archaeometry

Archaeometry **58**, 2 (2016) 177–200 doi: 10.1111/arcm.12154

PETROCHEMICAL IDENTIFICATION AND INSIGHTS ON CHRONOLOGICAL EMPLOYMENT OF THE VOLCANIC AGGREGATES USED IN ANCIENT ROMAN MORTARS*

F. MARRA†

Istituto Nazionale di Geofisica e Vulcanologia, Via di Vigna Murata 605, 00143 Rome, Italy

E. D'AMBROSIO

Via Cupa 5, 00048 Nettuno, Rome, Italy

M. GAETA

Dipartimento di Scienze della Terra, Sapienza—Università di Roma, Piazzale Aldo Moro 5, 00185 Rome, Italy

and M. MATTEI

Sovrintendenza Capitolina ai Beni Culturali, Via delle Tre Pile 3, 00186 Rome, Italy

Through the assistance of trace element and petrographic analyses on 14 samples of mortar aggregates from Roman monuments, including the Porticus Aemilia*, the Temple of Concordia, the Temple of the Dioscuri, Temple B and other structures of the Area Sacra di Largo Argentina, and the Villa di Livia, we establish the source area and we investigate the chronological employment of the volcanic materials used in ancient Rome's masonry. In contrast to previous inferences, the petrochemical data presented here show that systematic exploitation of the local 'Pozzolane Rosse' pyroclastic deposit has occurred since the early development of concrete masonry, at the beginning of the second century* BC*, through the early Imperial age. Subsequently, exploitation was extended to the overlying Pozzolane Nere and Pozzolanelle deposits. Only during the early phase of development of the concrete masonry in Rome, volcaniclastic sediments outcropping near the construction sites were mixed with the sieved remains of the tuff employed as the coarse aggregate, to produce the fine aggregate. The results of the study on the investigated monuments suggest the possibility of establishing the chronological identification of three different types of mortars, as a function of the composition of the volcanic material employed in the fine aggregate, which, when implemented by future studies, may contribute to the dating of monuments and archaeological structures.*

KEYWORDS: ANCIENT ROMAN MORTARS, ROMAN MASONRY, MATERIAL PROVENANCE, VOLCANIC ROCKS, TRACE ELEMENT ANALYSES, GEOLOGY OF ROME

INTRODUCTION

Since the beginning of the 20th century, a number of scholars (e.g., Van Deman 1912; Curtis 1913; Frank 1924; Blake 1947; Lugli 1957; Chiari *et al*. 1992; Oleson *et al*. 2004; Lancaster 2005; Jackson *et al*. 2006, 2007, 2010; Miriello *et al*. 2010) have agreed that the *harenae*

---

*Received 20 May 2014; accepted 8 July 2014

†Corresponding author: email fabrizio.marra@ingv.it

fossiciae (quarry sands), described as the best aggregate for mortars by the first-century BC Roman architect Vitruvius in Book II of *De architectura* (1997), are to be identified with the loose ash and scoria pyroclastic deposits (pozzolan) erupted by the volcanic districts of central Italy, which outcrop extensively in Tuscany, Latium and Campania (see Fig. S1). According to Curtis (1913), who argued that it would have been easier to bring this material by ship from the harbours of Campania rather than exploit the local pozzolan and transport it across the inland terrain, many historians and archaeologists have thought that the concretes in Rome during the Republican age were realized using pozzolan imported from the Phlegraean Fields (e.g., Lugli 1957), while recent studies (Jackson *et al*. 2007, 2010) have identified the presence of the local pozzolan (Pozzolane Rosse pyroclastic-flow deposits) only in the mortars of several Imperial-age buildings. However, the lithified pyroclastic-flow deposits (tuffs) outcropping in Rome and in its surroundings (Fig. 1; see also Table 1) have been exploited intensively since early human settlement to produce building stones. Similarly, in the present work we demonstrate that the local incoherent, pyroclastic-flow deposits (pozzolan) have also been mixed with lime, along with the rubble stone derived from the cutting of the lithified tuffs, to produce mortar and concrete since the development of concrete masonry in the early second century BC. An up-to-date litho-chronostratigraphic scheme of these volcanic products, along with the description of their use in ancient Roman masonry and the related archaeological names, is provided in Table 1.

With the aim of identifying the provenance of the volcanic aggregates, we have performed geochemical analyses on 12 samples of mortars and concretes from several Roman monuments (Table 2), spanning from the second century BC through to the third century AD, to compare their Zr/Y versus Nb/Y and Th/Ta versus Nb/Zr compositions with those of the volcanic products of central Italy that have been published in the recent literature (Marra *et al*. 2011, 2013; Marra and D'Ambrosio 2013). Moreover, in order to clarify some uncertain attributions, we introduce an alternative classification diagram using TiO_2 abundance instead of Y, since the latter element has revealed a greater mobility with respect to Zr and Nb, in the case of strong alteration affecting the analysed samples, such as that induced by bathing in HCl, which is mandatory in order to separate the volcanic aggregate of the analysed mortar samples from the lime matrix (see the Methods section). Indeed, the present study is focused on the identification of the volcanic material employed in the mortar aggregate; therefore, we do not investigate the physical and mechanical characteristics of the mortars, nor the chemical properties of the binder component, which is destroyed during aggregate separation.

METHODS

Sample preparation

Fourteen samples of bedding mortar were collected from original concrete masonry structures (walls, podiums etc.) of the Roman epoch (Table 2), under the supervision of the archaeologists of the Soprintendenza Speciale per i Beni Archeologici di Roma and of the Sovrintendenza Capitolina ai Beni Culturali, who were in charge of the different monuments. Thin sections of each mortar sample were then prepared for preliminary petrographic observations at the optical microscope. Subsequently, the clastic component employed as the aggregate in 12 of these samples (Table 2 (a)) was separated from the lime manually (whenever possible), or by bathing the samples in hydrochloric acid (HCl) for 4–5 days. 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 ratios are used to classify the materials (i.e., Zr,

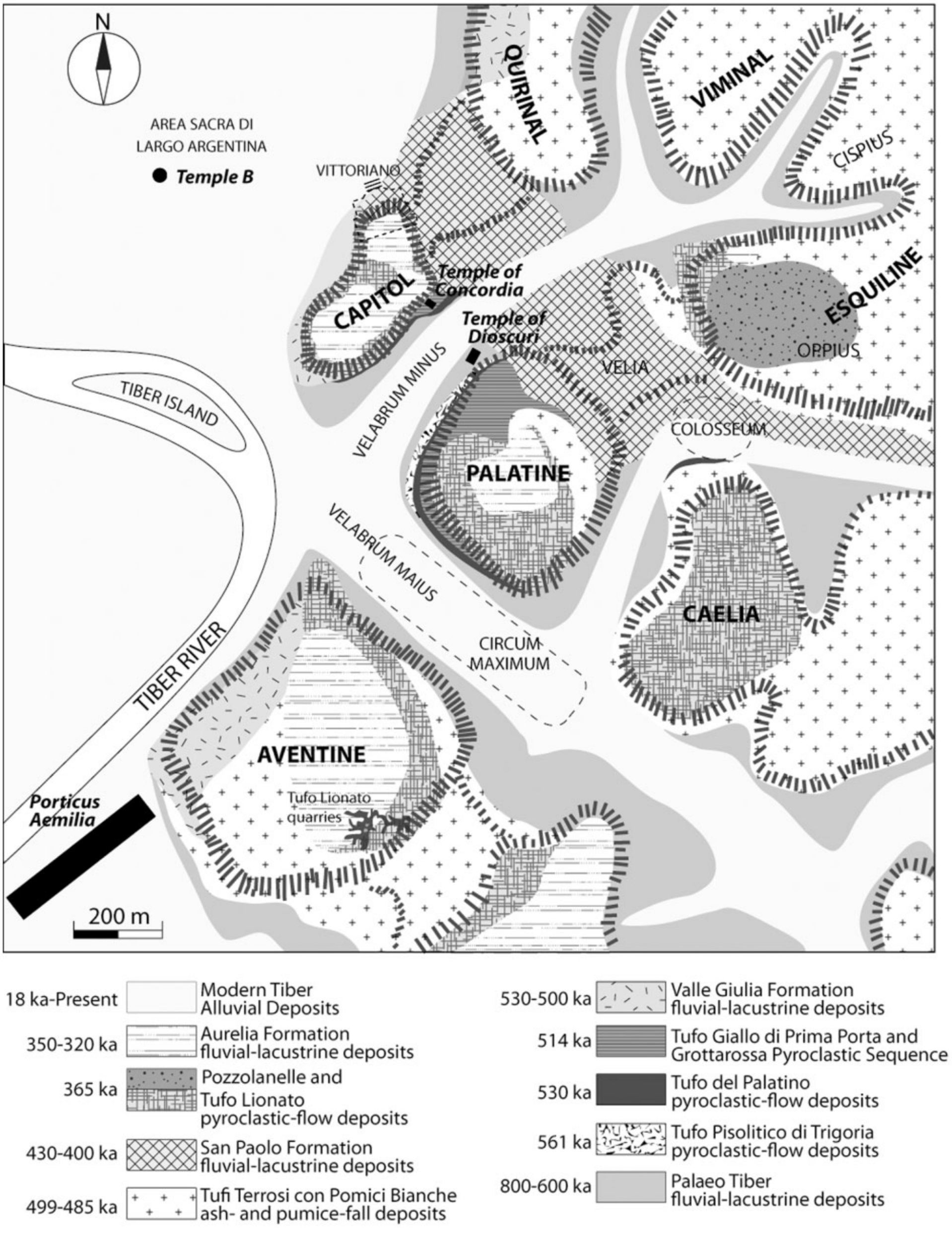

Figure 1 *A geomorphological map of ancient Rome (modified from Marra and Rosa 1995), showing the famous Seven Hills, which represent the remnants of a volcanic plateau (Heiken* et al. *2005) eroded by the Tiber River and its tributaries during the middle-to-late Pleistocene periods of sea-level fall (Alvarez* et al. *1996): chronostratigraphy after Karner and Marra (1998), Marra* et al. *(2014) and Marra and Florindo (2014). The locations of the monuments investigated in the present study are also shown.*

Table 1 *The litho-stratigraphic scheme*

AGE[4] (ka)	MONTI SABATINI VOLCANIC DISTRICT eruptive units [4]	ARCHAEOLOGICAL NAME	USE (AGE OF EARLIEST DOCUMENTED EMPLOYEMENT)	ARCHAEOLOGICAL NAME	ALBAN HILLS VOLCANIC DISTRICT eruptive units[5]	AGE[5] (ka)
					ALBANO CRATER Scond hydromagmatic cycle	
			Dimension stone (III c BCE)[1]	*Lapis Albanus*	**Peperino Albano pyroclastic-flow deposit**	36
						41
					ALBANO CRATER First hydromagmatic cycle	69
86						
	HYDROMAGMATIC ACTIVITY					
170					NEMI CRATER Hydromagmatic activity	150
					ARICCIA CRATER Hydromagmatic activity	203
249	TUFO DI PIZZO PRATO pyroclastic-flow deposit				FAETE PHASE scoria cone deposits, lava-flow deposits:	252
286	TUFO GIALLO DI SACROFANO pyroclastic-flow deposit		Paving slabs, coarse aggregate (IV c BCE)[1]		**Capo di Bove leucititic lava**	280
					hydromagmatic surge deposits:	
310	MAGLIANO ROMANO pumice-fall deposit		Dimension stone (III c BCE)[1]	*Lapis Gabinus*	**Castiglione Crater (Gabi)**	285 310
316	TUFO DI BRACCIANO pyroclastic-flow deposit					
			Only in XXth century restorations[3]	*Sperone*	TUSCOLANO-ARTEMISIO scoria cone deposits	368-353
			Fine aggregate (early II c BCE)[3]		**POZZOLANELLE pyroclastic-flow deposit**	368
			Dimension stone (III c BCE),[1] coarse aggregate	*Tufo dell'Aniene, Tufo di Monteverde*	**TUFO LIONATO pyroclastic-flow deposit**	

390	SAN ABBONDIO ash-fall succession		
447	FALL F pumice-fall deposit		
450	FALL E pumice-fall deposit		
451	**TUFO ROSSO A SCORIE NERE** **pyroclastic-flow deposit**	*Tufo di Fidene*	Dimension stone (IV c BCE)(1)
	FALL D pumice-fall deposit		
	FALL C pumice-fall deposit		
485	FALL B pumice-fall deposit		
499	**FALL A pumice-fall deposit**		Fine aggregate (II c BCE)(3)
	GROTTAROSSA PYROCLASTIC SEQUENCE **pyroclastic-flow deposit**	*Cappellaccio*	Dimension stone (VII c BCE),(2) Fine aggregate (II c BCE) (3)
517	TUFO GIALLO DI PRIMA PORTA pyroclastic-flow deposit		Fine aggregate (II c BCE)(3)
546	**TUFO GIALLO DELLA VIA TIBERINA** **pyroclastic-flow deposit**	*Tufo di Grottaoscura*	Dimension stone (IV c BCE),(1) coarse aggregate
	FAD3 pumice-fall deposit		
565	FAD2 pumice-fall deposit		
589	FAD1 pumice-fall deposit TUFO GIALLO DI CASTELNUOVO DI PORTO pyroclastic-flow deposit		

Fine aggregate (I c CE) (3)		**POZZOLANE NERE** **pyroclastic-flow deposit**	409
Fine aggregate (late II c BCE)(3)		**POZZOLANE ROSSE** **pyroclastic-flow deposit**	530
Paving slabs, coarse aggregate(?)(1)		VALLERANO lava-flow deposit	533
		CAVE ash-fall succession	503 520
		TUFO DI ACQUE ALBULE pyroclastic-flow deposit	530
Dimension stone (VII c BCE),(1) coarse aggregate	*Cappellaccio*	**TUFO DEL PALATINO** **pyroclastic-flow deposit**	533
		TUFO PISOLITICO DI TRIGORIA pyroclastic-flow deposit	565
		TUFO DI FOSSO COLLERASO pyroclastic-flow deposit	612

The age of the earliest documented employment of volcanic materials in Roman masonry is taken from (1) Lugli (1957), (2) Karner *et al*. (2001b) or (3) this work.

The chronostratigraphy of the Monti Sabatini and Alban Hills volcanic districts is taken from (4) Marra *et al*. (2014) and Sottili *et al*. (2010) or (5) Marra *et al*. (2003, 2009) and Freda *et al*. (2006).

Table 2 *(a) Mortar samples analysed in this work for trace elements (the full data is provided in the Appendix, as supplementary online material)*

Mortar sample	*Sampling site*	*Structure*	*Age*	*Separation*	*Sample composition*	*Whole aggregate composition*	*Group*
PAE	*Porticus Aemilia*	Wall	193 BC	HCl	TL	TL	A
TCO-1	Temple of Concordia	*Podium*	121 BC	M	PR	AU Fm + TL	A
TCO-2	Temple of Concordia	*Podium*	121 BC	M	TL/PL		
CAST	Temple of the Dioscuri	Wall	117 BC	M	TP	TP + TL	A
LA-C2	Largo Argentina Cell of Temple B	Foundation wall	Late second century BC	HCl	PR	PR	B
LA-C40P	Largo Argentina Temple B	*Podium*	Late second century BC	HCl	Fall A	PR + Fall A	B
LAC-15	Largo Argentina Temple B	Foundatio of *donario*	Early first century BC	M	PR	PR	B
LA-C10	Largo Argentina	Brick-faced wall	Late first century AD	HCl	PR	PR	B
LA-C29	Largo Argentina	Nucleus of brick-faced wall	Third century AD	M	PN	PR + PN	C
TPP	Torre di Prima Porta	*Opus incertum* wall	First century BC	HCl	GRPS	GRPS	B
LIV-R	Villa di Livia	*Opus raeticolatum* wall	*c.* 30 BC	HCl	GRPS	GRPS	B
LIV-L	Villa di Livia	Brick-faced wall	Second to third centuries AD	HCl	PL	PL	C

Abbreviations: LA, Area Sacra di Largo Argentina; TL, Tufo Lionato; AU Fm, Aurelia Formation; PR, Pozzolane Rosse; PN, Pozzolane Nere; PL, Pozzolanelle; TP, Tufo del Palatino; GRPS, Grottarossa Pyroclastic Sequence; HCl, separation through bathing in HCl; M, manual separation.

(b) Outcrop samples analysed in this work for trace elements (the full data is provided in the Appendix, as supplementary online material)

Rock sample	*Sampling site*	*Volcanic/sedimentary unit*
TPP-GRPS	Torre di Prima Porta	GRPS
GRPS-a	Prima Porta	GRPS-a
GRPS-b PAL	Palatine Hill	GRPS-b*

*Karner et al. (2001b).

Y, Nb, Th, Ta and TiO_2) 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 (see, e.g., Rubin *et al*. 1993; Salaün *et al*. 2011). In particular, it is likely that specific mineral phases may be removed by acid attack and, in the event that one of the investigated elements should be present in a selective way within these phases, a variation of the ratios may occur. For this reason, and especially when very small amounts of sampled material are concerned, the results of the analyses must be discussed with care. To overcome this limitation, we have integrated the Zr/Y versus 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.

Methods of analysis

Bulk samples of the volcanic component separated from the mortar aggregates—either single scoria and pumice clast or, when the grain size of the aggregate was too small, several clasts selected for their homogeneous texture—were analysed, along with four rock samples collected in the field, for trace element composition at Activation Laboratories, Canada, by lithium metaborate/tetraborate fusion ICP–MS. The fused samples were diluted and analysed using the PerkinElmer Sciex ELAN 6000, 6100 or 9000 ICP–MS. Three blanks and five controls (three before the sample group and two after) were analysed 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.

RESULTS

In this section, we present the geochemical and petrographic data of mortars sampled from the *Porticus Aemilia*, which is the earliest (beginning of the second century BC) still preserved example of concrete masonry in Rome, and from two other structures of the second century BC: the Temple of Concordia and the Temple of Castor and Pollux (the *Dioscuri*). We also present petrographic studies and trace element analyses on seven mortar samples collected from different structures of the Area Sacra di Largo Argentina, spanning from the second century BC through to the third century AD. Finally, we have performed geochemical analyses on two samples of volcanic scoria and pumice collected in an ancient Roman quarry in Prima Porta, north of Rome, to compare their composition with those of the mortars sampled nearby at the Villa di Livia, built under Emperor Augustus in around 30 BC, along with another mortar sample from a local building of late Republican age.

Colour photographs of mortar samples and separated volcanic aggregates, the sampling location, and scan images and microphotographs of thin sections are provided as supplementary online material (Figs S2–S6).

Petrochemical data

Figure 2 shows an overall plot of the analysed mortar aggregates in the Zr/Y versus Nb/Y and the Th/Ta versus Nb/Zr diagrams, to compare with the compositional fields of the Alban Hills and

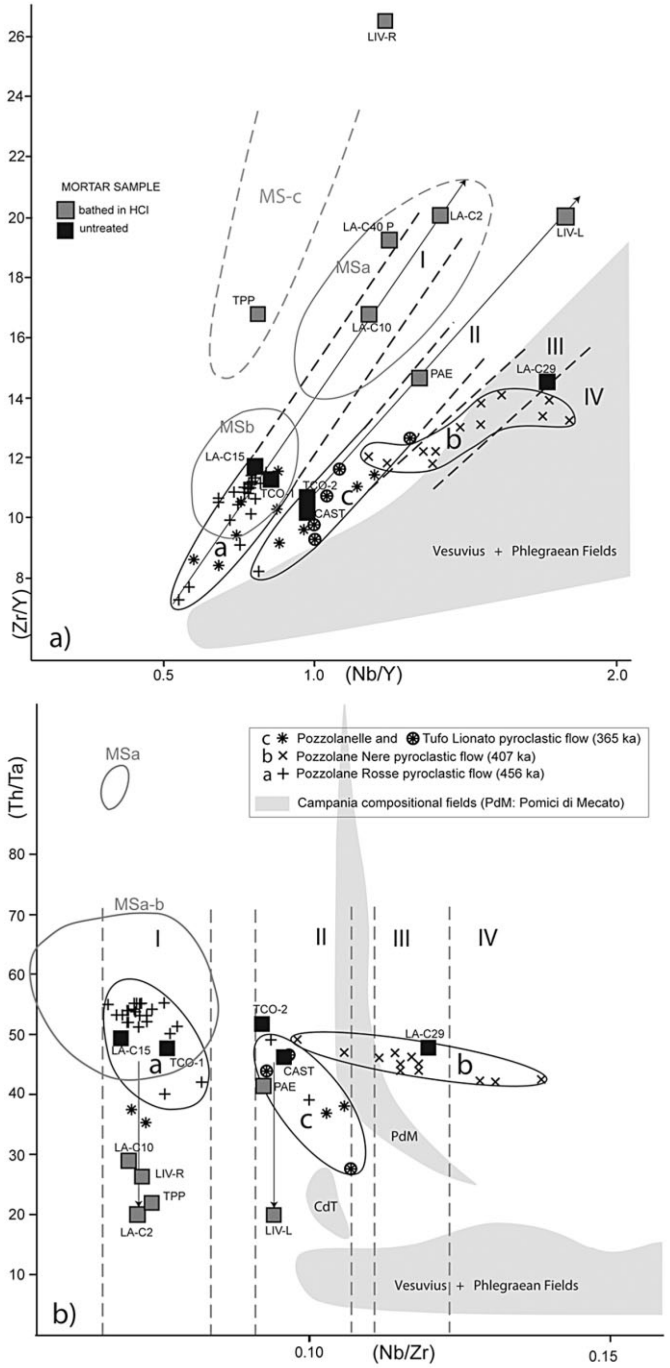

Figure 2 *Zr/Y versus Nb/Y (a) and Th/Ta versus Nb/Zr (b) diagrams comparing the compositions of the analysed mortar samples with those of the three pyroclastic-flow deposits (a–c) erupted by the Alban Hills volcanic district (after Marra* et al. *2011; Marra and D'Ambrosio 2013). The overall compositional fields of the explosive products of the Monti Sabatini and of the Campanian districts (Marra and D'Ambrosio 2013) are also shown.*

Monti Sabatini products outcropping around Rome, as well as with those of the Campanian magmatic region (Peccerillo 2005, and references therein), previously computed and presented graphically (Marra *et al*. 2011, 2013; Marra and D'Ambrosio 2013). In interpreting the results, it has to be taken into account that these previous studies have provided evidence of the great stability of the Zr/Nb ratio characterizing each specific volcanic product, with respect to a larger variability of the Y content, determining a series of sub-rectilinear compositional fields, stretching radially from the origin of the axis towards the outer Zr/Y versus Nb/Y diagram. The compositional fields defined in Figure 2 (a) after the literature data are therefore to be taken as indicative of the distribution trend of the Zr/Y versus Zr/Y values of each product or district, with an undefined upper limit, as indicated by the dashed portion of the contour lines of the fields.

The samples analysed in this work indeed display a systematic tendency to plot beyond or close to the upper limit of the sub-rectilinear compositional fields defined by the literature data. A likely explanation of this fact is that the apparent depletion in Y may be a consequence of the strong acid attack undergone by the small amount of analysed material. With the aim of testing the effective problem with Y abundances, we have tentatively replaced Y with TiO_2: an immobile element the abundances of which are commonly used to assess the uniformity of pre-pedogenic parent material in geochemical studies of palaeosols (Ashley and Driese 2000; Driese *et al.* 2000). Unlike Y, TiO_2 revealed a greater stability in the samples treated with HCl, and the alternative Nb/TiO_2 versus Zr/TiO_2 diagram has also proved to be extremely useful in separating several compositions of products that were overlapping in the other trace element diagrams, enhancing the possibility of attributing the mortar aggregate samples to specific volcanic units (Fig. 3).

The Porticus Aemilia The *Porticus Aemilia*, built in 193 BC, was a wide complex of warehouses connected to the nearby river port (*Emporium*); completed in the late third century BC south of the Aventino Hill (Fig. 1), it is the earliest still preserved monument in Rome to record the use of the *opus caementicium* (with the exception of a small portion of the original structure of Temple of Saturn, built in 380–360 BC, incorporated within later restorations of the monument). The aggregate separated from one sample of mortar collected in the original second-century BC structure (sample PAE; Figs S2 (b) and S2 (b′), and Table 2 (a)) is constituted by angular, lithoid tuff fragments (Fig. S2 (c)), showing in thin section the presence of orange glass fragments of the lithified pyroclastic-flow deposit known as Tufo Lionato (Gaeta 1998; Marra *et al*. 2009), along with several more scoriaceous clasts, rich in pyroxene and leucite crystals, displaying an intermediate aspect between the Tufo Lionato and the unlithified facies of the same pyroclastic-flow deposit ('Pozzolanelle'; Freda *et al*. 1997: see Fig. S3 (a). The trace element composition of the aggregate constituting mortar sample PAE matches the Tufo Lionato compositional field defined by Marra and D'Ambrosio (2013) (Fig. 2). Sample PAE is well aligned to the Zr/Y versus Nb/Y trend II (Fig. 2 (a)), defined by the compositional field 'c' given by the distribution of all the analysed samples from the literature data (Marra *et al*. 2011). It plots consistently inside the equivalent field 'c' in the Th/Ta versus Nb/Zr diagram of Figure 2 (b). As previously noted, the greater distance from the origin of the axes in the Zr/Y versus Nb/Y diagram with respect to the average TL composition reflects a certain depletion in Y, probably as a consequence of the acid treatment of sample PAE. Consistent with this hypothesis, PAE plots well inside the TL compositional field in the alternative Zr/TiO_2 versus Nb/TiO_2 classification diagram of Figure 3.

The temple of Concordia The temple dedicated to the Roman goddess Concordia was probably built in 218 BC; it was restored in 121 BC and completely rebuilt between 7 BC and AD 10 (Coarelli

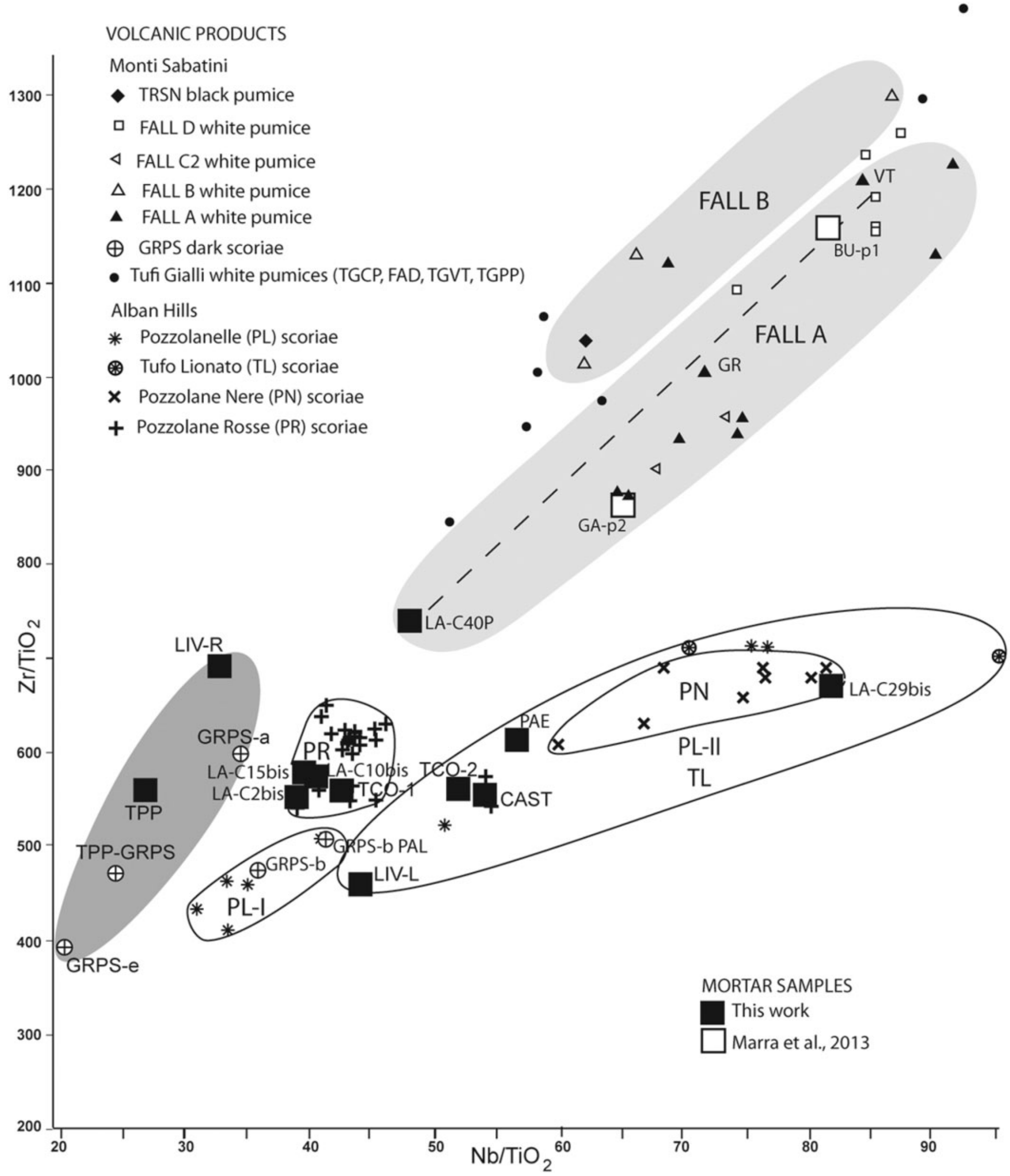

Figure 3 *A Zr/TiO_2 versus Nb/TiO_2 diagram comparing the compositions of mortar samples analysed in this and previous work with those determined here for the principal pyroclastic-flow and pumice-fall deposits of the Alban Hills and Monti Sabatini volcanic districts.*

2008, and references therein). One mortar sample (TCO) from a remnant of the 121 BC restoration was analysed at the optical microscope. The aggregate (Fig. S2 (e)) is composed of yellow sand with pyroclastic and sedimentary (carbonate) grains and coarser (~1 cm), vacuolar, calcareous rock fragments. Besides loose sanidine crystals and pumices clearly derived from the Monti Sabatini products outcropping on the banks of the Tiber River Valley in central Rome (i.e., Tufo

Giallo di Prima Porta and the Grottarossa Pyroclastic Sequence; Karner *et al.* 2001a), the majority of the volcanic scoriae displays a texture typical of the Pozzolanelle, with high crystallinity and the presence of abundant clinopyroxene, or of the Pozzolane Nere pyroclastic-flow deposit (Marra *et al.* 2009), characterized by subheudral leucite phenocrysts and acicular mica microlites (Fig. S3 (c)). Moreover, several orange glass fragments of Tufo Lionato are also present (Fig. S2 (d)). Two selected samples of scoria clasts were analysed for trace element composition: one rounded, red scoria showing evidence of transport and re-sedimentation (TCO-1), and several small, orange tuff fragments (TCO-2) (Table 2 (a)). Due to the very friable character of the mortar, separation of the aggregate was possible without bathing the sample in HCl. Consistent with previous inferences about the effect of acid attack, both samples display an apparent Y depletion (Fig. 2), and plot within the Pozzolane Rosse and within the TL-Pozzolanelle fields of the Zr/Y versus Nb/Y and the Zr/TiO_2 versus Nb/TiO_2 diagrams, respectively (Fig. 3). These observations allow us to identify the aggregate of the mortar of the Temple of Concordia as deriving from the volcaniclastic sedimentary deposit of the Aurelia Formation (350–320 ka; Karner and Marra 1998), which outcrops extensively on the north-eastern flanks of the Capitoline Hill (Fig. 1).

The temple of Castor and Pollux A sample of mortar (CAST, Table 2 (a)) was collected from the 117 BC construction in *opus incertum* incorporated in the AD 6 restoration of the Temple of Castor and Pollux (the *Dioscuri*) (Coarelli 2008, and references therein) and analysed for its geochemistry. Due to its incoherent character, it was unnecessary to bath the sample in acid.

The aggregate is entirely composed of millimetre-sized dark grey, poorly vesicular volcanic scoriae along with several fragments of orange and dark grey tuffs, probably deriving from the coarse aggregate employed in the concrete. Poorly vesicular scoriae as well as brownish glass fragments with small leucite crystals characterized by starry habit are observed in the aggregate of this mortar at the optical microscope, similar to those observed in the basal fallout (Marra *et al.* 2009) and in the distal facies (Freda *et al.* 2011) of the Pozzolane Rosse pyroclastic-flow deposit. However, the presence of apatite crystals in the glass (Fig. S3 (e)) seems to exclude such correlation, whereas the macroscopic features of the dark grey, leucite-bearing tuff fragments (Fig. S2 (f)) suggest that it may be Tufo del Palatino. Small fragments of Tufo Lionato tuff, with characteristic elongated glass shards ('fiammae'; see Fig. S3 (f)), are also present in the thin section.

Grey scoria clasts were selectively handpicked from a mortar sample (CAST), avoiding bathing in HCl. Geochemical analysis of this aggregate yielded a TL-Pozzolanelle composition in the Zr/Y versus Nb/Y, Zr/TiO_2 versus Nb/TiO_2 and Th/Ta versus Nb/Zr diagrams (Figs 2 and 3); however, the lack of reference analyses on Tufo del Palatino prevents us from attributing it to one tuff or the other.

The Area Sacra di Largo Argentina (LA) Seven mortar samples from different structures of the Area Sacra di Largo Argentina (see the inset map in Fig. S4), spanning in age from the second century BC through to the first century AD, have been investigated. The oldest mortars analysed for the present work were sampled from the foundation in *opus incertum* of the *cella* (sample LA-C2, Table 2 (a)) and from the foundation of the *podium* (sample LA-C40, Table 2 (a)) of Temple B, the construction of which is assumed to follow the severe fire of 111 BC (Caprioli 2010; and references therein). Two other mortar samples (LA-C30 and LA-C15) are from the nucleus and from the foundation of the *donario* (a low structure made of tuff blocks, probably a basement for groups of statues) that was completed in the first half of the first century BC on the southern side of Temple B, with a symmetrical construction on the northern side. A fifth mortar sample (LA-C18) was collected in the nucleus of the first *contropodio*: a circular retaining wall that was constructed during the second half of the first century BC to consolidate the *podium*, which was suffering lateral failure, probably due to the subsidence of the underlying alluvial soil on which the temple is founded. Samples LA-C30 and LA-C18 were analysed only at the optical microscope, while LA-C15 was analysed for its trace element composition (Table 2 (a)). Finally, two more mortar samples were collected from the brick-faced wall adjacent to column 7 of Temple B (LA-C10, Table 2 (a)), constructed in the second half of the first century AD, and from the brick-faced wall belonging to building 'E' (LA-C29, Table 2 (a)), to the west of Temple B, built in the third century AD (the era of Caracalla; 211–217 BC—see Coarelli *et al.* 1981). The aggregate of these mortar samples is prevalently constituted by sub-centimetre sized, red and black scoria (Figs S4 (a) – S4 (e)). Only the aggregate of sample LA-C40, from the Temple B *podium* foundation, revealed a roughly proportional mixing of red scoriae and white pumices (Figs S4 (b) and S4 (b′)).

Thin-section observation of five mortar samples (LA-C2, LA-C10, LA-C15, LA-C18 and LA-C30; Fig. S5) showed that the fine aggregate of all these mortars is essentially composed of scoria clasts of the Pozzolane Rosse pyroclastic-flow deposit, characterized by leucite crystals with a starry habit, along with occasional crystals and lithics, which also occur in this volcanic deposit. The allochthonous constituents of these mortars are represented only by occasional, tiny orange tuff and brick fragments (Figs S5 (b) and S5 (b′)), probably deriving from the coarse aggregate (*caementa*) of the concrete. In contrast, several millimetre-sized, altered (zeolitized) fragments, as well as granular ash containing sanidine (Figs S5 (b′) and S5 (d′)), are most probably derived from the uppermost, pedogenized portion of the pyroclastic-flow deposit, and from the colluvially reworked ash-fall deposit from the Monti Sabatini volcanic district, that ubiquitously overlies the Pozzolane Rosse eruptive unit (PR) in outcrops (Jackson *et al.* 2007, 2010), respectively.

When plotted in the Zr/Y versus Nb/Y identification diagram, samples LA-C15, LA-C2 and LA-C10 define a linear trend (the thin black arrow in Fig. 2 (a)) that is aligned with trend I (bordered by the dashed lines), which in turn is determined by the distribution of the literature data samples within compositional field 'a' of the PR. However, similar to sample PAE, two of these samples display an anomalous distance from the origin of the axis (i.e., Y depletion) with respect to the literature data samples. Comparison with the Th/Ta versus Nb/Zr diagram of Figure 2 (b) shows that LA-C2 and LA-C10 indeed have a tight Nb/Zr clustering within the PR trend I, but—unlike sample PAE, which plots within the compositional field 'c' of Tufo Lionato in this diagram—they also display Th depletion (the vertical arrows in Fig. 2 (b)) and plot lower with respect to the compositional field 'a' defined based on the literature data for the PR. Remarkably, both of these effects (Y and Th depletion) have been recognized as the consequence of particularly strong alteration processes affecting volcanic rock (Marra *et al.* 2011). A more direct identification of the volcanic product is achieved using the Zr/TiO_2 versus Nb/TiO_2 identification diagram of Figure 3, where samples LA-C15, LA-C2 and LA-C10 are tightly clustered to each other and plot inside a small compositional field defined by the other PR samples from the literature data set (Marra *et al.* 2011). In contrast, the composition of LA-C29 in the three diagrams of Figures 2 and 3 shows a correlation with the Pozzolane Nere pyroclastic-flow deposit.

The Zr/Y versus Nb/Y composition of the mortar pumice sample LA-C40P clearly indicates a Monti Sabatini provenance, ruling out a Campanian origin for this sample (Fig. 2; see also Fig. S6). Moreover, the Zr/TiO_2 versus Nb/TiO_2 diagram of Figure 3 suggests a correlation with the

Fall A1 layer of the Tufi Terrosi con Pomici Bianche eruptive sequence (Karner *et al*. 2001a; Sottili *et al*. 2004), erupted by the Monti Sabatini district. Pumice from this volcanic district has also been identified in the mortars of the Forum of Caesar, and in those of the Basilica Ulpia and the Grande Aula of Trajan's Markets, mixed with other pumice of Campanian origin (Marra *et al*. 2013). Based on their Zr/Y versus Nb/Y composition, which is almost identical to that of two pumice samples collected from outcrops in Rome, these mortar pumice samples were also attributed (Marra *et al*. 2013) to the Fall A1 layer (see also Fig. S6). The sub-rectilinear spread of all the samples analysed in previous work (Marra *et al*. 2013) (VT, GR, BU-p1, GA-p1 and FC) and LA-C40P is consistent with their attribution to Fall A1 (Fig. 3).

The Villa di Livia The Villa di Livia in Prima Porta, located on the western side of the Tiber River, north of Rome (Fig. S7 (a)), is named after Emperor Augustus' wife, Livia Drusilla, and it was probably built between 30 and 25 BC. Later enlargements and reconstructions were carried out, mainly in the second-to-third and third-to-fourth centuries AD (Messineo 2004).

Ancient tunnels in the pozzolanaceous deposits of the Grottarossa Pyroclastic Sequence (GRPS) and of the unlithified facies of the Tufo Giallo di Prima Porta (TGPP) pyroclastic-flow deposit (Karner *et al*. 2001a) have been discovered on the hill in front of the villa, during the excavation of an archaeological site close to a medieval tower (the Torre di Prima Porta; Fig. S7 (b)). The excavations also exposed the remains of concrete masonry structures, among which is a retaining wall in *opus incertum* dating to the second-to-first centuries BC, from which mortar sample TPP was collected (Figs S7 (e) and S7 (e′)). Two other mortar samples, one from the early Augustan era and the other from the second and third construction phases of the Villa di Livia, were collected from an *opus raeticolatum* retaining wall (LIV-R; Figs S7 (c) and S7 (c′)) and from a brick-faced wall (LIV-L; Figs S7 (d) and S7 (d′)) pertaining to the first century BC and to the second-to-third century AD construction phases, respectively.

One sample of pozzolan outcropping in the ancient quarry (TPP-GRPS; Table 2 (b) and Figs S7 (g) and S7 (g′)) was collected to compare with the mortar samples. Another pozzolan sample was collected at an outcrop of GRPS close to the villa (GRPS-a; Fig. S7 (b) and Table 2 (b)).

The trace element compositions of mortar samples from the Villa di Livia and the Torre di Prima Porta indicate different provenances for the late Republican and the Augustan-age samples (TPP and LIV-R) with respect to the second-to-third century AD sample (LIV-L) (Figs 2 and 3). The mortar samples TPP and LIV-R plot close to TPP-GRPS in the Zr/TiO_2 versus Nb/TiO_2 diagram of Figure 3, where a well-constrained compositional field is also defined for the GRPS by other outcrop samples analysed in this and in previous work (the dark grey area). Moreover, these samples plot within the MS compositional field C in Fig. S6, which is characteristic of the dark grey scoria occurring in the MS products (Marra and D'Ambrosio 2013; Marra *et al*. 2014). In contrast, LIV-L plots within field II, defined by TL and PL-II compositions, ruling out correlation with any MS product, in agreement with petrographic observation, which identifies this aggregate as Pozzolanelle. Indeed, observation in thin section provided evidence of the high crystallinity of these scoriae (Fig. S3 (b)) and the presence of abundant clinopyroxene crystals and accessory mica, which is typical of the Pozzolanelle scoriae. The presence of characteristic leucite + clinopyroxene holocrystalline lithics ('Italite'; Freda *et al*. 1997—see Fig. S3 (g)) definitively supports the attribution of these scoriae to the Pozzolanelle pyroclastic-flow deposit. In contrast, observation in thin section of the GRPS-b scoria clasts shows that these are characterized by a lesser crystallinity and by the presence of rare sanidine crystals (Fig. S3 (h)), which do not occur as xenocrystals in the Pozzolanelle, allowing us to eliminate any possible ambiguity in the identification of these scoriae.

DISCUSSION

The statistical significance of the investigated data set

The investigated data set of mortar samples includes all the still preserved masonry structures of the early period of development of this construction technique (second century BC) in Rome (i.e., the *Porticus Aemilia* and the original portions of Temple of Concordia and Temple of Castor and Pollux), with the exclusion of the remnants of the original *podium* of the Temple of Saturn (380–360 BC), for which we rely on observations reported in Jackson *et al.* (2010). Moreover, we investigated a selected number of monuments spanning from the first century BC through to the second century AD, which integrate previous observations on mortar components of the Forum of Caesar, the Tomb of Caecilia Metella, the Portico d'Ottavia, the Theatre of Marcellus, the Colosseum, Trajan's Forum and Markets, the Basilica Argentaria and the Temple of Adrian. All the mortars of this later set of monuments contain Pozzolane Rosse as the main aggregate, exclusively, as established on the basis of thin-section observation at the optical microscope (Jackson *et al.* 2010).

However, despite the apparent homogeneity of the mortar types so far investigated, the reduced amounts of samples analysed are not sufficiently statistically significant to extrapolate general rules of employment of raw materials by the Romans over such an extended chronological span. For this reason, the following considerations should be regarded as inferred on the basis of the investigated set of monuments, whereas further investigations are required in order to improve our knowledge on the chronological employment of different volcanic aggregates in Rome.

Types of mortar aggregates

In contrast with inferences of the early (Van Deman 1912) as well as the most recent studies (Jackson *et al.* 2007, 2010) on the composition of Roman mortars of the Republican epoch, the results of the present study on seven samples of mortar collected from monuments spanning from the end of the second century BC through to the beginning of the first century AD demonstrate that all these mortars contain a fine aggregate that was realized using the local Pozzolane Rosse granular volcanic ash. Only the mortars of the three earliest examples of concrete masonry in Rome (the *Porticus Aemilia*, the Temple of Concordia, and the Temple of Castor and Pollux, 193 through 117 BC) do not contain Pozzolane Rosse in the fine aggregate, which was obtained from the scrap material derived after cutting the tuff employed as the coarse aggregate, mixed with volcaniclastic material of sedimentary origin.

Moreover, the mortar of the foundation of the *podium* of Temple B in the Area Sacra di Largo Argentina (constructed soon after 111 BC) revealed the presence of a mix of Pozzolane Rosse scoriae and white pumices, for which the geochemical signature provides evidence of a provenance from the Fall A pumice deposit erupted by the Monti Sabatini volcanic district, occurring in the subsurface of Rome, below the Pozzolane Rosse layer (Fig. 4 (a)). Besides predating its employment in the early phase of development of the concrete masonry in Rome, the occurrence of this pumice in the mortar of *podium* of Temple B also testifies to the consolidated use and refinement of this material, despite its scarce availability due to the paucity of pumice deposits among the volcanic products outcropping in the surroundings of Rome (Marra *et al.* 2011).

Finally, the mortar of a third-century AD brick-faced wall in the Area Sacra di Largo Argentina revealed the presence of black scoriae of the Pozzolane Nere, a pyroclastic-flow deposit that has never been identified in mortars of Imperial age in previous work (Jackson *et al.* 2010, and references therein). The occurrence of Pozzolanelle in the aggregate of a brick-faced wall of the Villa di Livia ascribed to the second-to-third centuries AD suggests that by the end of the second century AD, the exploitation of pozzolan had been extended to the two pyroclastic-flow deposits overlying the Pozzolane Rosse.

Chronological interpretations

The composition of the earliest mortars reflects the near-site geological setting, revealing the use of materials occurring in the adjacent outcrops, or directly exposed by excavations in the construction yard, suggesting the lack of an established system for the refinement of pozzolan at that time. Indeed, to produce the fine aggregate of the mortar of the *Porticus Aemilia*, the constructors used the crushed material resulting from the rough cutting of the decimetre-sized Tufo Lionato blocks that constitute the coarse aggregate of the concrete. Moreover, they probably integrated it with the less coherent fraction of the pyroclastic-flow deposit occurring at the excavation site where the Tufo Lionato was quarried. A transitional facies between the lithified pyroclastic-flow deposit and the incoherent Pozzolanelle deposit is usually associated with the Tufo Lionato outcrops occurring on the hills in the City of Rome (see Fig. 4 (a)). In particular, such a facies occurs on the Aventino Hill, rising immediately north-east of the alluvial plain of the Tiber River, where the *Porticus Aemilia* was built (Fig. 1). Here, ancient tunnels for the excavation of Tufo Lionato have been detected by means of subsurface geotechnical investigations (Federici and Santoro 1997).

The concrete of the Temple of Concordia, built at the south-eastern foot of the Capitol Hill (Fig. 2), contains a complete record of its stratigraphy, revealing the same approach used by constructors of the *Porticus Aemilia* for supplying the building materials. Indeed, the mortar of the Temple of Concordia contains the whole range of volcanic and sedimentary materials occurring in the deposit of the Aurelia Formation, outcropping to the rear of the temple. Moreover, the abundant fragments of Tufo Lionato (Fig. S2 (e′)) provide evidence that, similar to that of the *Porticus Aemilia*, the mortar for the Temple of Concordia was realized using the crushed material resulting from the cutting of the *caementa*, mixed with abundant volcaniclastic fraction, derived from the sedimentary deposit of the Aurelia Formation overlying the Tufo Lionato at the Capitol Hill. Also, as at the Aventino Hill, a wide network of tunnels is excavated within the Tufo Lionato deposit on the Capitol Hill, revealing its intensive and long-lasting exploitation (Corazza *et al.* 2004).

According to these observations, Jackson *et al.* (2010) also indicated the sedimentary deposit of the Aurelia Formation as the source of the aggregate employed in the original *podium* of the Temple of Saturn (380–360 BC).

Finally, the mortar of Temple of Castor and Pollux (117 BC) is also realized with the crushed material deriving from the tuffs employed as rubble stone in the concrete: Tufo del Palatino and Tufo Lionato.

The mortar from Temple B of Area Sacra of Largo Argentina, dating after the fire of 111 BC, represents the turning point in the development of the concrete masonry in Rome, based on

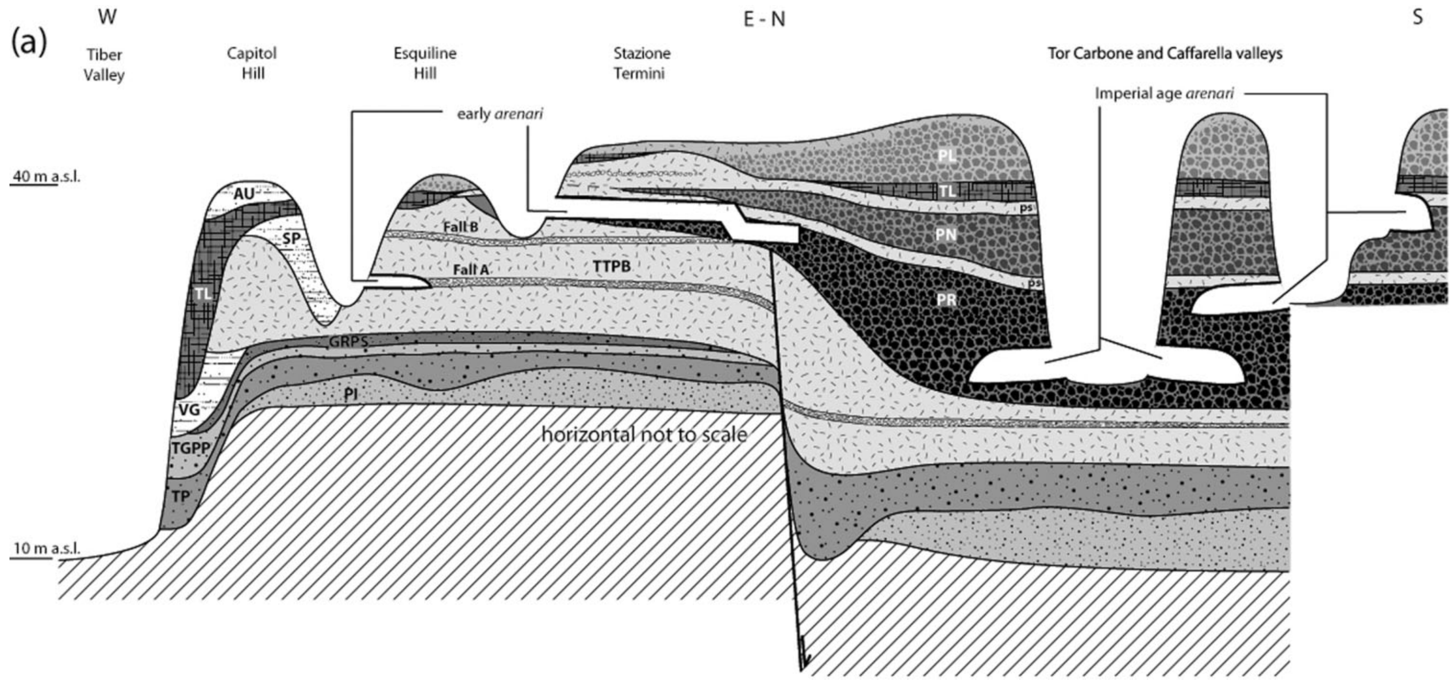

Figure 4 *(a) Rome's stratigraphic scheme, showing the subsurface geology and the geometry and depositional features of the pyroclastic-flow deposits providing the source for pozzolan. The possible locations of tunnels for the exploitation of pozzolan (arenarii) in the different epochs are also shown. (b) A geological map showing the outcrops of Pozzolane Rosse that have been identified through a dedicated study, based on the reinterpretation of the stratigraphic section of Stazione Termini (see Fig. S8), on the new chronostratigraphic data on the volcanic products of the Alban Hills and Monti Sabatini districts (Karner* et al. *2001a; Marra* et al. *2009, 2014) and on geomorphological reconstruction. Key to stratigraphic abbreviations: TL, Tufo Lionato; TSVLS, Tufi Stratificati Varicolouri di La Storta; PN, Pozzolane Nere; CG, Gonglomerato giallo (= SP Fm: San Paolo Formation); PR, Pozzolane Rosse; TTPB, Tufi Terrosi con Pomici Bianche; GRPS, Grottarossa Pyroclastic Sequence; TdP, Tufo del Palatino (= 'Cappellaccio'); PT4 (SC Fm), Palaeo-Tiber 4 unit (Santa Cecilia Formation); PT3 (PG2 Fm), Palaeo-Tiber 3 unit (Ponte Galeria 2 Formation).*

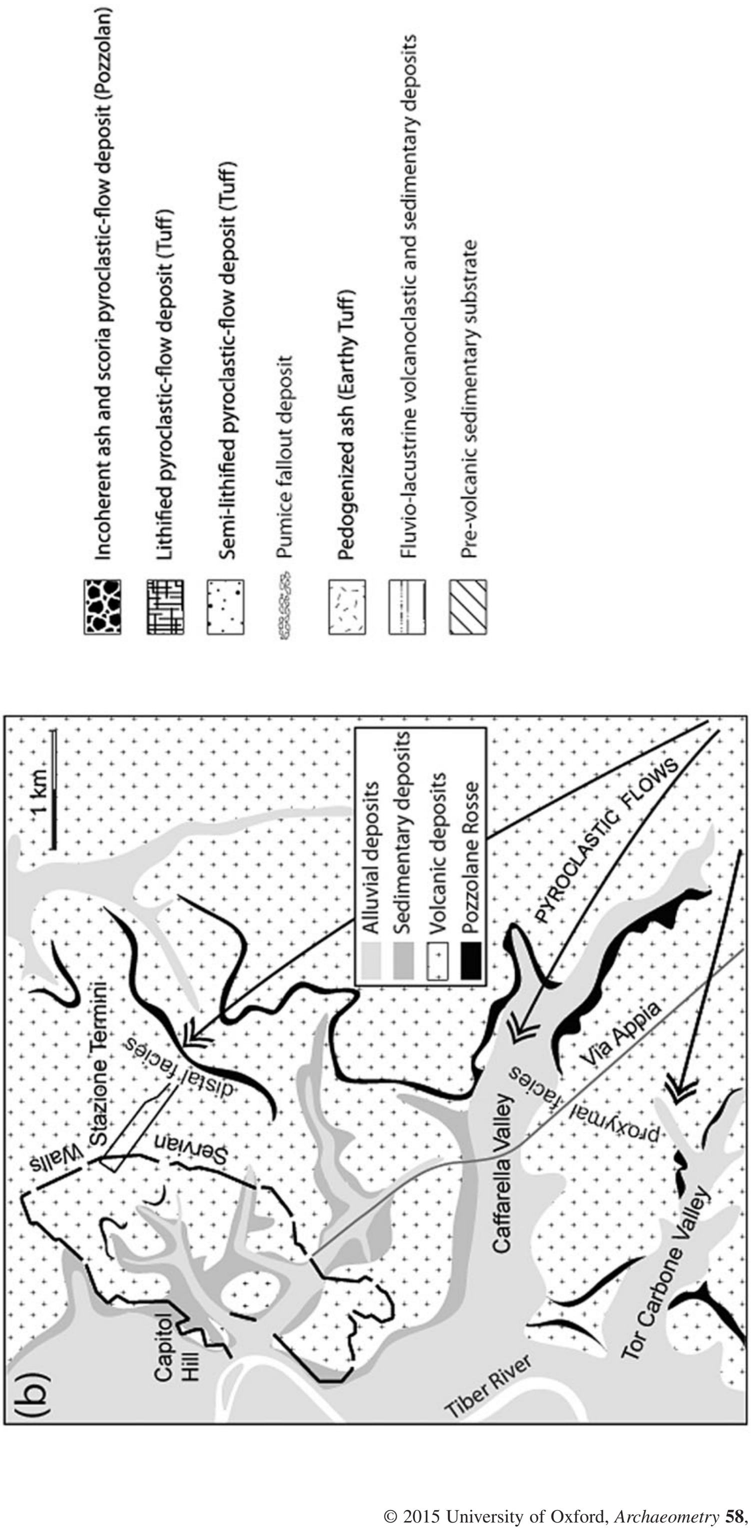

Figure 4 (*Continued*)

observations on the available set of monuments of this early age. This is the first mortar, among those investigated so far, to use Pozzolane Rosse in the aggregate, a material that was refined specifically for this purpose, instead of the more accessible sandy material outcropping in the vicinity of the construction yard. Remarkably, all the investigated mortars of the Area Sacra di Largo Argentina, dating from after the fire of 111 BC through to the second half of the first century BC, contain a fine aggregate realized using quarried volcanic sand (*harena fossicia*), in which the occasional presence of tiny Tufo Lionato fragments has to be considered to derive from the friable external surface of the *caementa*, or is purely accidental.

That this technical revolution occurs after the great fire of 111 BC, which destroyed a large number of buildings in Rome (Lugli 1952), does not seem accidental. The successive reconstructions required the availability of large amounts of building materials, probably leading to the exploitation of new sources and to the development of more systematic extraction methods. It is probable that the exploitation of the Pozzolane Rosse deposits by means of tunnels (*arenarii*) began in this epoch. Tunnel exploitation of tuffs had already been in progress since the archaic epoch, as testified by the large network of '*latomiae*' (cuts) affecting the Tufo del Palatino (Cifani 2008, and references therein) in the underlying geological strata of Rome, from which were cut the blocks of 'cappellaccio' (the archaeological name for Tufo del Palatino; Table 1), which were largely employed from the early settlement on the Palatine Hill through to the early Republican epoch (Lanciani 1897; Lugli 1957). The stratigraphic section of the Stazione Termini in Rome reported by Italian geologist De Angelis D'Ossat (1948) (Fig. S8) shows tunnels excavated in the pozzolan deposits directly overlying the *latomiae* in the Tufo del Palatino. We have reinterpreted the stratigraphy of the Stazione Termini section (see Fig. S8) in the light of the most recent achievements on the volcanic stratigraphy of this region (Karner *et al.* 2001a; Marra *et al.* 2009, 2014), showing that the Pozzolane Rosse deposit occurring within the centre of Rome has probably been exploited by means of *arenarii* since the end of the second century BC, as suggested by occurrences of this pozzolan in the mortars of monuments of this age.

In this light, the quarries for exploitation of the Grottarossa Pyroclastic Sequence pozzolan deposit in Prima Porta may be regarded as the local equivalent of the *arenarii* dug into the Pozzolane Rosse within the city of Rome, possibly attesting to the establishment of tunnel excavation as a means of supplying raw material for masonry since around the end of the second century BC.

Amongst the mortars analysed in this work, the occurrence of scoriae of the Pozzolane Nere and Pozzolanelle deposits only in those of the third century BC suggests that exploitation of these upper pozzolan layers began at a later date, as a probable consequence of the growth of the city and the increasing demand for building materials during the Imperial age. It is likely that by this time, tunnel excavation in the underlying geological strata had been extended to the Pozzolane Nere, as the uppermost tunnel in the Stazione Termini section suggests, as well as to the southern sector of the area of Rome, where thicker strata of the three pyroclastic-flow deposits outcrop extensively along the flanks of the Caffarella and Tor Carbone Valleys (Figs 4 (a) and 4 (b)).

CONCLUSIONS

Based on the results of the petrographic and geochemical study on the investigated set of monuments, is possible to establish the chronological use of different types of mortars, as a function of the composition of the volcanic material employed in the fine aggregate. However, given the statistically limited significance of the analysed number of mortar aggregates, the possibility of considering this chronology as representative of the evolution of the masonry technique in Rome, and its reliability with regard to indicating the construction date, relies on the implementation of the data set and on the availability of new archaeological information.

A chronological framework for the different aggregate compositions identified in the present study can be outlined by the following three groups (see also Table 2):

(a) Early second century BC: no use of Pozzolane Rosse; the fine aggregate is realized using the remains of the Tufo Lionato tuff, employed as coarse aggregate, mixed with the volcaniclastic sediments associated with it and outcropping near the construction sites.

(b) End of the second century BC to first century AD: the almost exclusive use of Pozzolane Rosse, exploited locally by means of tunnel excavation (*arenarii*), or its local equivalent in the sectors where this pyroclastic-flow deposit is missing (e.g., the Grottarossa Pyroclastic Sequence in Prima Porta, north of Rome). Mixing with the local Fall A pumice deposit is occasionally observed.

(c) Second-to-third centuries AD: combined or alternative use of Pozzolane Rosse, Pozzolane Nere and Pozzolanelle, with Pozzolane Rosse deposits remaining the main source.

ACKNOWLEDGEMENTS

We thank the Soprintendenza Speciale per i Beni Archeologici di Roma, the Sovrintendenza Capitolina ai Beni Culturali and the archaeologists in charge of the studied monuments for authorizing the collection of mortar samples. We are particularly grateful for the guidance and assistance offered during the sampling by Ida Sciortino (Temple of Concordia and Temple of Castor and Pollux), Andrea Venier (Villa di Livia) and Roberta Cellini (Torre di Prima Porta).

REFERENCES

Alvarez, W., Ammerman, A. J., Renne, P. R., Karner, D. B., Terrenato, N., and Montanari, A., 1996, Quaternary fluvial-volcanic stratigraphy and geochronology of the Capitoline Hill in Rome, *Geology*, **24**, 751–4.

Ashley, G. M., and Driese, S. G., 2000, Paleopedology and paleohydrology of a volcaniclastic paleosol interval: implications for early Pleistocene stratigraphy and paleoclimate record, Olduvai Gorge, Tanzania, *Journal of Sedimentary Research*, **70**, 1065–80.

Blake, M. E., 1947, *Ancient Roman construction in Italy from the prehistoric period to Augustus*, Publication 570, Carnegie Institution, Washington, DC.

Cann, J. R., 1970, Rb, Sr, Y, Zr, Nb in some ocean floor basaltic rocks, *Earth and Planetary Science Letters*, **10**, 7–11.

Caprioli, F., 2010, Problematiche del Tempio B di Largo Argentina attraverso la sua decorazione architettonica: Roma 2008—International Congress of Classical Archaeology. Meetings between cultures in the ancient Mediterranean, *Bollettino di Archeologia* online, special volume, 48–58.

Chiari, G., Santarelli, M. L., and Torracca, G., 1992, Caratterizzazione della malte antiche mediante l'analisi di campioni non frazionati, *Materiali e Strutture*, **2**, 111–37.

Cifani, G., 2008, *L'architettura romana arcaica: edilizia e società tra monarchia e repubblica*, L'Erma di Bretschneider, Roma.

Coarelli, F., 2008, *Roma—guide archeologiche Laterza*, Editori Laterza, Roma.

Coarelli, F., Kajanto, I., Nyberg, U., and Steinby, M., 1981, *L'Area Sacra di Largo Argentina*, Poliglotta Vaticana, Roma.

Corazza, A., Lombardi, L., and Marra, F., 2004, La geologia del Colle Capitolino, *Il Quaternario*, **17**(2/2), 413–41.

Curtis, C. D., 1913, The difference between sand and pozzolana, *Journal of Roman Studies*, **3**, 197–203.

De Angelis D'Ossat, G., 1948, Osservazioni di geologia applicata sugli scavi alla Stazione Termini di Roma, *Ingegneria Ferroviaria*, **8**, 443–50.

Driese, S. G., Mora, C. I., Stiles, C. A., Joeckel, R. M., and Nordt, L. C., 2000, Mass-balance reconstruction of a modern vertisol: implications for interpretations of geochemistry and burial alteration of paleovertisols, *Geoderma*, **95**, 179–204.

Duzgoren-Aydin, N. S., Aydin, A., and Malpas, J., 2002, Distribution of clay minerals along a weathered pyroclastic rock profile, Hong Kong, *Catena*, **50**, 17–41.

Federici, V., and Santoro, V. M., 1997, Antiche cave sotterranee sul Colle Aventino (Roma): indagini, studi e rilievi eseguiti nella zona di Via San Giosafat e valutazione delle caratteristiche di potenzialità di dissesto, *Geologia Tecnica & Ambientale*, **3**, 63–78.

Floyd, P. A., and Winchester, J. A., 1975, Magma type and tectonic setting discrimination using immobile elements, *Earth and Planetary Science Letters*, **27**, 211–18.

Frank, T., 1924, *Roman buildings of the Republic: an attempt to date them from their materials*, American Academy in Rome, Rome.

Freda, C., Gaeta, M., Palladino, D. M., and Trigila, R., 1997, The Villa Senni eruption (Alban Hills, central Italy): the role of H_2O and CO_2 on the magma chamber evolution and on the eruptive scenario, *Journal of Volcanology and Geothermal Research*, **78**, 103–20.

Freda, C., Gaeta, M., Giaccio, B., Marra, F., Palladino, D. M., Scarlato, P., and Sottili, G., 2011, CO_2-driven large mafic explosive eruptions: the Pozzolane Rosse case study from the Colli Albani Volcanic District (Italy), *Bulletin of Volcanology*, **73**, 241–56; doi:10.1007/s00445-010-0406-3

Freda, C., Gaeta, M., Karner, D. B., Marra, F., Renne, P. R., Taddeucci, J., Scarlato, P., Christensen, J. N., and Dallai, L., 2006, Eruptive history and petrologic evolution of the Albano multiple maar (Alban Hills, central Italy), *Bulletin of Volcanology*, **68**, 567–91.

Gaeta, M., 1998, Petrogenetic implications of Ba-sanidine in the Lionato Tuff (Colli Albani Volcanic District, central Italy), *Mineralogical Magazine*, **62**, 697–701

Heiken, G., Funiciello, R., and De Rita, D., 2005, *The Seven Hills of Rome—a geological tour of the Eternal City*, Princeton University Press, Princeton, NJ.

Jackson, M. D., Deocampo, D., Marra, F., and Scheetz, B., 2010, Mid-Pleistocene volcanic ash in ancient Roman concretes, *Geoarchaeology*, **25**(1), 36–74; doi:10.1002/gea.20295

Jackson, M. D., Kosso, C., Marra, F., and Hay, R. L., 2006, Geological basis of Vitruvius' empirical observations of material characteristics of rock utilized in Roman masonry, in *Proceedings of the Second International Congress of Construction History, Queen's College, University of Cambridge, 29 March–2 April 2006* (eds. M. Dunkeld, J. Campbell, H. Louw, M. Tutton, B. Addis and R. Thorne), 1685–702, The Construction History Society, London.

Jackson, M. D., Marra, F., Deocampo, D., Vella, A., Kosso, C., and Hay, R., 2007, Geological observations of excavated sand (*harenae fossiciae*) used as fine aggregate in ancient Roman pozzolanic mortars, *Journal of Roman Archaeology*, **20**, 1–30.

Karner, D. B., and Marra, F., 1998, Correlation of fluviodeltaic aggradational sections with glacial climate history: a revision of the classical Pleistocene stratigraphy of Rome, *Geological Society of America Bulletin*, **110**, 748–58.

Karner, D. B., Marra, F., and Renne, P. R., 2001a, The history of the Monti Sabatini and Alban Hills volcanoes: groundwork for assessing volcanic–tectonic hazards for Rome, *Journal of Volcanology and Geothermal Research*, **107**, 185–219.

Karner, D. B., Lombardi, L., Marra, F., Fortini, P., and Renne, P., 2001b, Age of ancient monuments by means of building stone provenance: a case study of the Tullianum, Rome, Italy, *Journal of Archaelogical Science*, **28**, 387–93.

Lancaster, L. C., 2005, *Concrete vaulted construction in imperial Rome: innovations in context*, Cambridge University Press, New York.

Lanciani, R., 1897, *The ruins and excavations of ancient Rome*, Macmillan, London,.

Lugli, G., 1952, *Fontes ad topographiam veteris urbis Romae pertinentes*, vol. 1, Istituto di Topografia Antica, Università degli Studi di Roma.

Lugli, G., 1957, *La tecnica edilizia romana con particolare riguardo a Roma e Lazio*, Bardi, Rome.

Marra, F., and D'Ambrosio, E., 2013, Trace-element classification diagrams of pyroclastic rocks from the volcanic districts of central Italy: the case study of the ancient Roman ships of Pisa, *Archaeometry*, **55**, 993–1019; doi:10.1111/j.1475-4754.2012.00725.x

Marra F., and Florindo, F., 2014, The subsurface geology of Rome (Italy): sedimentary processes, sea-level changes and astronomical forcing, *Earth-Science Reviews*; doi:10.1016/j.earscirev.2014.05.001

Marra, F., and Rosa, C., 1995, Stratigrafia e assetto geologico dell'area romana, in *La geologia di Roma: il centro storico* (ed. R. Funiciello), 49–118, Memorie Descrittive della Carta Geologica d'Italia, **50**.

Marra, F., D'Ambrosio, E., Sottili, G., and Ventura, G., 2013, Geochemical fingerprints of volcanic materials: identification of a pumice trade route from Pompeii to Rome, *Geological Society of America Bulletin*, **125**, 556–77; doi:10.1130/B30709.1

Marra, F., Deocampo, D., Jackson, M. D., and Ventura, G., 2011, The Alban Hills and Monti Sabatini volcanic products used in ancient Roman masonry (Italy): an integrated stratigraphic, archeological, environmental and geochemical approach, *Earth-Science Reviews*, **108**, 115–36; doi:10.1016/j.earscirev.2011.06.005

Marra, F., Karner, D. B., Freda, C., Gaeta, M., and Renne, P. R., 2009, Large mafic eruptions at the Alban Hills Volcanic District (central Italy): chronostratigraphy, petrography and eruptive behavior, *Journal of Volcanology and Geothermal Research*, **179**, 217–32.

Marra, F., Sottili, G., Gaeta, M., Giaccio, B., Jicha, B., Masotta, M., Palladino, D. M., and Deocampo, D., 2014, Major explosive activity in the Sabatini Volcanic District (central Italy) over the 800–390 ka interval: geochronological–geochemical overview and tephrostratigraphic implications, *Quaternary Science Reviews*; doi:10.1016/j.quascirev.2014.04.010

Marra, F., Freda, C., Scarlato, P., Taddeucci, J., Karner, D. B., Renne, P. R., Gaeta, M., Palladino, D. M., Trigila, R., and Cavarretta, G., 2003, Post-caldera activity in the Alban Hills Volcanic District (Italy): ^{40}Ar/^{39}Ar geochronology and insights into magma evolution, *Bulletin of Volcanology*, **65**, 227–47.

Messineo, G., 2004, *La Villa di Livia a Prima Porta, Roma*, Libreria dello Stato, Istituto Poligrafico dello Stato, Roma.

Miriello, D., Barca, D., Bloise, A., Ciarallo, A., Crisci, G. M., De Rose, F., Gattuso, C., Gazineo, F., and La Russa, M. F., 2010, Characterization of archaeological mortars from Pompeii (Campania, Italy) and identification of construction phases by compositional data analysis, *Journal of Archaeological Science*, **37**, 2207–23.

Oleson, J. P., Brandon, C., Cramer, S. M., Cucitore, R., Gotti, E., and Hohlfelder, R. L., 2004, The ROMACONS project: a contribution to the historical and engineering analysis of hydraulic concrete in Roman maritime structures, *The International Journal of Nautical Archaeology*, **33**(2), 199–229; doi:10.1111/j.1095-9270.2004.00020.x

Pearce, J. A., 1996, A users' guide to basalt discrimination diagrams, in *Trace element geochemistry of volcanic rocks: applications for massive sulphide exploration, Winnipeg, 24–26 May 1996* (ed. D. A. Wyman), 79–113, Geological Association of Canada, Short Course Notes, **12**, 79–113, Geological Association of Canada, St. John's, Newfoundland.

Peccerillo, A., 2005, *Plio-Quaternary volcanism in Italy: petrology, geochemistry, geodynamics*, Springer-Verlag, Berlin.

Rubin, J. N., Henry, C. D., and Price, J. G., 1993, The mobility of zirconium and other 'immobile' elements during hydrothermal alteration, *Chemical Geology*, **110**, 29–47.

Salaün, A., Villemant, B., Gérard, M., Komorowski, J.-C., and Michel, A., 2011, Hydrothermal alteration in andesitic volcanoes: trace element redistribution in active and ancient hydrothermal systems of Guadeloupe (Lesser Antilles), *Journal of Geochemical Exploration*, **111**, 59–83.

Sottili, G., Palladino, D. M., and Zanon, V., 2004, Plinian activity during the early eruptive history of the Sabatini Volcanic District, central Italy, *Journal of Volcanology and Geothermal Research*, **135**, 361–79.

Sottili, G., Palladino, D. M., Marra, F., Jicha, B., Karner, D. B., and Renne, P. F., 2010. Geochronology of the most recent activity in the Sabatini Volcanic District, Roman Province, central Italy, *Journal of Volcanology and Geothermal Research*, **196**, 20–30.

Van Deman, E. B., 1912, Methods of determining the date of Roman concrete monuments (first and second papers), *American Journal of Archaeology*, **16**, 230–51, 387–432.

Vitruvius, 1997, *De architectura*, ed. P. Gros, Einaudi, Torino.

SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article at the publisher's web-site:

Figure S1 Map of Central Italy showing the location of the volcanoes of the Roman Co-magmatic Region and the outcropping areas of the pyroclastic rocks employed in ancient Roman masonry.

Figure S2 A – Porticus Aemilia

a) Map and sampling location; b-b′) Particular of the southeastern wall where one mortar sample (PAE) was collected from the lower, older portion of the original structure, characterized by an overall dusky aspect, with a prevailing lime matrix and a finer aggregate, which ranges in color from dark grey to brown and orange, binding the coarse aggregate made of Tufo Lionato (TL) fragments; c) Aggregate of mortar sample PAE, separated from the lime matrix after bathing in

HCl, which was analyzed for trace-element; d) Scan image of a thin section of sample PAE, before separation of the aggregate, showing the occurrence of large fragments of Tufo Lionato (TL) and crystalline scoriae (TL/PL) that at the optical microscope revealed transitional texture between Tufo Lionato and Pozzolanelle (see microphotograph of Supplementary Figure 3a); loose, pale green clinopyroxene crystals (cpx) also occur.

Figure S2 B – Temple of Concordia

e) aggregate separated from mortar sample TCO, from which selected scoria clasts were handpicked and analyzed for trace-element; e′) Scan image of a thin section of sample TCO, before separation of the aggregate, showing the occurrence of several fragments of Tufo Lionato (TL), crystalline scoriae of Pozzolanelle (PL) and Pozzolane Nere (PN), and abundant loose crystals, including clinopyroxene (cpx) and sanidine, as well as rare pumice clasts (see text and Supplementary Figure 3c). The occurrence of these heterogeneous volcanic components, along with the abundant sedimentary fraction (including cm-sized travertine fragments: TR in (e)), indicate provenance from the Aurelia Formation cropping out on the flanks of Capitol Hill, at the back of the Temple of Concordia (see Supplementary Figure 1).

Figure S2 C – Temple of Castor and Pollux

f) aggregate separated from mortar sample CAST; f′) Scan image of a thin section of sample CAST, before separation of the aggregate, showing the occurrence of several grey scoriae displaying macroscopic texture similar to that of Tufo del Palatino (TP) and large fragments of Tufo Lionato (TL) (see Supplementary Figure 3f).

Figure S3 – Microphotographs of mortar samples

Horizontal field of view is 2 mm for all pictures.

a) Volcanic glass showing intermediate feature between Tufo Lionato and Pozzolanelle in the IInd century b.C. mortar sample PAE from Porticus Aemilia; b) Image at crossed nichols highlighting abundant clinopyroxene crystals (cpx) within a typical Pozzolanelle scoria, occurring in the IInd-IIIrd century A.D. mortar of sample LIV-L from Villa di Livia: c) Pozzolane Nere scoria with characteristic, subhedral leucite phenocrysts (L) and acicular mica microlites (not shown), occurring as the reworked, volcaniclastic fraction of the of Aurelia Formation sedimentary deposit, in the IInd century b.C. mortar sample TCO of Temple of Concordia; d) Typical Pozzolane Rosse scoria, showing a poorly crystalline texture and the characteristic starry habit of leucite crystals, from the Ist century b.C. mortar sample LA-C18 of Temple B of Area Sacra di Largo Argentina; e) Interstitial volcanic glass with starry leucite and apatite crystals in the IInd century b.C. mortar sample CAST from the Temple of Dioscuri, attributed to Tufo del Palatino; f) Typical Tufo Lionato glass shard with characteristic elongated vesicules (“fiammae”) in mortar sample CAST; g) Holocrystalline leucite + clinopyroxene inclusion (“Italite”), typically occuring in the Pozzolanelle pyroclastic-flow deposit (Freda *et al*., 1997), in mortar sample LIV-L; h) Crystalline scoria clast with characteristic sanidine crystals (s) in an outcrop sample of Grottarossa Pyroclastic Sequence unit b (GRPS-b).

Figure S4 A – Area Sacra di Largo Argentina – Republican age mortars

Inset map shows location of mortar samples that have been analyzed for trace elements.

a) Aggregate extracted after HCl bathing from sample LA-C2, collected in the IInd century b.C. wall of the *Cella* of Temple B (a′);

b) Aggregate extracted after HCl bathing from sample LA-C40, collected from the Ist century b.C. foundation of the podium of Temple B (b″-b′″); white pumice clasts (b′) were separated from the red scoriae and analyzed for trace-elements;

c) Dark grey scoriae handpicked from sample LA-C15, collected from the nucleus of the *Donario* (c′);

Figure S4 B – Area Sacra di Largo Argentina – Imperial age mortars.
d) Red scoriae collected from the nucleus (d′) of a Ist century A.D. brick faced wall (d″); the scoriae were bathed in HCl to remove the lime adhering to the external surface, before underwent geochemical analysis;
e) large scoriae handpicked from the nucleus of a IIIrd century brick faced wall (e′); only the black scoria (2), which required no HCl bathing, was analyzed for trace-elements.
Figure S5 Thin sections of mortar samples from the Area Sacra di Largo Argentina. See inset map of Supplementary Figure 4 for location. Description of the volcanic components is provided in the text. Legend: PR = Pozzolane Rosse; I-II-III indicate three progressive degrees of increasing alteration of the scoriae, based on their color and corresponding to weathering indexes established by Jackson *et al*., 2010; TL: TufoLionato; Cpx: clinopyroxene; Lc: leucite; Lv: lava lithic fragment; Ps: altered ash deriving from pedogenized layer (paleosol); Br: brick fragment.
Figure S6 Zr/Y vs Nb/Y compositions of the pumice sample LA-C40 P and of the aggregates of the mortars from Villa di Livia and Prima Porta are compared to the compositional fields determined from literature data (Marra and D'Ambrosio, 2013) for the Monti Sabatini and the Alban Hills pyroclastic products, and to other compositions determined for this (GRPS-a, GRPS-b PAL) and previous work (Marra *et al*.; 2011, 2014) (GRPS-b, GRPS-e). In particular, composition of ancient Roman mortar pumice samples analyzed in this and previous (Marra *et al*., 2013) work, are compared to those of the pumice deposits Fall A and Fall B, occurring in the subsurface of Rome (see Figure 4).
The compositional fields of the pumice-fall deposits of Vesuvius and Phlegraean Fields (light grey areas)[3] are also reported to show the lack of correlation with the investigated mortar samples.
Figure S7 A – Villa di Livia and Torre di Prima Porta mortar samples
a–b) Sampling location; c) Ist century b.C. *opus raeticolatum* wall, d) IInd-IIIrd century A.D. brick faced wall and e) early Ist century b.C. *opus incertum* wall, from which mortar samples LIV-R, LIV-L and TPP were collected; c′, d′ and e′ show the correspondent aggregates extracted after HCl bathing;
Figure S7 B – Ancient Roman quarries in Torre di Prima Porta
g) Remnants of Roman age tunnels for exploitation of the local pozzolan (incoherent facies of Tufo Giallo di Prima Porta -TGP- and Grottarossa Pyroclastic Sequence -GRPS[6]); a pumice layer (p) occurs at the base of the exposed pyroclastic succession;
g′) sample of scoriae collected from the GRPS layer excavated at Torre di Prima Porta quarries and analyzed in this work for trace-elements.
Figure S8 The stratigraphic section of Stazione Termini reported by De Angelis D'Ossat[7] shows tunnels excavated in the pozzolan deposits directly overlying the *latomiae* in the Tufo del Palatino. Although De Angelis D'Ossat did not recognize these pozzolan layers as the Pozzolane Rosse and Pozzolane Nere, our re-interpretation of the section, based on comparison with the stratigraphic logs of boreholes drilled in this area, and on the new achievements on the chronostratigraphic features of the Alban Hills and Monti Sabatini volcanoes (Karner *et al*., 2001; Marra *et al*., 2009; Marra *et al*., 2014), demonstrates he was wrong. We have recognized the typical succession occurring in Rome (see stratigraphic scheme of Figure 4a), with the Tufi Terrosi con Pomici Bianche (including either Fall A and Fall B: P1a and P1b) between Tufo del Palatino and Pozzolane Ross (Karner *et al*., 2001; Sottili *et al*., 2004). Moreover, according to their temporal range, we have attributed the thick succession of fallout deposits above the Pozzolane Nere to the "Tufi Stratificati Varicolori della Storta" (Corda *et al*., 1978). In particular, based on its stratigraphic position between Pozzolane Nere (407 ka) and Tufo Lionato (365 ka), we correlate the pumice layer [15] that De Angelis D'Ossat identified as "Granturco" with the

distal deposit of the Vico β pumice fallout (P2), which is dated at 404 ± 7 ka (Cioni *et al*., 1993). Similarly, we correlate the air-fall deposit between Pozzolane Rosse and Pozzolane Nere with Fall E and Fall F, erupted 350 ± 4 and 347 ± 7 ka, respectively, during thew final sateges of the Tufo Rosso a Scorie Nere eruption cycle (Marra *et al*., 2014), as well as with VIco α, erupted 419 ± 7 ka from the Vico Volcano (Cioni *et al*., 1993).

Appendix Mortars

SUPPLEMENTARY REFERENCES