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Provenance materials for Vitruvius' *harenae fossiciae* and *pulvis puteolanis*: Geochemical signature and historical–archaeological implications

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ABSTRACT

In this paper we present new geochemical and petrographic data aimed at identifying the volcanic materials used in Roman times to produce the fine aggregate of mortars employed in the construction of terrestrial (*harenae fossiciae*) and maritime (*pulvis*) masonry structures, described by Vitruvius in *De Architectura*. Using trace-element discrimination diagrams, this study establishes the lithological provenance of a selected dataset of mortar aggregates sampled from Roman edifices in the ancient Etruscan towns of Sutri, Vulci and Volsinii (Bolsena), from Rome (Temple of Castor and Pollux, Temple B of Largo Argentina, Forum of Trajan), and from the Roman harbors of *Anxur* (Terracina) and of *Claudius* (Fiumicino). We show that Vitruvius was referring to the loose pyroclastic products (pozzolan) erupted by the volcanoes of the Roman Magmatic Province, cropping out in Tuscany, Latium and Campania, that were selectively and systematically exploited to produce the aggregate in the different regions of central Italy. In particular, we identify the specific volcanic products occurring in northern Latium and in Rome from which the aggregates of the investigated mortars were exploited, and we correlate them to the four kinds of *harenae fossiciae* defined by Vitruvius as *carbunculus*, *rubra*, *nigra* and *cana*. We also show that the material extracted from the mortars of the Roman ports sampled for this work, that Vitruvius calls *pulvis*, corresponds to the pumice-fall deposits erupted by the Phlegrean Fields volcanic district, and we discuss the archaeological implications and the historical background of the leadership held by the Roman town of *Puteoli* (Pozzuoli) in the construction technique and exportation of materials for maritime structures.

1. Introduction

Marcus Vitruvius Pollio (born c. 80–70 BC, died after c. 15 BC) was charged for the supervision on the military machines during the rule of Julius Caesar, at the beginning of his career. Despite that he was commonly accounted for being an architect and an engineer, he was more likely a member of the *apparitores* (Gros, 1982, 2007), a professional order formed by advisors of the Roman Magisters, who acted as intermediaries and referents in the realization of public works and for their administrative management, in which he covered the specific role of *scriba armamentarii* (secretary of arsenals). After the end of his service he was appointed for the superintendence on the construction of the Basilica of Fano, a fact that accounts for his expertise in the field of the building sciences. Around 31–27 BC he wrote an exhaustive essay of architecture (*De Architectura*, dedicated to the new emperor Augustus). In this text he gives an overview of the Roman technology, construction methods and building materials. Among many other topics, Vitruvius describes the criteria of selection of the materials and the methodology to produce mortar that have remained substantially unchanged until the introduction of the Portland cement in the XIXth century (Blezard, 1998; Ringbom and Hohlfelder, 2011). In particular, Vitruvius provides a list and the description of the best sandy materials to be employed as fine aggregate in the *opus caementicium* (concrete masonry), that he calls *harenae fossiciae* (quarry sands).

Vitruvius distinguishes four kinds of *harenae fossiciae*: "(…) *sunt haec* (*are these*): *nigra*, *cana*, *rubra*, *carbunculus*". According to Gros (2007) these terms are translated as "black", "gray", "red" and "charcoal", with the last term interpreted to reflect the aspect of the black volcanic scoria, which is similar to that of the charcoal (cfr. Frank, 1924; Lugli, 1957; Jackson et al., 2006). A straight interpretation of this classification appears problematic; indeed, in the first three cases he merely makes a distinction based on the color, suggesting that this is the only physical parameter that differentiates the same material, while in the fourth one he presents an *excursus* in which he describes several physical characteristics and the geographic origin from a specific area (Etruria).

Several scholars since the beginning of the last century (e.g. Van Deman, 1912a,b; Curtis, 1913; Frank, 1924; Blake, 1947; Lugli, 1957; Chiari et al., 1992; Oleson et al., 2004; Lancaster, 2005; Miriello et al., 2010; Jackson et al., 2006; 2007; 2010a) agreed that the *harenae fossiciae* described by Vitruvius in book II of *De Architectura* are to be

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identified with the loose, scoriaceous ash–lapilli pyroclastic deposits (pozzolan), erupted by the volcanic districts of Central Italy, which extensively crop out in Tuscany, Latium and Campania (Fig. 1), and that are considered responsible for conferring the extraordinary resistance and durability to the ancient Roman mortars.

In particular, two elements strongly support this hypothesis:

i. Vitruvius writes that the sand quarries (*fossicia harenaria*) are found "(…) Especially, one can see that where the Apennine range encloses the regions of Italy and Etruria [corresponding to the modern Tuscany and northern Latium] there is no lack of sand deposits in almost every locality. Across the Apennines, however, in that part which faces the Adriatic Sea, not one can be found, nor can I name a single one across the sea in all Achaea or Asia. (…)" (2.6.5). This area matches the Tyrrhenian Sea margin of central Italy (Fig. 1), and corresponds to the Roman Magmatic Province (Conticelli and Peccerillo, 1992; Peccerillo, 2005), comprising the volcanic provinces of Latium (Vulsini, Vico, Monti Sabatini, Alban Hills and Ernici volcanic districts). It is not clear, instead, if it should include also Campania, where the other volcanic districts (Roccamonfina, Phlegrean Fields and Vesuvius) of the larger Roman Co-magmatic Region (sensu Washinghton, 1906) are located.
ii. According to Vitruvius, in order to produce a good mortar when mixed with lime, the best *harena fossicia*: "(…) when rubbed in the hands it causes screech (…), (…) it shouldn't be earthy but rough (…)" (2. 4.1), and "(…) if wrapped in a white cloth, when shaken away, it has not left any dirt nor any earth in there (…)" (2. 4. 1) (cfr. Lugli, 1957; Jackson et al., 2006, 2007).

The definition of the geographical area and the physical–mechanical characteristics confirm the identification of the *harenae fossiciae* with the sand- to gravel-sized, siliceous volcanic scoriae which form the incoherent pyroclastic deposits, nowadays called "pozzolan", widely used to produce mortar from Roman times to the Present.

The term pozzolan derives from the town of Pozzuoli (*Puteoli*), in the Phlegraean Fields (Fig. 1), and entered in use probably only in the late Roman epoch. The adjective *puteolanus* (i. e. "from *Puteoli*") is used around the first century AD by Plinio the Elder (Natural History 16.202; 35.166), Strabo (Geography 5.4.6) and Seneca (*Quaest. Nat.* 3.20.3) to identify the material that Vitruvius calls "*pulvis*" (powder), and describes as occurring in the region of Baiae (a village few km from *Puteoli* on the coast of the homonymous Gulf) and in the area around the Vesuvius, which "mixed with lime and rock fragments not only confers strength to the constructions, but is capable to solidify under water" (2. 6. 1). This property characterizes those that nowadays are called "hydraulic mortars", as opposite to the "aerial mortars", which cannot set underwater. A broad literature showed that the particular chemical reactions with lime of zeolite minerals occurring in the volcanic aggregate (pozzolanic reaction) confer to a mortar the strong binding power and the hydraulic character (e.g.: Mertens et al., 2009, and references therein). Remarkably, this feature belongs to all the volcanic pozzolan of Central Italy, and not only to that occurring in Campania. However, many scholars have assumed that the pozzolan from the Phlegraean Fields, exploited along the coast of the Gulf of Pozzuoli, was used in Roman times as the aggregate to construct harbor structures throughout the Mediterranean region (e.g. Oleson et al., 2004; Hohlfelder, 2008; Stanislao et al., 2011). Vitruvius doesn't seem to consider this volcanic ash from *Puteoli* one type of *harena fossicia*, since he uses a specific term: powder (*pulvis*), as opposite to sand (*harena*), for it (Lugli, 1957). Besides the alternative terms he uses, indeed, we remark that the geographical region he reports as the source area of the *harenae fossiciae*, as mentioned before, seems to be restricted to the central Tyrrhenian Sea margin of Italy (Tuscany and Latium).

In this paper, through a selected geochemical dataset on mortar samples, we present an overview of the source area of the volcanic

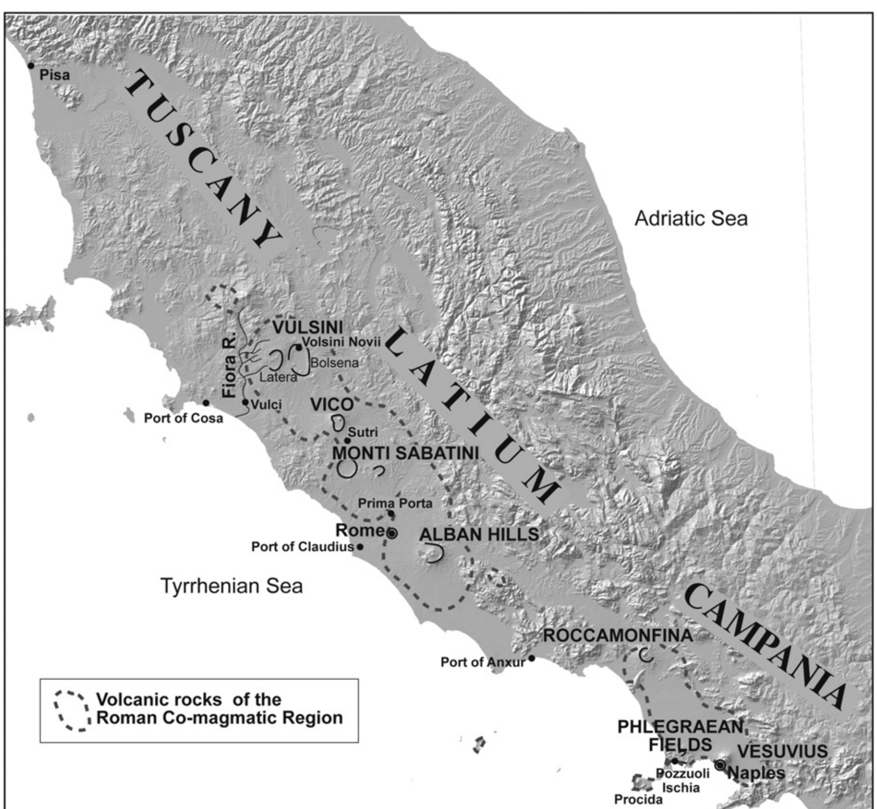


Fig. 1. Map of central Italy showing location of the volcanic districts of the Roman Province.

materials employed to produce mortar in the different regions of central Italy in Roman times, with a particular focus on Latium. In particular, we discuss the implications of the new geochemical and petrographic data of mortars sampled from Roman edifices in the ancient Etruscan villages of Sutri, Vulci and Volsinii (Bolsena), from Rome (Temple of Castor and Pollux, Temple B of Largo Argentina, Forum of Trajan), and from the Roman harbors of *Anxur* (Terracina) and of *Claudius* (Fiumicino), which provide new evidence to the identification of the volcanic products that correspond to the different types of *harenae fossiciae* and to the *pulvis* from the Gulf of Pozzuoli, described by *Vitruvius* in his *De Architectura*.

2. Methodological approach

In order to establish a simple and objective methodological approach, which may be easily and inexpensively adopted by everyone who is intended to study the origin of the volcanic components of the Roman concretes and mortars, we adopt a recent method based on the ratio of several trace elements (i.e.: Zr, Y, Nb, TiO_2, Th, Ta), that are poorly sensitive to alteration processes (Marra et al., 2011; 2013; Marra and D'Ambrosio, 2013; Marra et al., 2015).

It has to be remarked that the siliceous volcanic component, which was the subject of the geochemical analyses, is faintly affected by acid attack and, in any case, the elements whose ratio are used to classify the materials (i.e.: Zr, Y, Nb, Th, Ta) are substantially immobile ones (Cann, 1970; Floyd and Winchester, 1975; Pearce, 1996; Duzgoren-Aydin et al. 2002). Therefore, their mutual abundances are expected to remain stable, when the bulk composition is determined. However, recent studies have shown that even these “immobile” elements can be involved in the alteration processes under particular conditions (e.g.: Rubin et al., 1993; Salaun et al., 2011). In particular, it is likely that specific mineral phases may be removed by acid attack and, in case one of the investigated elements should be present in selective way within them, a variation of the ratios may occur. For this reason results of the analyses, especially when very small amount of sampled material is concerned, must be discussed with care. To overcome this limitation, we have integrated the Zr/Y vs Nb/Y diagram with another diagram, where Y is replaced by TiO_2 for those cases in which we suspected the occurrence of selective depletion of the former element due to acid attack (Marra et al., 2015).

Moreover, we analyzed at the electron microprobe (EMP) the matrix glass of several pumices that have been identified in the thin sections performed from pristine mortar samples from the ports of *Claudius* and *Anxur*, in order to compare their composition to that of the Campanian products provided in the literature.

3. Sample preparation

Samples of mortar were collected from the original structures of Roman epoch under the supervision of the archaeologists of the different Italian archaeological “Soprintendenze”, in charge for the different monuments.

Thin sections of each mortar sample were performed for preliminary petrographic observations. Subsequently, the clastic components employed as the aggregate were separated from the lime by bathing the samples in cloridric acid (HCl) for 4/5 days. As shown in Marra et al. (2015) this treatment does not affect the Zr/Nb ratio of the samples, whereas it is able to produce more or less significant Y depletion. In contrast, a more stable behavior is observed for the TiO_2 content. For these reasons, we will use the Zr/TiO_2 vs Nb/TiO_2 diagram for the correlation of the mortar aggregates with specific volcanic products, while we will rely on the Zr/Y vs Nb/Y compositional trends (essentially ruled by the Zr/Nb ratio) to attest the volcanic region from which the aggregates come.

4. Trace element analysis

Bulk samples of the volcanic component, either single scoria or pumice clast, or, when the grain size of the aggregate was too small, several clasts selected for their homogeneous texture, were analyzed for trace element at the Activation Laboratories, Canada by Lithium Metaborate/Tetraborate Fusion ICP-MS. Fused sample is diluted and analyzed by Perkin Elmer Sciex ELAN 6000, 6100 or 9000 ICP/MS. Three blanks and five controls (three before sample group and two after) are analyzed per group of samples. Wet chemical techniques were used to measure the loss on ignition (LOI) at 900 °C. International rock standards have been used for calibration and the precision is better than 5% for Rb and Sr, 10% for Ni, Zr, Nb, Ba, Ce, and La, and 15% for the other elements.

5. EMP analyses of matrix glass

Electron microprobe (EMP) analyses were performed at Istituto Nazionale di Geofisica e Vulcanologia (Rome, Italy) with a JEOL JXA 8200 equipped with five wavelength-dispersive spectrometers, using 15 kV accelerating voltage, 4.27 nA beam current, and counting time of 10 and 5 s were used on background and peaks, respectively. To reduce alkali loss the spot size was enlarged to 5 μm and Na and K were counted first and simultaneously with Al, Si and Ca. The following standards were adopted for the various chemical elements: anorthoclase (Al, Si, Na), augite (Mg), fayalite (Fe), rutile (Ti), Kfs (K), barite (Ba), apatite (P), rhodonite (Mn).

6. Sampling

6.1. Vulci, Volsinii, and Sutri

Vulci, thanks to its ports on the Fiora River and on the Tyrrhenian coast, represented an important Etruscan town since the VIII–VI centuries BC. In 273 BC, along with the nearby town of Volsinii, it was conquered by Rome and, after the construction of the harbor of Cosa 20 km north of the Fiora mouth, it became a key point for commercial exchanges between Etruria and the Mediterranean region. We collected two mortar samples from the walls of ambient 21 and 43 (Sample VU1, VU2, see Fig. 2a–a′, b–b′) and a third one from the garden wall (sample VU3, ambient 34, Fig. 2c–c′) of the II–I century BC Roman architectural complex within the archaeological park of Vulci (Moretti Sgubini, 1993).

Volsinii, an ancient Etruscan town defeated and conquered by Romans in 264 BC, is located on the banks of the Bolsena Lake, which constitutes a volcano-tectonic depression originated by the collapse of the edifices responsible for the early activity of the Vulsini volcanic district. We collected two mortar samples (CP1 and CN1, Fig. 2d–d′ and e–e′) from the walls of two houses (“Casa delle Pitture” and “Casa del Ninfeo”) erected in the first half and at the end of the IInd century BC, respectively (Timperi, 2010, and reference therin). Moreover, we collected one sample of mortar from the vaults of the coeval *tabernae* (Fig. 2f–f′) which contains well visible, large pumices.

Sutri (Latin *Sutrium*), etruscan town conquered by Romans in the IV century BC and colonized in the I century BC. (Morselli, 1980; Del Lungo, 2008). The most outstanding monument of Sutri is its amphitheater that was built between the second half of the Ist century BC and the beginning of the Ist century CE. Although it is completely dug into the tuff, some structural elements in masonry were realized, as testified by a few remnants. Among these is a nucleus of a wall adjacent to the north-western entrance, from which we collected one mortar sample (SUT ANF, Fig. 3a).

6.2. Villa di Livia in Prima Porta

Based on its location on the western side of the Tiber River north of Rome, the area of Prima Porta can be considered the southernmost

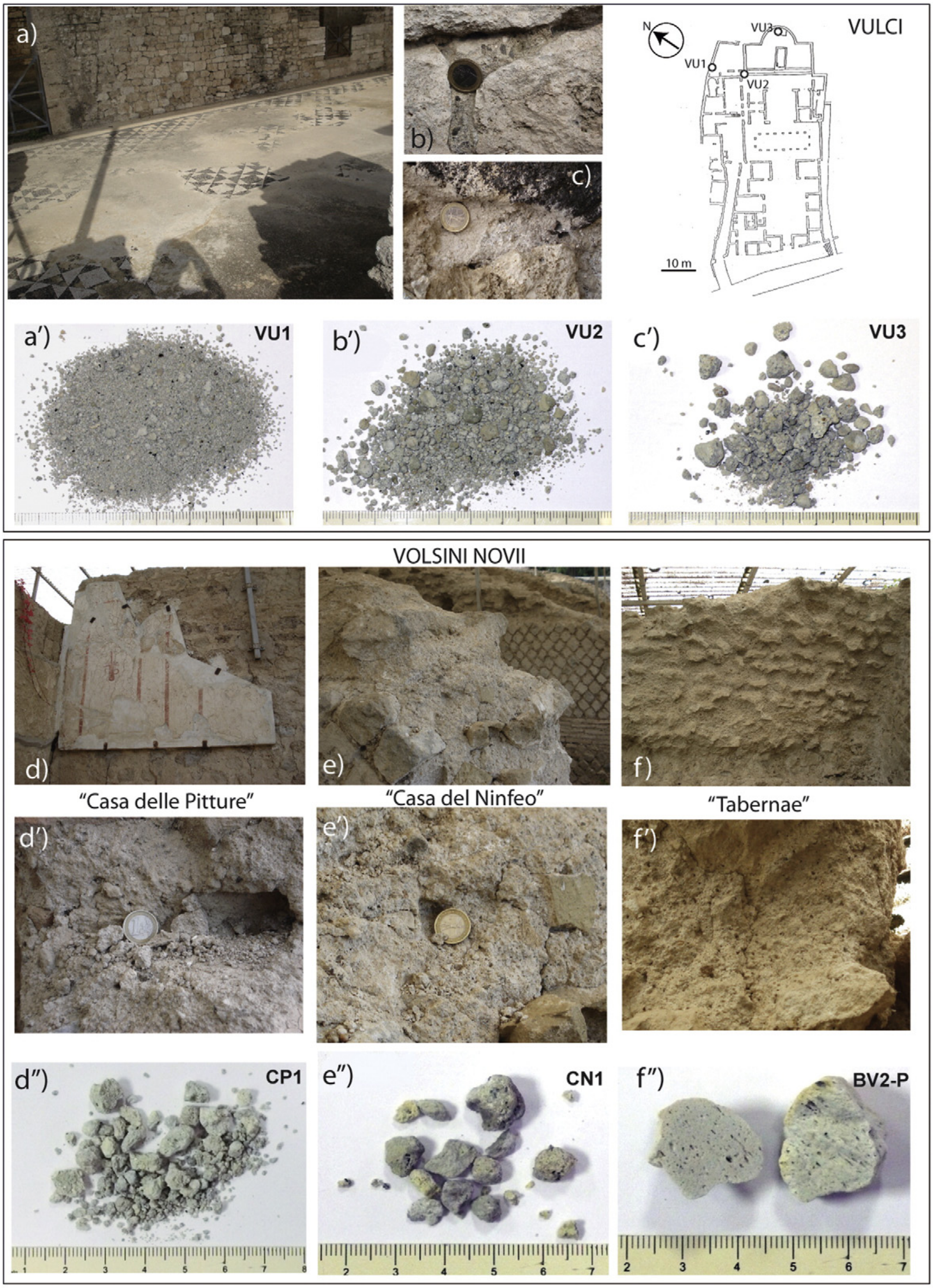


Fig. 2. Mortar aggregates from the ancient Etruscan towns of Vulci and Volsinii. a)–a′), b)–b′), c)–c′): sampling site and aggregate after separation from the lime of mortar samples VU1, VU2, VU3, collected from as many II–I century BC masonry structures in the architectonic complex of the Archaeological Park of Vulci (see inset map); d)–d′)–d″), e)–e′)–e″), and f)–f′)–f″): sampling site and aggregate after separation from the lime of mortar samples CP1, CN1, BV2-P collected from the II century BC structures of Casa delle Pitture, Casa del Ninfeo and the associated *tarbernbae* within the archaeological site of Volsinii.

portion of Etruria, at the boundary with Rome's territory until the conquest of Veii in 396 BC. The Villa of Livia in Prima Porta is named after Emperor August's wife, Livia Drusilla and it was probably built between 30 and 25 BC. Later enlargements and re-constructions were performed, mainly in the IInd–IIIrd and in the IIIrd–IVth centuries (Forte, 2007; Messineo, 2004, De Franceschini, 2005).

The aggregates of two mortar samples of the early Augustan and of the IInd–IIIrd constructive phases analyzed in Marra et al. (2015)

yielded geochemical compositions attesting their correlation with the deposit of the Grottarossa Pyroclastic Sequence (Karner et al., 2001), cropping out and exploited near the Villa di Livia in Prima Porta. In contrast, all the III–IV century mortars are characterized by the presence of large (2–3 cm) black scoriae (Fig. 3b) that are very similar to those occurring in the local, incoherent facies of Tufo Rosso a Scorie Nere (Marra et al., 2011, 2014). For the present study, we have manually separated and analyzed a fragment of one black scoria collected from a brick faced wall of a III–IV century CE structure of the Villa.

6.3. Rome

The selective use of the local Pozzolane Rosse pyroclastic-flow deposit in the mortars and concretes of several monuments of ancient Rome spanning in age the II century BC through the IIIrd century CE has been documented by geochemical data presented in Marra et al. (2015). Here we provide new petrographic evidence for the mortars of Temple of Castor and Pollux (Coarelli, 2008) and for Temple B of Largo Argentina (Caprioli, 2010) (II c. BC). Moreover, in order to integrate the existing geochemical dataset, we have performed trace-element analyses on one mortar sample collected from a fallen remnant of the vaulted ceiling of the Sala Trisegmentata of Forum of Trajan (96–115 CE). The occurrence within the mortars of Sala Trisegmentata of Pozzolane Rosse scoriae, mixed with pumices of uncertain attribution was documented through thin section analysis at the optical microscope in Bianchi et al. (2009). The provenance of these pumices from the volcanic districts of Campania was successively determined based on Zr/Y vs Nb/Y signature by Marra et al. (2013). However, no pumice has been found in the mortar sampled for this study, which was collected from a vault fragment displaying gradational density stratification, confirming observation by Bianchi et al. (2009) that the pumice was selectively employed only in the central portion of the vaults to decrease the specific weight of this portion of the structure. The sampled mortar aggregate is entirely composed of two apparently different types of red and gray scoriae; the latter, when split revealed a black core (Fig. 3i). The red and the black clasts have been separated and the two samples (ST-R and ST-B, respectively) were analyzed for trace-element composition.

6.4. Port of Claudius (Fiumicino) and Port of Anxur (Terracina)

According to *Vitruvius*' precepts, it is generally believed that the Roman builders of the harbors that punctuated the coasts of the Mediterranean Sea under the hegemony of the Empire used only pozzolan exploited in the Bay of Naples, deriving from the eruptions of the Phlegraean Fields and Somma–Vesuvius volcanic districts (e.g. Oleson et al., 2004). Marra and D'Ambrosio (2013) have recently demonstrated, based on geochemical data reported in Jackson et al. (2010b), that the aggregate used in the II c AD Trajanic port of Ostiae yielded a Zr/Y vs Nb/Y signature attesting its provenance from the Phlegrean Fields, whereas that of a ca. 60 BC structure of the Cosa harbor (Tuscany) yielded a Campanian composition which has an only equivalent in the products of the 79 AD eruption of Vesuvius, which occurred well after the supposed construction of the portion of the harbor from which the pumice was sampled, thus leaving its actual identification uncertain.

Here we have investigated the composition of the mortar aggregates from two important harbors of the early Imperial Age close to Rome: the port of *Claudius* in Fiumicino, started by Emperor Claudius in 42 CE and inaugurated by Emperor Trajan in 64 CE (Morelli et al., 2001), and the port of *Anxur* (the modern Terracina), built by Trajan at the beginning of the IInd century CE (Di Mario, 1994).

The mortar sample collected at the Port of Claudius (PC) contained three different types of pumice, displaying different textural features, that we have handpicked separating them from a minor component of heterogeneous volcanic fragments (PC1-A, PC1-PV, PC2, Fig. 4a–a′–a″).

At Terracina, the fine aggregate that has been separated from the matrix, in addition to several whitish, microvesicular pumices (sample TER-W, Fig. 4b′) that are identical to those separated from sample PC2, contains moderately vesicular, mm-sized gray scoriae (sample TER-G, Fig. 4b″).

7. Results

Geochemical data for the 13 investigated mortar samples and 3 outcrop rock samples are reported in Appendix A, whereas a summary showing the attribution of the mortar aggregates to the volcanic product of origin is provided in Table 1.

7.1. General plots of the geochemical data

Fig. 5 shows an overall plot of all the analyzed mortar aggregates in the Zr/Y vs. Nb/Y and in the Th/Ta vs Nb/Zr diagrams, to compare their composition with the compositional fields of the different volcanic districts of Central Italy, determined in Marra et al. (2011, 2013), and Marra and D'Ambrosio (2013).

In interpreting the results it has to be taken into account that these previous work have evidenced the great stability of the Zr/Nb ratio that characterizes each specific volcanic product, with respect to a larger variability of the Y content, determining a series of sub-rectilinear compositional fields, radially stretching from the origin of the axis towards the extern of the Zr/Y vs. Nb/Y diagram. The compositional fields defined in Fig. 5 after data reviewed in Marra and D'Ambrosio (2013) are therefore to be intended as indicative of the distribution trend of the Zr/Y vs Zr/Y values of each product or district, with an undefined upper limit, as indicated by the arrows on the contour lines of each field. The analytical uncertainty for Zr and Nb is 10% (lower than for Y) and the sub-linear trends in the diagrams evidence that the variability is small and do not affect the possibility to recognize representative trends for the different products, allowing us to distinguish one from the other.

In contrast, more clustered distributions characterize the eruptive products in the Zr/TiO_2 vs Nb/TiO_2 diagram (Figs. 6, 7), which can be used more confidently to identify the provenance of the mortar aggregates. Based on these features, the Zr/Y vs. Nb/Y and Th/Ta vs. Nb/Zr diagrams of Fig. 5 allow for a ready attribution of the different mortar aggregates to the volcanic region of origin (i.e. Latium vs. Campania) and, in most instances, to the volcanic district, whereas the correlation with a specific volcanic deposit can be validated with the Zr/TiO_2 vs Nb/TiO_2 diagrams of Figs. 6 and 7.

As an example, there is no doubt that the four samples of mortar collected from the harbors of *Claudius* and Terracina (PC1-A, PC1-PV, TER-W, TER-G) contain pumices coming from the Campanian districts, as opposite to all the volcanic aggregates of mortar samples from the monuments of Rome and Etruria, which plot within the Latium compositional fields in Fig. 5a, b. Moreover, the mortar samples from northern Latium plot in the left, upper portion of the diagram in Fig. 5a, with BV2-P, VU2, VU3, and CN1 aligned to the trend pertaining to the compositional field of the Vulsini district, whereas SU ANF plot in the area where all the compositional fields of the Latium districts overlap, and CP1 plots far from the literature compositions. However, the compositional fields of the products of the different volcanic districts of Latium are distinguished better in the Zr/TiO_2 vs Nb/TiO_2 diagram of Fig. 6, allowing attribution of several mortar samples from Etruria, including sample SU ANF, to specific products of Vulsini and Vico. In conclusion, when all the diagrams are used in combination, each mortar sample analyzed in this paper can be more or less confidently attributed to a specific volcanic deposit, as discussed in the following sections.

8. Geochemical and petrographic data of mortar aggregates

8.1. Vulci and Volsinii

The thin sections realized for preliminary petrographic observation from mortar samples VU1, VU3, CN1 and CP1 revealed the predominance of poorly vesicular, gray scoria clasts with leucite, sanidine, clinopyroxene and biotite, along with other minor pumice clasts and tuff fragments characterized by the same mineralogic assemblage, which also occurs in form of loose crystals. These textures and compositions are compatible with the most part of the volcanic products of the larger Roman Magmatic Province, including Latium and Campania, whereas they rule out the sole provenance from the Colli Albani district, where sanidine and plagioclase are extremely rare (Gaeta, 1998; Marra et al., 2011). The pumice sample BV2-P, besides a quasi-aphiric texture, also revealed the undiscriminating presence of rare sanidine and plagioclase among the phenocrystal assemblage.

In contrast, the Zr/TiO_2 vs Nb/TiO_2 compositions of samples VU1, VU3, CN1 and BV2-P (Fig. 6) restrict their attribution to the Vulsini district, with the only other possible match represented by a minority of Monti Sabatini products characterized by a particular composition (field MS-C; Marra and D'Ambrosio, 2013; Marra et al., 2014). However, comparison with Fig. 5, where these samples are well-aligned along a different linear trend (dashed gray line) with respect to that of the Zr/Y vs Nb/Y compositional field MS-C, allows the inferring of a common provenance from the local Vulsini volcanic district for all these "Etruscan" mortar samples.

A restricted set of samples from the Vico district, either from literature (Perini et al., 2004) or performed for the present study, plots in intermediate position between the Vulsini and Monti Sabatini compositions (tightly dashed line in Fig. 6), suggesting the possibility of using the Zr/TiO_2 vs Nb/TiO_2 diagram for more safe identification of provenance from the different volcanic districts, with respect to the Zr/Y vs Nb/Y diagram.

Remarkably, Zr/TiO_2 vs Nb/TiO_2 composition of mortar aggregate VU2 displays a striking similarity with that of the pozzolan recovered in the wrecked Roman ship at the ancient port of Pisa (Pecchioni et al., 2007; cross in Fig. 6), that based on Zr/Y vs Nb/Y signature Marra and D'Ambrosio (2013) identified as the deposit of the Onano pyroclastic-flow unit, erupted by the Latera volcanic complex at the Vulsini district, and cropping out in the area of Vulci and Vulsini Novii (Palladino et al., 2010). The samples of the Onano unit (o in Fig. 6; data from Conticelli et al., 1987) plot along with the pozzolan of ship B and close to VU2 also in the Zr/TiO_2 vs Nb/TiO_2 diagram of Fig. 6, confirming inferences of Marra and D'Ambrosio (2013).

The compositional field defined by VU2 and the Onano samples include also the samples from the Valentano scoria cones (v in Fig. 6) that is located on the southern rim of the Latera caldera. Another good match is observed between composition of mortar sample VU3 and those of the samples of the Sovana pyroclastic-flow deposits (s in Fig. 6; data from Conticelli et al., 1987). This pyroclastic deposit crops out in correspondence of the higher hydrographic network of the Fiora River and its tributaries, immediately north of Vulci (Fig. 1). The gray scoria sample CN1 from Volsinii yielded very similar composition as that of VU3, whereas that of CP1 might reveal a mix of Latera units compositions (e.g. Onano, Sorano and Sovana, see Fig. 6).

Finally, the pumice sample BV2-P shows a markedly different Zr/Y vs Nb/Y composition with respect to the other Etruscan mortars but still strictly aligned with the other samples, to define a very tight "Vulsinian" compositional trend (dashed gray line in Fig. 6), which accounts for the high reliability of the trace-element discrimination method to recognize the volcanic district of origin. Composition of BV2-P plots close to that of the pumice deposits of Farnese and Canino (Fig. 6), which represent the more widespread Plinian-fall deposits of the Latera volcanic complex (Palladino et al., 2010).

8.2. Sutri

Sample SU ANF displays an offset position with respect to the linear trend defined by samples from Vulci and Volsinii in both diagrams of Figs. 5a and 6, suggesting a best correlation with the Vico volcanic districts. In Fig. 6 we have plotted the Zr/TiO_2 vs Nb/TiO_2 compositions of the products whose pyroclastic-flow deposits are characterized by the presence of black vesicular scoriae within a loose ash matrix. These include the Sutri (Vico's Tufo Rosso a Scorie Nere), Ronciglione and Carbognano formations from Vico volcano (Perini et al., 2004), and the unlithified facies of the Tufo Roso a Scorie Nere from Monti Sabatini (Marra et al., 2014). Comparison of sample SU ANF composition with those of the different volcanic deposits suggests correlation with the Carbognano and Ronciglione Formations. The observation in a thin section of sample SU ANF evidenced a mineral assemblage with plagioclase and sanidine, ruling out attribution to the leucite-bearing Carbognano Formation, as opposite to the leucite-free scoriae of the Ronciglione Formation (Perini et al., 2004). Moreover, the characteristic presence of 0.3–2.0 mm long, euhedral plagioclase phenocrysts, showing normal zoning and containing inclusion-rich zones and occasionally sieve-textured, glass inclusion-rich cores (Fig. 3f), which is typical of the Ronciglione Formation deposit, definitely provides correlation with this volcanic unit.

Based on the good reliability of the correlations made here by means of the Zr/TiO_2 vs Nb/TiO_2 diagram, we also note that samples VCO 15 and VCO 167 from the Perini et al. (2004) dataset might have been miscorrelated, because they show good correlation with the sabatinian TRSN and with the Ronciglione Formation, respectively (Fig. 6).

8.3. Villa di Livia

In contrast to the Augustan age mortars of the earliest Villa di Livia structures, in which the Roman builders employed the pyroclastic-flow deposit of the Grottorossa Pyroclastic Sequence exploited locally (Marra et al., 2015), a pervasive use of the loose, pozzolanaceous facies of the Tufo Rosso a Scorie Nere Sabatino in the later mortars of the III and IV century AD is confirmed by the Zr/TiO_2 vs Nb/TiO_2 composition of the black scoria sample (LIV-B) analyzed in this work (Fig. 6).

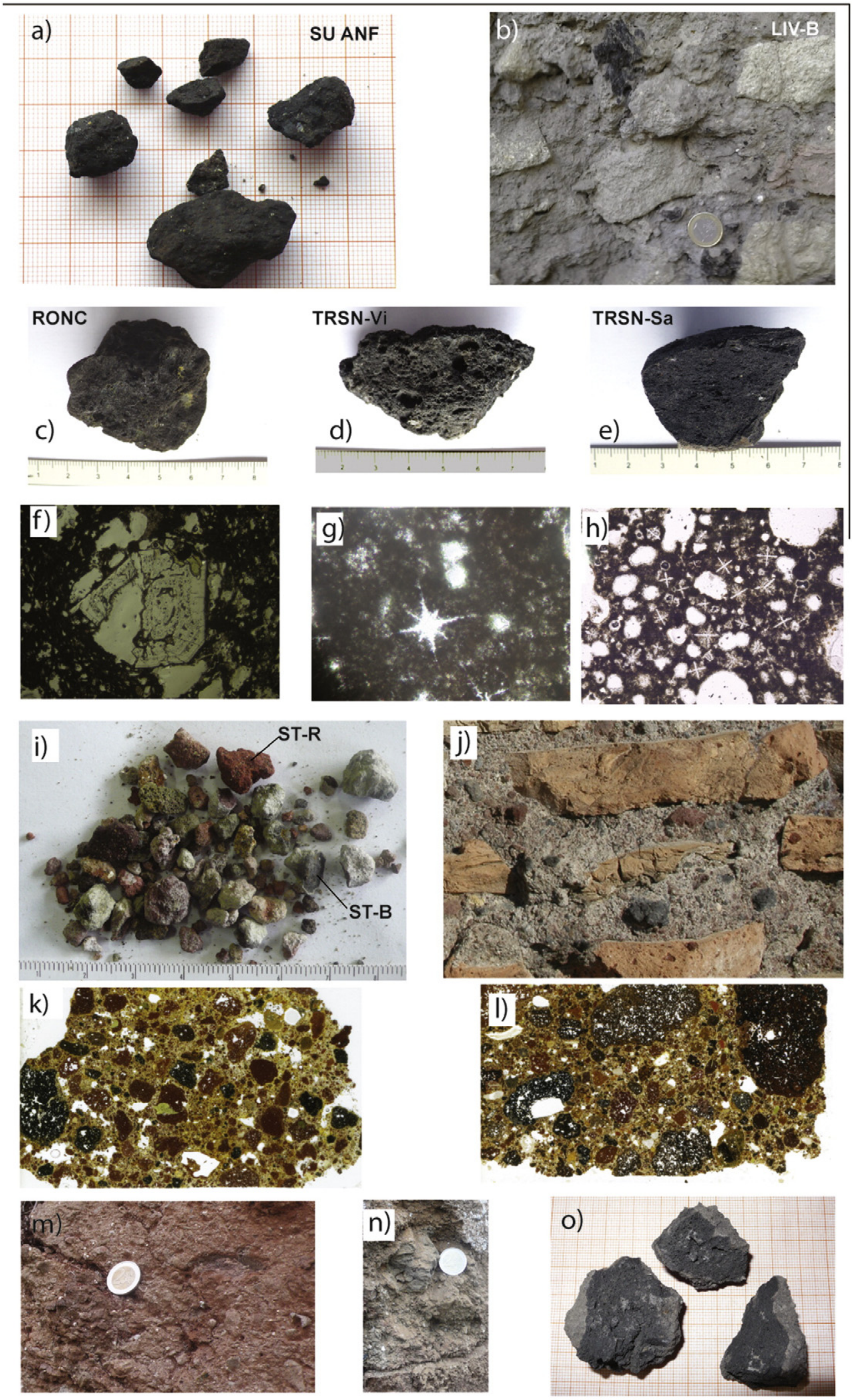
8.4. Rome

8.4.1. Temple of Castor and Pollux and Temple B of Largo Argentina

Zr/Y vs Nb/Y and Zr/TiO_2 vs Nb/TiO_2 signature of mortar samples from the II century BC Temple of Castor and Pollux and Temple B of Largo Argentina analyzed in Marra et al. (2015) provided evidence of the selective and continuative use of Pozzolane Rosse volcanic aggregate in Rome since the early development of concrete masonry. Here we substantiate this evidence showing two microphotographs in thin sections of these mortars, revealing the presence of characteristic leucite crystals with starry habit (Fig. 3g, h):, which is an exclusive feature of the Pozzolane Rosse matrix glass (Marra et al., 2009; Freda et al., 2011).

8.4.2. Forum of Trajan

When plotted in the Zr/Y vs Nb/Y identification diagram of Fig. 5a the samples ST-R and ST-B fall in the upper extreme of compositional field I (bordered by the dashed lines) which is defined by the literature data for Pozzolane Rosse (Marra et al., 2011), evidencing that these samples display anomalous distance from the origin of the axis (i.e.: Y depletion). Comparison with the Th/Ta vs Nb/Zr diagram in Fig. 5b shows that ST-R and ST-B have indeed a tight Nb/Zr within the Pozzolane Rosse trend I (bounded by the dashed vertical lines), but also display Th depletion and plot lower with respect to the compositional field I defined based on literature data for the PR. Remarkably,


a)
SU ANF
b)
LIV-B
RONC
c)
TRSN-Vi
d)
TRSN-Sa
e)
f)
g)
h)
i)
ST-R
ST-B
j)
k)
l)
m)
n)
o)

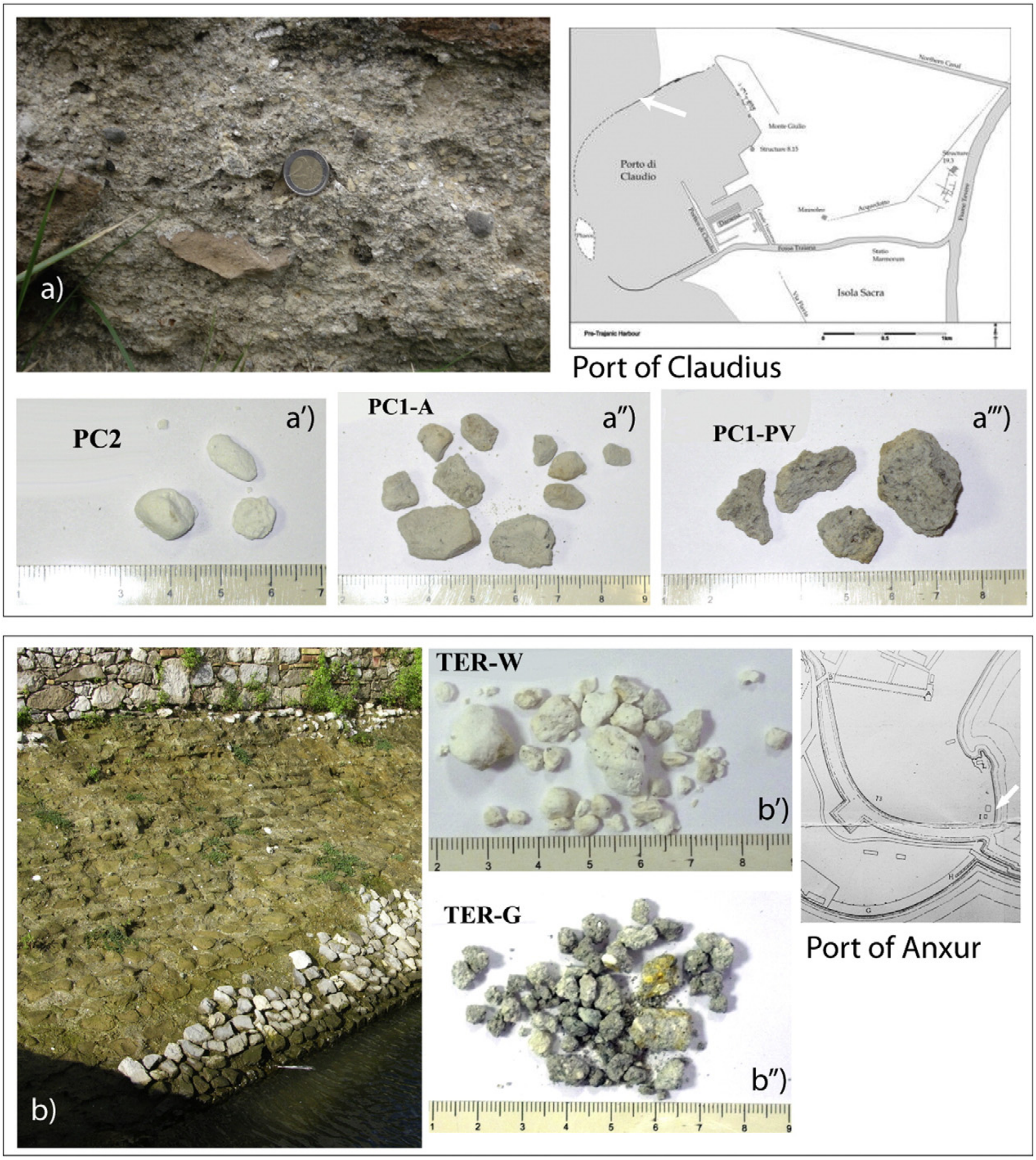


Fig. 4. a) Sampling location and detail of the quay concrete of Molo Foraneo at the Port of Claudius; a′), a″), a‴): three different types of pumice occurring in the aggregate of the concrete were handpicked after HCl bathing of the sample (PCL), and analyzed separately (samples PC2, PC1-A, PC1-PV); b) breakwater of the quay of the Port of *Anxur* from which a concrete sample (TER) was collected; and b′)–b″) two different types of pumice occurring in the aggregate were separated and analyzed (TER-W, TER-G).

Fig. 3. a) Mortar aggregate after separation from lime of sample SU ANF collected from a dividing wall at the entrance room of the Sutri Amphitheater; b) large black scoriae occurring in the mortar of the III–IV century structures of Villa di Livia in Prima Porta: one scoria sample (LIV-B) was collected and analyzed for the present work; c), d), e): scoria samples collected from the outcropping volcanic deposit of Ronciglione Formation (RONC), Sutri Formation (=Tufo Rosso a Scorie Nere Vicano, Tufo Grigio Vicano) (TRSN-Vi), and Tufo Roso a Scorie Nere Sabatino (=Tufo Grigio Sabatino) (TRSN-Sa), respectively, and analyzed in the present work; f) microphotograph of a plagioclase crystal showing texture (see text) characteristic of the Ronciglione Formation volcanic scoriae, occurring in a thin section of mortar sample SU ANF; horizontal field of view is 2 mm for all microphotographs. g), h): microphotographs of thin sections of mortar samples of Temple of Castor and Pollux, and Temple B of Largo Argentina, respectively, showing idiosyncratic leucite crystals with starry habit, which are characteristic of the Pozzolane Rosse pyroclastic-flow deposit; i) red and black scoria occurring in the aggregate of the mortar collected from a fallen vault of the Sala Trisegmentata of Forum of Trajan: red and black fragments were separated and the respective samples (ST-R and ST-B) were analyzed in the present work; j) large red and black scoria occurring in the nucleus of a I century AD wall in the Area Sacra of Largo Argentina. k–l) thin sections of mortar samples from a Ist century AD brick-faced wall (k) and from the IInd century BC *donario* of Temple B (l) in the Area Sacra of Largo Argentina, Rome, in which red and black scoriae of the Pozzolane Rosse pyroclastic-flow deposits constitute the volcanic aggregate. Other large pyroclastic-flow deposits cropping out in Rome characterized by the presence of reddish and grey to black volcanic scoriae are the "Pozzolanelle" (m, n) and the "Pozzolane Nere" (o); and scoriae from these deposits have been identified in the aggregate of two mortars of the II–IIIrd century AD at Villa di Livia in Prima Porta, and in Largo Argentina, respectively (Marra et al., 2015).

Table 1
Mortar samples analyzed in this work. Attribution to the volcanic district and, when possible, to the volcanic product of origin of the mortar aggregate is made based on the classification diagrams in Figs. 5 through 8.

Sample	Sampling site	Age	Region	Volcanic district	Volcanic product
VU2	Vulci ambient 43	II–I BC	Northern Latium	Vulsini, Latera	Onano Fm
VU3	Vulci ambient 34	II–I BC	Northern Latium	Vulsini, Latera	Sovana Fm
CN1	Volsinii Casa del Ninfeo	End of II BC	Northern Latium	Vulsini, Latera	Sovana Fm-?
CP1	Volsinii Case delle Pitture	First half of II BC	Northern Latium	Vulsini, Latera	Probably a mix of different products
BV2-P	Volsinii vault of tabernae	End of II BC	Northern Latium	Vulsini, Latera	Farnese Fm-?
SU ANF	Dividing wall, Sutri amphitheater	Prob. I BC	Northern Latium	Vico	Ronciglione Fm
LIV-B	Brick-faced wall of Villa di Livia in Prima Porta	III–IV AD	Northern Rome	Monti Sabatini	Tufo Rosso a Scorie Nere
ST-G	Sala Trisegmentata of Forum of Trajan	96–115 AD	Rome	Colli Albani	Pozzolane Rosse
ST-PR	Sala Trisegmentata of Forum of Trajan	96–115 AD	Rome	Colli Albani	Pozzolane Rosse
PC1-PV	Port of Claudius	42 AD	Rome's coast	Phlegraean Fields	Astroni-?
PC1-A	Port of Claudius	42 AD	Rome's coast	Phlegraean Fields	Astroni?
TER-G	Port of Terracina	Prob. II AD	Southern Latium coast	Phlegraean Fields	Astroni
TER-W	Port of Terracina	Prob. II AD	Southern Latium coast	Phlegraean Fields	Trefola unit f

Sample	Sampling site	Unit
RONC	Ronciglione	Ronciglione Fm (Vico C)
TRSN-Vi	Foglia	Sutri Fm (vican TRSN)
TRSN-Sa	Prima Porta	Sabatinian TRSN

Rock sample analyzed in this work.
Full geochemical data in Appendix A.

both of these effects (Y and Th depletion) have been recognized and have the consequence of particularly strong alteration processes affecting a volcanic rock (Marra et al., 2011), and are a likely consequence of the HCl bathing to separate the aggregate of these samples. A more straight identification of the volcanic product is achieved using the Zr/TiO_2 vs Nb/TiO_2 identification diagram of Fig. 6, where samples ST-R and ST-B are tightly clustered to each other and plot inside the small compositional field defined by the other Pozzolane Rosse samples (dark gray area in Fig. 6), computed after the literature dataset (Marra et al., 2011).

8.5. Ports of Claudius and Anxur

Zr/TiO_2 vs Nb/TiO_2 compositions of the four mortar pumice samples of the Roman ports of Claudius (Ostiae) and Terracina (Anxur) are compared to a selected dataset (Peccerillo, 2005; Lustrino et al., 2011) of pumices erupted by the Somma–Vesuvius and by the Phlegraean Fields volcanic districts of Campania, in Fig. 7a and b, respectively. All these mortar pumices display clear campanian compositions, as opposite to mortar pumice sample LA-C40p from Largo Agentina, which plots outside of the Campania compositional field and matches well compositions of the Monti Sabatini volcanic district (MS-A in Fig. 7a, b), as also two other pumices from the mortars of Forum of Trajan analyzed in Marra et al. (2013) (GA-p2, BU-p1) do. A third mortar pumice from the Grande Aula of Trajan Markets (GA-p1), that Marra et al. (2013) attributed to the Vesuvius based also on its mineralogic composition, shows Zr/TiO_2 vs Nb/TiO_2 composition quite similar to that of the early explosive activity of Somma–Vesuvius ("Pomici di Base" and "Pomici Verdoline", Ayuso et al., 1998; Landi et al., 1999: Paone, 2006: Piochi et al., 2006; Fig. 7a). Three mortar pumices from the ports of Claudius and Terracina (PC1-A, PC1-PV and TER-G) are aligned to the compositional trend defined by pumices from Sarno eruption (Pomici di Base), but plot outside of this field; while sample TER-W plots within the compositional field defined by two pumices of the Avellino eruption unit (Fig. 7a). However, when the Zr/TiO_2 vs Nb/TiO_2 compositions are cross-checked with the total alkali silica (TAS) compositions from the same selected dataset of Somma–Vesuvius products (Fig. 8a), an almost complete mismatch is evidenced, ruling out attribution of the analyzed mortar pumice samples to anyone of these products. Indeed, matrix glass compositions of several pumice contained in the thin sections of two mortar samples (PCL and TER) analyzed at the electron microprobe concentrate in the phono-trachytic field, with a minority spreading in the lower part of the tephri-phonolitic field in Fig. 8a, covering a compositional area in which no Somma–Vesuvius product plots.

The comparison of the Zr/TiO_2 vs Nb/TiO_2 compositions of the mortar pumice samples with the products of the Phlegraean Fields in Fig. 7b shows that the three samples aligned along the same trend (PC1-A, PC1-PV and TER-G) match the magma composition (above the thinner dashed line) that characterizes the products erupted after the large Campanian Ignimbrite eruption of 40 ka (Civetta et al., 1997), including the Neapolitan Yellow Tuff (Orsi et al., 1995) and the products of the later activity (Civetta et al., 1991; D'Antonio et al., 1999; De Astis et al., 2004; Smith et al., 2011), as opposite to TER-W, which according to its offset plotting has a different magma composition (Marra et al., 2013), matching that (below the thinner dashed line) of the Campanian Ignimbrite and of the older products of the Phlegraean Fields (Pappalardo et al., 1999; Pabst et al., 2008; Tomlinson et al., 2012). In particular, TER-W plots within the narrow compositional field defined by samples of the fallout deposit occurring at Trefola quarry (unit TLf, Pappalardo et al., 1999; Pabst et al., 2008; dark gray area in Fig. 7b). Other products of the pre-CI activity occurring in Trefola (TLh, i) and in Torregaveta (TGk, l) and analyzed in Pappalardo et al. (1999) have Zr/TiO_2 vs Nb/TiO_2 composition very similar to that of TER-W. In contrast, TER-G plots close to the compositions of several products of the post-NYT activity (D'Antonio et al., 1999; Smith et al., 2011), in particular those of Astroni (Fig. 7b). More in general, TER-G and the two pumice mortar samples from the port of Claudius (PC1-PV, PC1-A) display Zr/TiO_2 vs Nb/TiO_2 compositions matching those of the more offset products of the late phase of activity at the Phlegraean Fields (white and gray circles in Fig. 7b). The latter ones, according to what were discussed in Marra et al. (2014) about the Monti Sabatini products, display longer distance from the origin of the axis, which is consistent with the more differentiated character of their magma (D'Antonio et al., 1999; Smith et al., 2011). These include the products of Agnano, Astroni, Archiaverno, Pigna San Nicola, Capo Miseno, Baia and Fondi di Baia eruptive centers, which are all located near Pozzuoli (Fig. 7c). Finally, also several products of the post-CI activity from Trefola (TL r, s and Tlo) and Ponti Rosi (indicated by the light gray areas), have similar compositions.

However, comparison of the matrix glass TAS compositions of mortar samples PCL and TER with those of the products of the Phlegraean Fields activity in Fig. 8b, rules out correlation with the most differentiated, trachytic deposits of Trefola (units TLo, r, s), Baia, Fondi di Baia, Archiaverno and Ponti Rossi. In contrast, a very good match is observed in Fig. 8b either with the products of the Trefola fallout (TLf), as well as

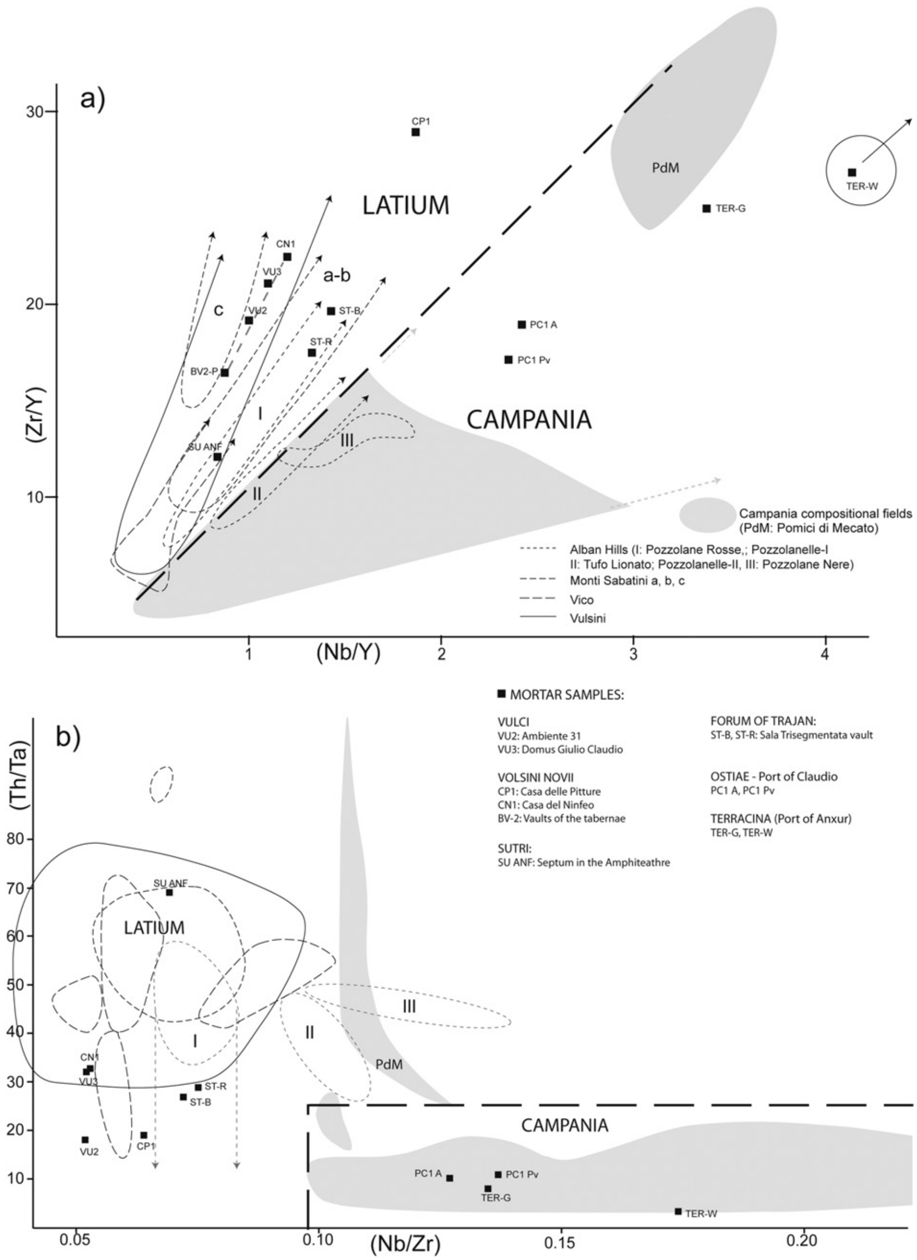


Fig. 5. Zr/Y vs Nb/Y (a) and Th/Ta vs Nb/Zr (b) compositional fields of the products of the volcanic districts of Latium and Campania after literature data analyses compiled in Marra and D'Ambrosio (2013), to compare compositions of the analyzed mortar samples. See text for explanations.

with those of the eruptive centers of Astroni, Capo Miseno and, at a lesser extent, Pigna San Nicola. The compositional spread, ranging the trachyphonolitic to the tephryphonolitic fields of the TAS diagram, suggests that two or more different products occur at the microscopic scale of the analyzed thin sections of mortar samples. This is particularly true for sample TER, for which two main average compositions, tephryphonolitic and phono-trachytic, may be hypothesized. Remarkably, the two types of pumice separated from the aggregate of this mortar (TER-W and TER-G) yielded a different magmatic composition in the diagram in Fig. 7b. The combined Zr/TiO_2 vs Nb/TiO_2 composition of mortar pumice sample TER-W and TAS compositions yielded by matrix glass of pumices in thin section TER, univocally indicate the fallout deposit of Trefola (TLf, Pappalardo et al., 1999; Pabst et al., 2008) as the product of origin. In contrast, pumice TER-G displays a less differentiated Zr/TiO_2 vs Nb/TiO_2 composition (closer to the origin of the axis), also with respect to the other pumice mortar samples PC1-PV and PC1-A, which is consistent with its correlation with the less differentiated TAS composition of several products of the late Phlegraean Fields activity, including those occurring at the eruptive center of Astroni (see also Fig. 8b), which are the best candidate as the source of this pumice.

Similarly, the combined observation of Zr/TiO_2 vs Nb/TiO_2 and TAS compositions of mortar samples from the Port of Claudius, evidences their correlation with the more differentiated deposits occurring at the eruptive centers of the Phlegraean Fields, and a best fit with those of Astroni.

8.6. Discussion: identification of the source areas of the harenae fossiciae

In interpreting Vitruvius it is fundamental to be aware of the fact that, as many classicists have repeatedly pointed out, he refers to precepts, either verbal and written, which are not up to date with the time when he writes, despite that there is a clear evidence of "ideological" references to his times and, in particular, to the Caesarian ideology (Gros, 1982, 2007; Rawson, 1985; Coarelli, 1987; Schrijvers,

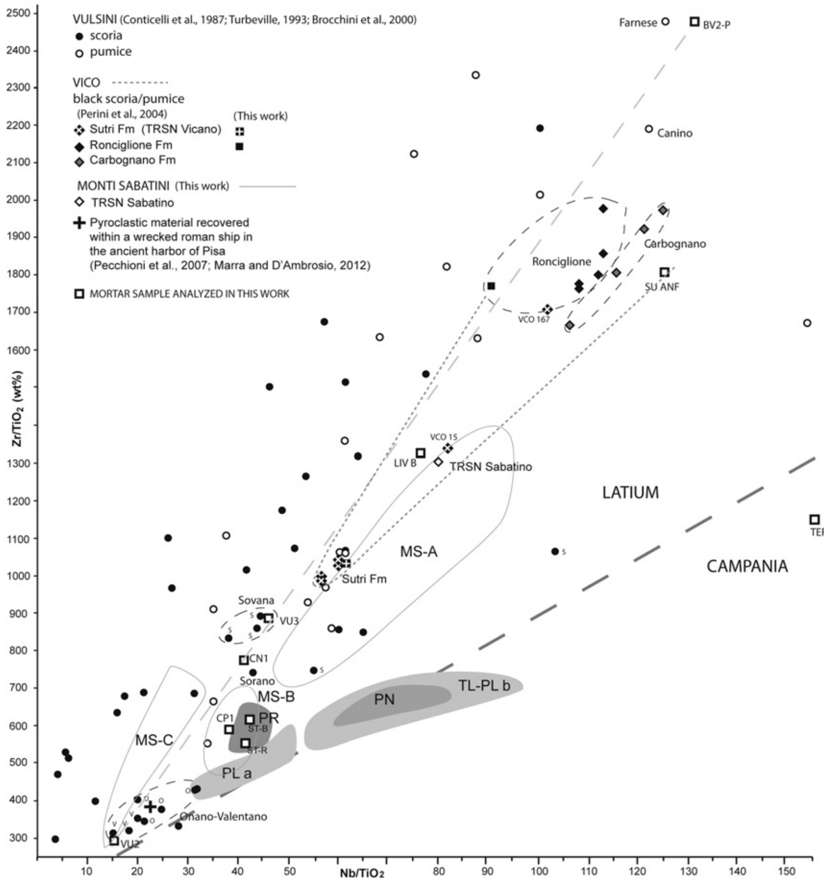


Fig. 6. Zr/TiO_2 vs $Nb//TiO_2$ individual compositions of selected products of the Vulsini and Vico districts (plotted after data in the reported literature) and compositional fields of the products of the Monti Sabatini and Alban Hills volcanic districts, and of the whole Campanian magmatic region (compiled after data reported in Marra et al., 2015), to compare compositions of the analyzed mortar samples. See text for explanations. Legend: MS-A, MS-B, MS-C: Monti Sabatini compositional fields, as defined in Marra et al. (2014) and Marra and D'Ambrosio (2013); PR: Pozzolane Rosse pyroclastic-flow deposit, PN: Pozzolane Nere pyroclastic-flow deposit, TL: Tufo Lionato pyroclastic-flow deposit, and PL: Pozzolanelle pyroclastic-flow deposit (groups a and b, as defined in Marra and D'Ambrosio, 2013; Marra et al., 2015).

1987; Romano, 1994). According to a definition by Gros, he was a "*laudator temporis acti*" (he who praises past times) and wrote inspired by a strong "spirit of service", aimed at promoting a correct practice of architecture rather than at defining its theory, in order to give the many people who had the responsibility for the construction of public and private buildings (above all the politicians) a treaty which was to be as most complete as possible. At the end of his career as an architect, Vitruvius shows himself as the one who tries to codify and save the knowledge, both theoretical and practical, of the last two Hellenistic centuries, preserving it against the incoming architectural revolution of the imperial age (Gros, 2007). In particular, in the second book treatment on the building materials, the subject is arranged according to an outline going from the simple to what is considered complex, artificial or exceptional (Gros, 2007). So, as to the earths (chap. 3–6), it goes from crude bricks (chapter 3) to the sand (chapter 4), to the lime (chapter 5), to finish with the *harenae fossiciae* (chapter 6).

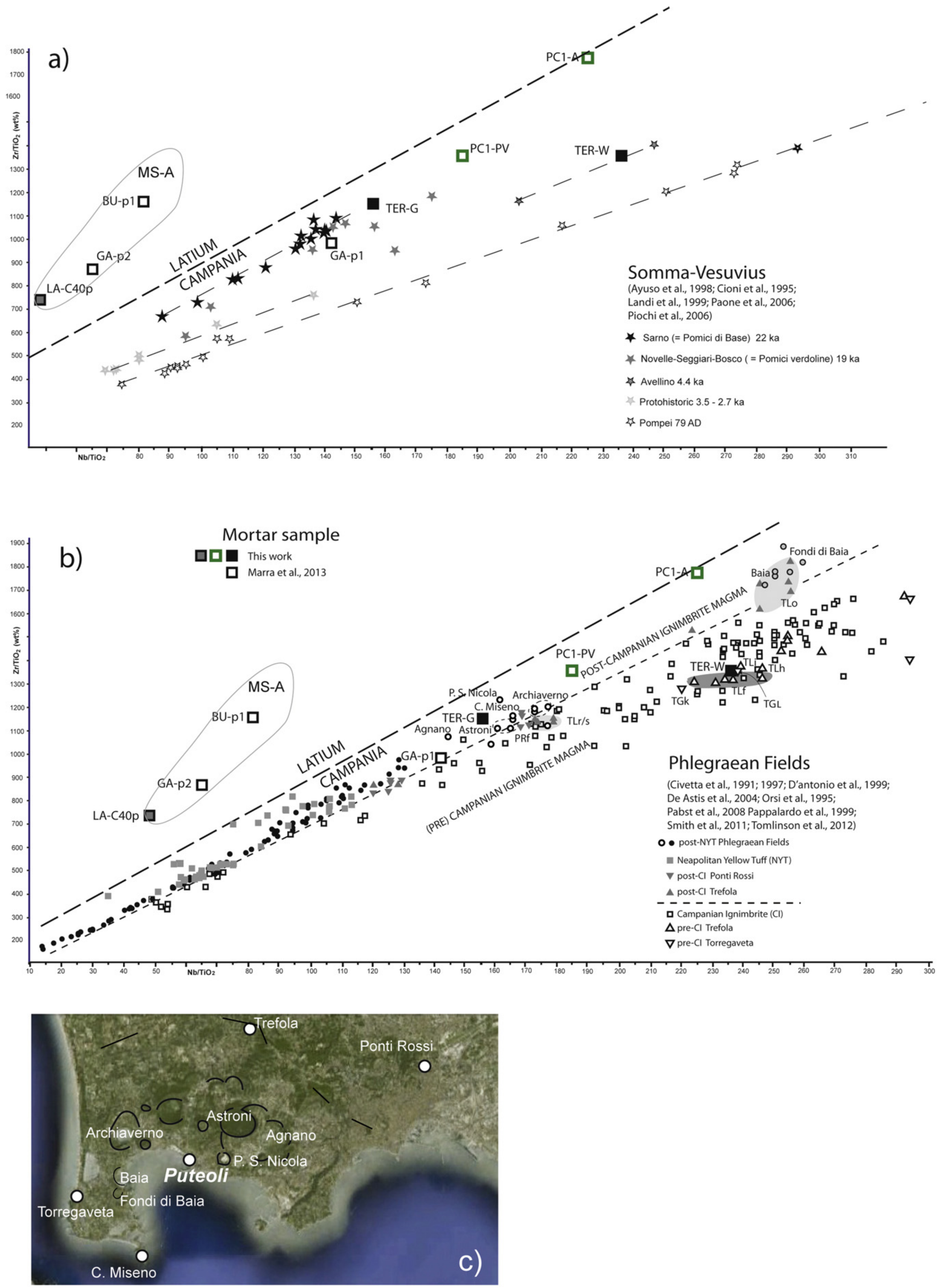
Based on the abovementioned considerations, in our opinion, when Vitruvius says "the *harenae fossiciae* are these", he wants to include in the four categories all the materials that were systematically exploited to produce fine aggregate for the mortars in the region that he refers as their sourcing area, at least since the IInd century BC. Therefore, the types *rubra*, *nigra*, *cana* and *carbunculus* have to comprise the different kinds of granular volcanic ash (pozzolan) that occurred in Tuscany and Latium, and, as discussed ahead, in Campania.

In contrast to this interpretation, Lugli (1957) thinks that the treatment of the quarry sands excluded the pozzolans of the Rome's area, and he argues that these were not exploited in the times when Vitruvius wrote his *De Architectura* and, also according to Curtis (1923), that the Roman builders employed pozzolan imported from the Phlegrean Fields in the mortars. However, data presented in this paper (Fig. 3g, h, l) demonstrate that Lugli is wrong: the Pozzolane Rosse volcanic ash was extensively employed as fine aggregate in the Roman mortars since the IInd century B.C., whereas there is no evidence of employment of any type of Campanian volcanic rocks in the buildings of Rome until the construction of Forum of Caesar (46–44 B.C.) (Marra et al., 2013).

8.6.1. Mortars from Etruria: carbunculus

Ancient Etruria corresponded for its most part to modern Tuscany and Northern Latium, a region comprehending the volcanic districts of Vulsini, Vico and Monti Sabatini, which, along with the Alban Hills and he Ernici districts in southern Latium, constitute the Roman Magmatic Province (Conticelli and Peccerillo, 1992; Fig. 1). Vitruvius makes explicit reference to Etruria as a source area of a particular *harena fossicia* that he calls "*carbunculus*" (= little piece of charcoal). The identification of this kind of *harena* with a local volcanic product has been widely debated (e.g. Jackson et al., 2006, and references therein), and in our opinion there is no doubt that the term *harena fossicia* of Vitruvius has to be considered a synonymous of the modern term pozzolan. In particular Lugli

Fig. 7. Zr/TiO_2 vs $Nb//TiO_2$ individual compositions of selected volcanic products of the Somma–Vesuvius (a) and Phlegraean Fields (b) districts (plotted after data in the reported literature) and compositional fields of the products of the Monti Sabatini district (MS-A), to compare compositions of the analyzed mortar samples. See text for explanations. c) Location map of the eruptive centers of the Phlegraean Fields.



a)
PC1-A
PC1-PV
TER-W
MS-A
BU-p1
TER-G
GA-p2
GA-p1
LATIUM
CAMPANIA
LA-C40p
Zr/TiO2 (wt%)
Nb/TiO2
Somma-Vesuvius
(Ayuso et al., 1998; Cioni et al., 1995; Landi et al., 1999; Paone et al., 2006; Piochi et al., 2006)
Sarno (= Pomici di Base) 22 ka
Novelle-Seggiari-Bosco (= Pomici verdoline) 19 ka
Avellino 4.4 ka
Protohistoric 3.5 - 2.7 ka
Pompei 79 AD
b)
Mortar sample
This work
Marra et al., 2013
Fondi di Baia
Baia
TLo
POST-CAMPANIAN IGNIMBRITE MAGMA
(PRE) CAMPANIAN IGNIMBRITE MAGMA
TER-W
TLh
TLf
P. S. Nicola
Archiaverno
C. Miseno
Agnano
Astroni
TLr/s
Phlegraean Fields
(Civetta et al., 1991; 1997; D'antonio et al., 1999; De Astis et al., 2004; Orsi et al., 1995; Pabst et al., 2008 Pappalardo et al., 1999; Smith et al., 2011; Tomlinson et al., 2012)
post-NYT Phlegraean Fields
Neapolitan Yellow Tuff (NYT)
post-CI Ponti Rossi
post-CI Trefola
Campanian Ignimbrite (CI)
pre-CI Trefola
pre-CI Torregaveta
c)
Trefola
Ponti Rossi
Astroni
Archiaverno
Agnano
P. S. Nicola
Puteoli
Baia
Fondi di Baia
Torregaveta
C. Miseno

(1957), in accordance with Blake (1947) who identifies the *carbunculus* with the "dry, porous black pozzolana which is still in use in the region of Viterbo", correlates it to the pyroclastic deposits of the Tufo Grigio Vicano (a local name to indicate the unlithified facies of "Tufo Rosso a Scorie Nere Vicano") (Fig. 1a), and points out the similarity between the black scoriae of this volcanic deposit and the charcoal, which probably induce Vitruvius (2.6.6) to think that this material is the product deriving from the burning of the matter: "(…) Therefore, where the mountains are not earthy but consist of soft stone, passing through the fissures in the stone, sets it afire. The soft and delicate part is burned out, while the hard part is left. And thus, just in Campania scorched earth becomes ash, so in Etruria the cocked matter becomes charcoal (…)".

However, also the loose pyroclastic-flow deposits of the Ronciglione Formation (Vico Ignimbrite B, Fig. 3c) and the smaller Carbognano Formation from Vico (Perini et al., 2004) are characterized by the presence of black scoriae, and may be regarded as potential equivalent of the *carbunculus*. Moreover, the unlithified, pozzolanic *facies* of the Tufo Rosso a Scorie Nere (Fig. 3e), erupted 450 ka by the Monti Sabatini volcanic district and cropping out to the north of Rome (Karner et al., 2001), displays identical texture as the Tufo Grigio Vicano (Fig. 3d) (Alvarez et al., 1975), with which it was commonly mistaken in the literature. In particular, as noted by Frank (1924), "the scoriae-filled ash found near Grottarossa a few miles beyond the Mulvian bridge" fits the description and the area of occurrence that Vitruvius gives for the *carbunculus*. Also the lithified facies of the Tufo Grigio Vicano is identical to that of its equivalent from Monti Sabatini and it is known in the literature as Tufo Rosso a Scorie Nere Vicano. However, it has a different eruption age at 150 ± 4 ka (Laurenzi and Villa, 1987); besides several other informal names, including Vico Ignimbrite C (Cioni et al., 1987), it is designated by the formal name of "Sutri Formation" (Perini et al., 2004).

Despite that the Sutri amphitheater is entirely dug into the lithified facies of the Sutri Formation (Tufo Rosso a Scorie Nere Vicano), Zr/TiO_2 vs. Nb/TiO_2 signature and mineralogic assemblage (without leucite and with characteristic plagioclase) of the black scoriae of the mortar aggregate sampled from a dividing wall at the entrance room (Fig. 3a) indicate provenance from the deposit of the Ronciglione Formation, which also extensively crops out in the area around Sutri, to the south of Vico volcano (Fig. 1).

In contrast, Zr/TiO_2 vs. Nb/TiO_2 composition of one large black scoria collected in the IV century AD mortar of Villa di Livia analyzed in the present study (Fig. 3b) matches that of the sabatinian Tufo Rosso a Scorie Nere pyroclastic-flow deposit (TRaSN), whose unlithified, pozzolanic facies crops out in Grottarossa, few km south of Prima Porta.

These data confirm that these black pozzolanic materials, representing the most widespread, loose scoriaceous deposits occurring at the Monti Sabatini and Vico volcanic districts, were exploited in Etruria and it is likely that they were called *carbunculus*, independent from the different volcanic units of provenance, which the Roman builders couldn't be aware of. Evidently, the exploited formation was the one cropping out in the area of the construction site, as the employment of TRaSN from the Monti Sabatini in Prima Porta shows. It is therefore evident that Vitruvius uses this word to refer to this type of *harena fossicia* largely employed in southern Etruria.

In contrast, in the northern towns of Vulci and Volsinii are employed the local products of the Latera activity at the Vulsini district, as attested by Zr/TiO_2 vs. Nb/TiO_2 composition of the aggregates analyzed in the present study. These aggregates are all characterized by a light gray color (Fig. 1) and, in our opinion, represent perfect examples of *harena cana*, as also discussed below.

8.6.2. Harenae cana, rubra and nigra

The identification of the *harena cana* with the ash-gray type aggregate of the mortars of the Republican Age (Van Deman, 1912a,b), in which the fine aggregate was supposed to consist of volcaniclastic sand of the sedimentary formations that crop out on the flanks of the Capitoline Hill (Jackscon et al., 2007, 2010a), is to be rejected, for a number of reasons that are illustrated hereby.

First of all for methodological reasons, since Vitruvius refers to the quality (in this case the color) of the material that is used as the fine aggregate, while Van Deman and Jackson et al. attribute the color of the resulting mortar (aggregate + lime) to the *harena*. Indeed, most of the Republican Age mortars, despite the grayish appearance resulting from an abundant fraction of lime, were made with Pozzolane Rosse aggregate (Marra et al., 2014). Moreover, the sedimentary successions cropping out at the Capitoline Hill (Valle Giulia, San Paolo and Aurelia Formations; Karner and Marra, 1998; Corazza et al., 2004) consist mainly of clays and silty sands, and the volcaniclastic fraction has undergone the process of erosion, transport and fluvial re-deposition, which caused argillification of the vitreous component, therefore it has an "earthy" aspect and does not show anymore the characteristics that the best *harenae fossiciae* must have (i.e.: screeching, roughness, cleanness) according to *Vitruvius*.

Based on the considerations above, we are likely to exclude that sedimentary deposits, even rich in the volcanoclastic component, though occasionally mixed in the fine aggregate of the mortars (e.g., in the IInd century B.C. Temple of Concordia, Marra et al., 2014, or in some mortars of Forum of Caesar, Bianchi et al., 2009), can be included among the *harenae fossiciae* and, in particular, in the category which Vitruvius calls "*cana*". In our opinion Vitruvius' attribute of *harena fossicia* is reserved to true volcanic deposits only.

Van Deman (1912 a–b) identified Vitruvius' *harena rubra* with the clean red pozzolana observed in the mortars of Forum of Caesar, and that was used during the Augustan through the Trajanic age, to produce extremely hard mortars. More recently, Jackson et al. (2007) have shown that petrographic features at the optical microscope of the mix of prevalently reddish, and subordinately black, granular ash and scoriae (Fig. 3k–l) employed in several monuments of the Imperial Age corresponds to the scoriae of the Alban Hill's ignimbritic eruption known as "Pozzolane Rosse" (456 ± 3 ka; Karner et al., 2001; Marra et al., 2009; Freda et al., 2011). The reddish scoriae are characteristic of the mid-upper portion of the deposit ("intermediate alteration facies"), while the black ones of the lowest portion (least alteration facies; Jackson et al., 2007). Following Van Deman's inference based on the analyses of the mortars from a restricted number of monuments of Republican Age (i.e. Porticus Aemilia, Temple of Concord, Temple of Castor and Pollux, Forum of Caesar), petrographic analyses by Jackson et al. (2010a) have suggested that the "Pozzolane Rosse" aggregate was introduced only around the mid Ist century B.C. in the concretes of Forum of Caesar (46–44 BC).

In contrast with this assumption, the study of the mortars from Temple B and several other structures of the Area Sacra di Largo Argentina (Marra et al., 2015), along with a revision of the attribution of the aggregate employed in the mortar of the Temple of Castor and Pollux (Marra et al., 2015, and this work) evidence that the Pozzolane Rosse aggregate was in use since the IInd century B.C. (Fig. 3g–h, l). Therefore, there can be no doubt that *Vitruvius* must have known the "Pozzolane Rosse" volcanic ash very well, and that in describing the *rubra* and *nigra* types among the best *harena fossiciae* he refers to those that are typical of this volcanic deposit.

It should be noted, however, that the scoriae of the other two large pyroclastic-flow deposits occurring in the sub-surface of Rome ("Pozzolane Nere" and "Pozzolanelle", Karner et al., 2001; Marra et al., 2009) range in color from black to gray and from brown to orange (Fig. 3m, n, o). Whereas the use of Pozzolane Rosse was almost ubiquitous during the Republican Age, as the extensive presence of exploitation tunnels ("*arenari*") within the city of Rome testifies, both these alternative deposits have been recognized in isolated cases (Marra et al., 2015). Therefore, the terms *rubra* and *nigra* by *Vitruvius* would include all the colors that are characteristic of the three

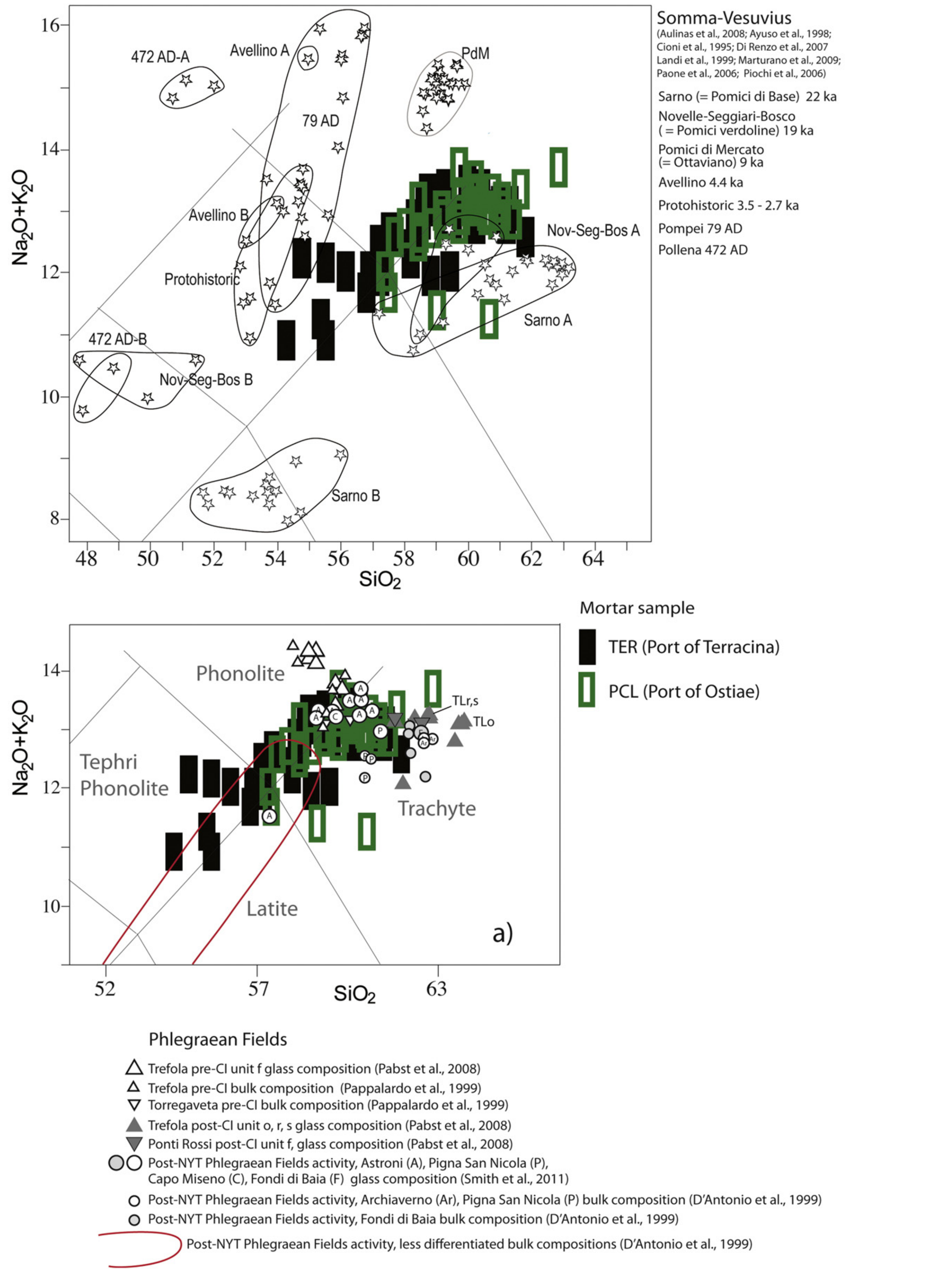


Fig. 8. TAS bulk and EMP glass individual compositions of selected products of the Somma–Vesuvius (a) and Phlegraean Fields (b) districts (plotted after data in the reported literature), to compare EMP glass compositions of pumice and shards occurring in thin section of the sampled mortar samples TER and PCL, analyzed in the present work. See text for explanations.

pozzolanaceous deposits erupted by the Alban Hills volcanic district, and the Latin author may as well be referring to all the Roman pozzolans by these two types. More in general, when also the gray color of the Etruscan mortar aggregates from Vulci and Volsinii (Fig. 2a′–c′, d″f″), as well as that of the Campanian pumice occurring in PC1-A, PC1-PV, and TER-G aggregates (Fig. 4a″–a‴, b″) is considered, it seems evident that the types *cana*, *rubra* and *nigra* may encompass the complete range of pozzolan deposits occurring in Tuscany, Latium and Campania. However, according to Vitruvius, the gray pumices occurring in the aggregate of the mortars of the ports of Claudius and Anxur should be included in the category he calls *pulvis*, rather than among the *harenae canae*, introducing an apparent contradiction as discussed in the following paragraph.

A second contradiction in the terminology used by Vitruvius to describe the *harenae fossiciae* is represented by the superposition between *carbunculus* and *harena nigra*: it may be explained by the different average granulometry that characterizes the coarser and more vesicular pyroclastic deposits of the Vican and Sabatinian incoherent facies of Tufo Rosso a Scorie Nere, with respect to the smaller size and higher density of the black scoriae of Pozzolane Rosse and Pozzolane Nere, combined with the likely use of the term *carbunculus* derived by the aspect of the local black pozzolan exploited in northern Latium.

8.6.3. Pulvis

The *pulvis* coming from the region including the gulf of *Puteoli* (Pozzuoli) and the bay of Naples, whose extraordinary attitude to produce mortars that have the capability to set under water is described by *Vitruvius*, has been broadly identified with the local pozzolan (e.g.: Oleson et al., 2004 and references therein); however, from a lithologic point of view, the Campanian pozzolan is indistinguishable from that occurring in Latium. This type of volcanic deposit is originated from highly explosive eruptions and is emplaced as airfall or density current pyroclastic-flow deposits. It is constituted by a loose to faintly coherent aggregate of granular solidified magma, ranging in size from ash, lapilli, and bomb and blocks (sub-millimeter to decimeters in diameter). Other components of the pyroclastic deposits are loose, mm-sized minerals, and mm- to dm-sized lithic inclusions, deriving from rock fragments of the substrate, which may be volcanic (tuff, lava, and holocrystalline lithics), as well as sedimentary ones. Based on the more or less vesicular texture (deriving from the bubble of gas entrained in the magma), the juvenile magmatic components are defined pumice or scoria, respectively. This is a qualitative distinction, which may be regarded as a subjective one; however, the lightweight pumice floats on water, as opposite to the denser scoria. Unless determining the mineralogical assemblage and the geochemical composition, which in Roman times was not possible to do, the pyroclastic products of Central Italy cannot be distinguished, if not based on their general aspect and color. In fact, such are the criteria that Vitruvius uses to classify them. It is therefore unclear why *Vitruvius* should use a different term to describe the pozzolan from Campania (*pulvis*) with respect to that of Etruria (*harena*), since he also recognizes the same "volcanic" origin for these materials: (…) And thus, just in Campania scorched earth becomes ash, so in Etruria the cocked matter becomes charcoal. Both of these are outstanding for constructions, but one works in buildings on land, while the other works as well for sea moles (…) (2.6.6) (cfr. Lugli, 1957; Jackson et al., 2006).

In the first analysis, it may be inferred that the material called powder (*pulvis*; cfr. *TLL*, X, 2, XVII) must have shown finer in size with respect to that called sand (*harena*). However, either in the whole mortar before separation of the aggregate, as well as in the clastic fraction resulting after HCl bathing, the grain size of the aggregate of the samples collected at the ports of Claudius and Anxur results quite a coarse one, even coarser with respect to several aggregates of mortars from terrestrial masonry structure sampled in Etruria (see Fig. 2) and in Rome (Fig. 3). Although a larger number of maritime mortars need to be investigated in order to validate this observation statistically, the results of the present study suggest that the distinction based on the grain size should be rejected.

In order to understand the reason of using the term *pulvis* for the pyroclastic deposits of Campania, in our opinion, it is fundamental that the following section of *De Architectura*, in which Vitruvius attributes the particular properties of the *pulvis* to the fact that (…) under these mountains (those surrounding the Vesuvius) are boiling earths and plentiful springs. These would not exist unless deep beneath there were huge fires, blazing with sulfur or alum or pitch. Therefore these interior fires and the vapor of their flames seep through veins in the ground and make this earth light (*Igitur penitus ignis et flammae uapor per interuenias permanans et ardens efficit levem eam terram*), and the tufa created there has risen up without any component of moisture (…) (2.6.1).

The adjective "*levem*" translates as "light" (cfr. *TLL*, VIII, 2) and might be intended by *Vitruvius* to describe the whitish to light gray, high vesicular pumice clasts that constitute most portion of the Campanian pyroclastic deposits (Fig. 4), as opposed to the denser, heavier scoriae that characterize the pyroclastic deposits of Vulsini, Vico, Monti Sabatini and Alban Hills districts (Figs. 2, 3). In fact, it is possible that Vitruvius considered the *pulvis* one particular, lightweight *harena fossicia*.

It remains to be established whether Vitruvius was aware that the thin pumice layers occurring in the sub-surface of Rome (Fall A of Tufi Terrosi con Pomici Bianche, Marra et al., 2015) were selectively exploited in Rome and mixed with Pozzolane Rosse scoriae since the IInd century BC, as evidenced by the mortar of the podium of Temple B in the area sacra of Largo Argentina (Marra et al., 2015). The selective use of pumice has been evidenced here to occur also in the mortar of the IInd century BC vaults of the *tabernae* in Vulsini, where it was exploited from the local fallout deposit of the Farnese formation, showing that this was a consolidated technique to realize vault concretes, in act in different regions of Italy already during the Republican Age. A possible answer is that *Vitruvius* considered the Roman pumice along with that from northern Latium as *harena cana*, while he might have referred to as *pulvis* the white, microvesicular pumice type of samples PC2 and TER-W (Fig. 4a′, b′).

Indeed, the term "powder" seems to apply better to these peculiar, white, brittle pumice clasts occurring in both the maritime mortars analyzed for this work, which are characterized by microvesicular texture conferring to them a powdery crumbliness. Geochemical data for sample TER-W have attested its provenance from a pumice fallout deposit occurring at the modern quarry of Trefola (Trefola unit f, Pappalardo et al., 1999), in the Phlegraean Fields. Despite *Vitruvius* refers to the *pulvis* as the specific aggregate to realize concrete for maritime structures, the Trefola pumices represent a minority portion of the aggregate of the investigated mortars, which is constituted of typical gray, vesicular pumice for its most portion (e.g. Fig. 4a″–a‴), or either denser scoriae (TER-G, Figure b″). A possible explanation may be that this peculiar pumice was originally the material employed in *Puteoli* to produce mortar for maritime structures, and that it was only in subsequent times integrated with other pumices from the widespread outcrops of the Phlegrean Fields, with aspect similar to those Vitruvius would have included in the *harena cana* type.

Indeed, it is clear that a large variety of Campanian pumices has been successfully employed to build the ports of the Tyrrhenian Sea, and that any other type of pumice from other volcanic regions would have fit the purpose. Therefore, the selective use of Campanian pumice in the harbors overall the central Tyrrhenian Sea coasts (Marra and D'Ambrosio, 2013; this work) in our opinion is due to a series of logistic, economic, industrial and historical reasons:

i: the large occurrence of pumice deposits in the inland of *Puteoli*, where since the beginning of the second century BC an important harbor system conveying the increasing traffic of the goods coming from the eastern Mediterranean region (mainly wheat) was created (Pomey and Tchernia, 1980–81; Zevi, 1994);

ii: it is very likely that the development of the technical expertise in the construction of maritime structures was facilitated here by the availability of this volcanic material, which is characterized by hydraulic properties;

iii: the Port of *Puteoli* soon became the most important harbor of the Mediterranean Region, from which a large variety of products were shipped worldwide;

iv: these factors probably allowed *Puteoli* to become the reference town for the technical expertise and the workmanship on harbor concrete masonry, developing a sort of monopoly on the production and the exportation of the materials for maritime construction.

9. Conclusions

The results of the present study show that the local incoherent volcanic materials (pozzolan) erupted during the Pleistocene activity of the volcanic districts of the Roman Magmatic Region, comprehending that Tuscany, Latium and Campania, were selectively exploited in these regions of Central Italy and employed to produce the aggregate for concretes and mortars.

In particular, the mortars from the ancient Etruscan towns of Vulci and Vulsinii novi investigated in this work were realized with the products erupted by the Vulsini volcanic district (e.g.: Onano, Sovana, Sorano, Farnese Formations, Conticelli et al., 1987), as evidenced by the Zr/Y vs Nb/Y and Zr/TiO_2 vs Nb/TiO_2 compositions of the aggregates. Among these products, it seems relevant the identification of the Onano pyroclastic-flow deposit in one mortar from a II–I century BC building in Vulci, which was already recognized (Marra and D'Ambrosio, 2013) as the source of the pozzolan transported by a Roman ship wrecked in the ancient port of Pisa. This fact suggests the continued and systematic exploitation of this volcanic deposit cropping out in the region drained by the River Fiora, and its exportation via the fluvial and maritime routes throughout the Tyrrhenian Sea.

A second relevant finding is the fact that the aggregate for the concrete of the vaults of the tabernae associated with the IInd c BC House of Ninfeo is entirely realized with pumice, a technique to produce lightweight concrete that in Rome has been observed at the Forum of Caesar (46–44 BC) in conjunction with the introduction of a particular vesicular lava imported from Pompei (Lancaster et al., 2010; Marra et al., 2013). The use of pumice at Volsinii pre-dates that in Rome and cast light on the high specialized masonry technique achieved by Roman constructors since the IInd c. BC.

In Sutri, and at the more southern location of Prima Porta, instead, the aggregate of the investigated mortars is realized with the local pyroclastic-flow deposits of the Ronciglione Formation (Perini et al., 2004) and the sabatinian Tufo Rosso a Scorie Nere (Marra et al., 2014), respectively.

In Rome, the petrographic observation in the thin sections of the IInd c BC mortars from the Temple of Castor and Pollux and from Largo Argentina, as well as the trace-element signature of the IInd c. AD aggregate of the mortars from the Forum of Trajan, have confirmed the continuative and selective use of the red and black scoriae of the local Pozzolane Rosse pyroclastic-flow deposit (Marra et al., 2009; Jackson et al., 2010) to produce the aggregate for mortars and concretes, already reported in Marra et al. (2015).

Finally, a systematic and selective use of pumice coming from the volcanic districts of the Phlegrean Fields, with a particular type strictly matching Zr/TiO_2 vs Nb/TiO_2 and TAS glass compositions of the fallout deposit TLf (Pappalardo et al., 1999; Pabst et al., 2008) cropping out at the locality of Trefola, and a second type having a best match with those of the deposit of the Astroni center (D'Antonio et al., 1999; Smith et al., 2011), has been evidenced by the analyses on the mortar samples collected in the ports of Claudius and Terracina, located on the central–southern coast of Latium.

Based on all the observations described above, it is inferred that the three kinds of *harenae fossiciae* defined by Vitruvius as *rubra*, *nigra* and *cana* (red, black, grayish) are comprehensive of all the central–southern Italy's pozzolans, either the ones occurring in the Latium volcanic region and those in the Campanian region, which were extensively cultivated and used to realize masonry structures since the IIIrd century BC (Miriello et al., 2010; Marra et al., 2015). The pyroclastic-flow deposits emplaced in the volcanic districts of central Italy are indeed characterized by loose, granular ash beds, ranging in size from fine sand to gravel, and displaying various colors ranging from red to orange to brown, and from black to gray to white. In particular, the red and black colors are characteristics of the "Pozzolane Rosse" pyroclastic-flow deposit (Jackson et al., 2010a) that was selectively cultivated in Rome, while the gray color is prevailing among the pyroclastic products exploited in northern Latium. The fourth type that Vitruvius calls *carbunculus* is also to be identified with a volcanic material, and in particular with the loose facies of the pyroclastic-flow deposits cropping out in northern Latium, including the Tufo Rosso a Scorie Nere (also known with the formal name of Sutri Formation) and the Ronciglione Formation, erupted from the Vico volcano (Perini et al., 2004) around 150 ka (Cioni et al., 1993), and the Tufo Tosso a Scorie Nere Sabatino (TRaSNS), erupted by the Monti Sabatini volcanic district 450 ka (Karner et al., 2001a; Marra et al., 2014). According to inferences by Lugli (1957) and Frank (1939), the occurrence of large, vesicular, black, charcoal-looking scoriae, whose trace element compositions were determined in the present study in mortars collected at the Sutri amphitheater and at Villa di Livia in Prima Porta north of Rome match those of the Ronciglione Formation and of the TRaSNS, respectively, confirms that the term *carbunculus* should be interpreted to reflect the aspect of the volcanic material that was exploited in the area north of Rome.

Finally, the material that Vitruvius calls *pulvis* and that he says "is found in the neighborhoods of Baiae," (in the Gulf of Pozzuoli, the modern *Puteoli*) "and in the lands of the municipalities around Mount Vesuvius" (Vitr.2.6.1), corresponds to the pumiceous deposits erupted by the activity of the Phlegraean Fields and cropping out in the inland of the port of *Puteoli*, as evidenced by the trace-element signature of the mortar aggregates analyzed in this work. In our opinion, the different term Vitruvius uses for this material, *pulvis*, despite the identical volcanic origin with respect to the other pyroclastic deposits that he calls *harenae*, is due to the highly vesicular, lightweight nature of this volcanic material, as opposite to denser scoriae which constitute the pozzolan deposits, according to the adjective *levem* (light) that he uses to describe it. In particular, the crumbly, powdery aspect of one peculiar type of pumice that occurs in both the investigated harbor mortars may be at the origin of the word *pulvis* that Vitruvius uses to describe the material employed to produce mortar for maritime structure.

However, the systematic employment of different types of pumice exploited in the Phlegraean Fields to produce hydraulic mortars for all the Roman ports, rather than to the distinctive mechanical and physical properties of these volcanic products with respect to those of the other volcanic districts of central Italy, is to be attributed to the large occurrence in the vicinity of one of the earliest, most important harbors of the Mediterranean Sea. This fact is likely at the base of the development of the constructive technique of maritime structures and the selection of the materials, providing *Puteoli* with a monopoly in this field.

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