Fig. 9B), may be due to the fact that they contain different kinds of pumiceous aggregates, as well as non-volcanic aggregates. However, all these samples plot within the broader field of the Campanian products, although many are located outside of the proper field for Vesuvius, and, remarkably, most of these "outliers" plot in the higher portion of the Zr/Y versus Nb/Y diagram, halfway toward the Camaldoli della Torre pumice samples (Fig. 9B). Being that the deposits of the late Phlegrean Fields activity are almost entirely lacking in the area of Pompeii, and it being unlikely that the builders of Pompeii used pozzolan imported from Puteoli, a possible interpretation of this feature may be that these mortars contain an admixture of outcropping Vesuvius pumice and now-buried "Camaldoli della Torre–like" pumice, supporting the hypothesis that local vents located near Pompeii provided volcanic aggregate with this peculiar geochemical signature (i.e., high Zr/Y) in Roman times. Further analyses are needed to verify such a hypothesis.

Historical and Archaeological Implications

Most authors agree that Vitruvius refers to the vesicular lava employed as coarse aggregate in the vaults of the Roman monuments by mentioning the *Pumex Pompeianus* in his *De Architectura* (e.g., Lancaster, 2005, and references therein). A possible provenance of the vesicular lava samples from the southeastern flanks of Vesuvius and in particular from the surroundings of Pompeii, suggested by their trace-element signature, is well supported by Vitruvius' use of the adjective *pompeianus* to define these scoriae (Vitruvius, *De Architectura* 2: 6.2, p. 132–134, *in* Gros, 1997), which should be considered to indicate a specific geographic origin from the town of Pompeii or neighboring territory (*Ager Pompeianus*). It is probable that the *Ager* developed since the third century BCE (Iorio, 1992, and references therein), and it must have reached its maximum extension by the first century BCE, when Publius Cornelius Silla founded a colony of veterans and Pompeii became a Roman town (Cicero, *Pro Sulla*, 60–62 in Boulanger, 1957, p. 141–143). The territory under the influence of Pompeii was bordered to the southeast by the Sarno River, which separated it from the territories of Stabiae and Nuceria, and extended westward to the Tyrrhenian Sea, including the town of Oplontis (the modern Torre Annunziata) (de'Spagnolis Conticello, 1994; Senatore, 2004; Soricelli, 2001). To the northeast, it reached the villages of Boscoreale, Boscotrecase, and Trecase, where several *villae rusticae* have been excavated (Asaka, 1993; Fig. 12); the economic importance of this area is also evidenced by the fact that the city door that opened toward it, Porta Ercolano, is the largest one, suggesting that it accommodated an intensive transit of people and chariots bringing goods. The *Ager Pompeianus* also included Terzigno and Ottaviano to the north, where large numbers of modern quarries are located (Fig. 12). The same area of Camaldoli della Torre, although farther eastward, likely was economically linked to Pompeii, since the closer town of Herculaneum was essentially a resort locality (Iorio, 1992).

Most of the villas that have been excavated within the *Ager Pompeianus* had implements and structures for the production, storage, and, in some instances, sale of oil, wine, and cereals (Łoś, 1992). Moreover, the industrial vocation of the *Ager Pompeianus* is also testified by the presence of some plants for the production of bricks and tiles (Fig. 12), beside amphorae and dolia used for the transportation of oil and wine (Steinby, 1984; Tchernia, 1996). The pyroclastic nature of the soil was at the base of the high fertility of the *Ager Pompeianus*, and it is very likely that also an intensive exploitation of the volcanic material to be employed in masonry, either for local use, at the beginning, as well as for exportation to Rome, successively, occurred in this area. The use in Rome of building material imported from Campania is evidenced for the first time in the Forum of Caesar (46–44 BCE); a few decades later, during the Augustan era, a backward flux of building material from Rome to Pompeii is testified: tiles produced in the *figlinae* in the surroundings of Rome were shipped to Pompeii, and probably in several other Campanian towns, in order to implement the local availability, which was largely increased by the great development of private as well as public architecture (Łoś, 2000).

The associated shipment of loose volcanic material such as pozzolan (to which the vesicular lava clasts and the pumice should be assimilated) and amphorae for transportation of foodstuffs has been documented in the case of a Hellenistic ship wrecked in the port of Pisa (Pecchioni et al., 2007), where a bed of volcanic scoriae served as stowage material wedging a cargo of amphorae. Similarly, the volcanic material exported to Rome may have been the secondary cargo of a shipment of oil and/or wine from Pompeii. However, the river port situated in the south of the city, between Porta Marina and Porta di Stabia, on a lagoon formed by the Sarno River (Curti, 2009), was probably unsuitable for mooring of large ships. It is seems more likely that shipments of large amounts of volcanic material were delivered from Puteoli (Pozzuoli), which was the reference port for Campania and, particularly, for the Bay of Naples. Commercial relationships between the two Campanian towns were very strict, Pompeii, along with Cuma, Naples, and Capua formed a regional trade complex having Puteoli as its center (Łoś, 1992; Purcell, 1984).

We cannot ignore, however, the importance of land transport in the context of production and export, during the winter (from October to April), when sea transport was impracticable. Land, sea, and river transport had a complementary nature in the ancient world (Laurence, 1998). A widespread road system linked Pompeii and its territory to bystander towns and, in particular, to Puteoli (Cerchiai, 2010; Varone, 1991). Ancient sources (Suetonius, *Titus* 7, 4, in Ailloud, 1957; Statius, *Silvae*, 3: 5, 72–75, 104, in Frère and Izaac, 1961; Cassius Dio. 66, 21–23, in Capps et al., 1925) and archaeological evidences (De Carolis, 1997; Cerulli Irelli, 1975; Soricelli, 1997) show that the territory around Pompeii was never completely neglected, even after the eruption of 79 CE. The road that linked the town to Nuceria, Neapolis, and Puteoli was quickly restored after the disaster, even before the "final" restoration of the road system (120–121 CE) testified by some milestones of the Emperor Hadrian. The geochemical signature of the archaeological lava samples employed in the monumental complexes built in Rome after 79 CE is still indicative of a provenance from the southern flanks of Vesuvius, whereas only one sample from Basilica Ulpia has a trace-element compositions compatible with that of the lava flows of the northern flanks, suggesting that the exploitation of the volcanic material cropping out in the surroundings of Pompeii, contextually to the restoration of the road system, may have been quickly recovered after the disaster. At the same time, the obliteration of most of the active quarries by the 79 CE flows certainly induced a renewing and an expansion of the area of exploitation, as far as to the northern flanks of Vesuvius.

CONCLUSIONS

Geochemical fingerprints of the analyzed specimens of pumice and lava employed in the Forum of Caesar and Forum of Trajan reveal their provenance from the southern flanks of Vesuvius, and the historical sources suggest that their exploitation occurred within the territory of Pompeii. In contrast, trace-element ratios of other specimens extracted from the same mortars indicate a local provenance from the Monti Sabatini Volcanic District.

The combined use of lightweight lava and pumice in the concrete of the vaulted ceilings indicates that these materials were employed to reduce the specific weight of the structures, and reveals the high level of knowledge that the Roman builders had about the physical properties of different volcanic products. Indeed, the addition of local pumice from Monti Sabatini to that coming along with the scoriaceous lava from Pompeii presumes a project study and knowledge on the nature of the outcropping volcanic products, allowing for a precise selection of the materials. This implies identification of the thin layers of pumice (Fall A and B) occurring within the "Tufi Terrosi con Pomici Bianche" volcanic deposit in the territory of Rome and the evaluation of the particular physical properties of this material, analogous to those of the pumice cropping out in Campania.

The selective and systematic exploitation of the local pumice is testified by the extensive use that the Roman builders made of it, since it occurs in all the investigated mortars of the Forum of Trajan (dedicated in 112 CE), one century and a half later than its first documented employment at the Forum of Caesar (46–44 BCE). Its cultivation might have been in order at some of the quarries located along the Tiber Valley north of Rome (e.g., in Grottarossa, Fig. 2), where Falls A and B discontinuously crop out below the Tufo Rosso a Scorie Nere pyroclastic flow, which was exploited to produce dimension stones. It seems more likely, however, that these pumice horizons were exploited by means of tunnel excavation within the City of Rome. Indeed, Falls A and B systematically underlie the Pozzolane Rosse pyroclastic-flow deposit in central Rome, through which several *arenarii* (exploitation tunnels sometimes reutilized as catacombs during the Christian Era; Testini, 1966; Ventriglia, 1971) occur. It is likely that dedicated *arenarii* for the cultivation of pumice may have been excavated in the Tufi Terrosi, which were also the preferred horizon, because of their lesser permeability with respect to the overlying pozzolans, for hydraulic tunneling, as observed in several zones of Rome (e.g., Casale del Marmo locality; Succhiarelli, 2002).

The dedicated use of specific lightweight mortars, to be employed in the vaulted ceilings, justifies the economic choice of cultivating local deposits, even if not much productive ones with respect to the ones occurring in Campania, in order to reduce the shipping costs of the materials. The earliest addition of pumice in the mortars of the steps and of the walls of the Forum of Caesar cannot, however, be explained in this way, and it probably reflects the innovative approach taken by the constructors of Forum of Caesar in introducing new materials and, maybe, a local workmanship from Pompeii that traditionally used Vesuvian pumice as fine aggregate in the mortar (Miriello et al., 2010). However, results of this test were not favorable for pumice in Rome, since the studies so far conducted on buildings of Imperial age have shown that it was used exclusively to produce lightweight concretes for the vaults, whereas only the local Pozzolane Rosse ash from the Alban Hills Volcanic District constitutes the fine aggregate in the concretes of all other structures (Jackson et al., 2010, and references therein).

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