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# Mid-Pleistocene Pozzolanic Volcanic Ash in Ancient Roman Concretes

## ABSTRACT

The hydrated lime-volcanic ash mortars of imperial age concrete construction in Rome owe their extraordinary durability to a specific alteration facies of scoriaceous ash from the Pozzolane Rosse ignimbrite, erupted at 456±3 ka from Alban Hills volcano. Stratigraphic, petrographic, and chemical investigations demonstrate that during the warm, humid period preceding marine isotope stage 11, hydrolytic pedogenesis produced an argillic horizon in Pozzolane Rosse, with thick illuvial clay that had little reactivity with hydrated lime, as shown by mortars from the Forum of Julius Caesar (46 to 44 BC). In the underlying soil horizon, however, translocated halloysite overlies opal and poorly crystalline clay surface coatings. Imperial age mortars, as from the Forum and Markets of Trajan (AD 96 to 115), show strong reactivity of these components, altered scoria groundmass, and zeolites with hydrated lime. Romans deliberately selected this alkali-rich ash for optimal performance of pozzolanic concretes.

## INTRODUCTION

The concrete masonry of the monuments of ancient Rome is composed of cobble-sized brick and tuff clasts (*caementa*), which are bonded by pozzolanic mortars (Figure 1) with alkali-rich, calcium-alumina-silicate hydrate cements (Langton & Roy, 1984) and altered, volcanic ash aggregate. Roman builders of the republican age, sixth century BC through first century BC, developed a good empirical understanding of the geographic distribution and material characteristics of the diverse volcanic tuffs they quarried for dimension stone masonry (Jackson et al., 2005). By second century BC, builders had begun to experiment with concrete construction, formulating moderately durable mortars with hydrated lime and pozzolanic aggregates excavated from ash deposited by the Tiber River at the foot of the Capitoline Hill (Jackson et al., 2007). During first century BC, Romans expanded their understanding of the various granular ash deposits of the Roman region, and they significantly improved the strength and durability of pozzolanic concretes during the Augustan era, 27 BC to AD 14, eventually a selecting specific alteration facies of the Pozzolane Rosse ignimbrite (Jackson et al., 2007), erupted at 456±3 ka from Alban Hills volcano (Figure 2) (Karner, Marra, & Renne, 2001; recalculated in Marra, Florindo, & Boschi, 2008). The robust mortars (Giavarini, Samuelli Ferretti, & Santarelli, 2006) that form the basis of the sophisticated concrete vaulted architecture of the imperial era, first through fourth century BC, systematically contain this Pozzolane Rosse ash (Tables I, II). For more than 100 years, archaeologists have speculated about the provenance of the aggregates that Roman builders selected for pozzolanic mortars (Van Deman, 1912a; 1912b; Blake, 1947; Lancaster, 2005), but have reached few firm conclusions. Previous studies have attempted to identify the lithological provenance of pozzolanic ash from various mortars through comparison of geochemical data, such as rare earth element and x-ray diffraction analyses, with those of Roman ash in outcrop, with limited success (Bakos et al., 1992; 1994; Chiari, Santarelli, & Torracca, 1992; Chiari et al., 1996).

The purpose of this paper is to describe the variations in the petrographic and chemical characteristics of the Roman volcanic ash deposits; to situate these characteristics within the mid-Pleistocene volcanic, climate, and pedogenic history of the Roman region; and to use these data to give a preliminary assessment of the compositions of pozzolanic aggregates and relative abundances of pozzolanic reactive components in the altered ash. Stratigraphic, petrographic, and geochemical data indicate that mid-Pleistocene paleopedological processes produced alterations in the Pozzolane Rosse ignimbrite that significantly enhanced its pozzolanic activity, or reactivity, with hydrated lime. The textures and compositions of the volcaniclastic mortar aggregates and cementitious complexes give insights into the reactive components of the ash aggregates and the state of preservation of the ancient mortars. These data provide new information with which archaeologists can begin developing hypotheses about the preferences and expertise of Roman builders in formulating aggregate mixes, as well as quarrying techniques, transport of materials, and organization of worksites (Delaine, 1997; Bianchi & Meneghini, 2002; Rea, 2002). Furthermore, they form a foundation for the study of other Mediterranean ashes that Romans used as pozzolanic aggregates.

## GEOLOGIC ENVIRONMENT

The Roman landscape exposes a complex aggradational sequence of volcanic tuffs and granular ash deposits, or pozzolane, which were erupted from the Alban Hills and Monti Sabatini volcanic districts between about 560 and 35 ka (De Rita, Funiciello, & Parotto, 1988; De Rita et al., 1995; Marra and Rosa, 1995; Karner, Marra, & Renne, 2001; Heiken, Funiciello, & De Rita, 2005; Marra, Florindo, & Boschi, 2008; Marra et al., 2008). These inter-layered ignimbrites, airfall, and reworked volcaniclastic deposits record episodes of pyroclastic eruption, pedogenesis, and fluvial deposition and erosion by the Tiber River during mid-Pleistocene sea level rise and fall (Figure 3) (Marra & Rosa, 1995; Karner & Marra, 1998; Marra, Florindo, & Boschi, 2008).

The highly-potassic scoriae of the Pozzolane Rosse ignimbrite may have erupted with a more-or-less uniform chemical composition (Fornaseri, Scherillo, & Ventriglia, 1963; Trigila et al., 1995). However, the major element chemistry of the ash shows a great deal of variation, even within a single quarry (Figure 4). Petrographic studies indicate that different processes or degrees of pedogenic alteration coupled with differences in the relative abundances of primary volcanic constituents produced substantial variations in bulk geochemistry, color, texture, and cementation of the ash. Furthermore, pedogenic alteration products such as poorly crystalline clay and opaline silica are amorphous and not easily detected through x-ray diffraction analyses. We therefore take an integrated stratigraphic, petrographic, and chemical approach to describing the volcanic and pedogenic stratigraphy, the micromorphological characteristics of alteration facies, and the chemical variability of Pozzolane Rosse, correlating the characteristics of the pozzolanic aggregate in mortars with the pedogenic processes observed in quarries (Tables I, II).

We first describe the volcanic stratigraphy and micromorphological characteristics of successive mid-Pleistocene volcanic ash deposits at Castèl di Leva quarry, and the paleosol that developed between 456 and 436 ka, during marine isotope stages 12 to 11 in Pozzolane Rosse (Marra, Florindo, & Boschi, 2008) (Figures 3, 4). We then give petrographic descriptions of the primary volcanic components and the secondary, or authigenic, components of Pozzolane Rosse ash from quarries through the Roman region. These data provide a straightforward method for determining the lithological provenance and the "alteration provenance" (Jackson et al., 2007) of various aggregates in the ancient mortars, the abundances of potential reactive authigenic components, and the long lasting durability of the imperial age mortars. In particular, the cementitious matrix of robust, indurated imperial age mortars has an alkali-rich composition (Roy & Langton, 1989), indicative of strong reaction of hydrated lime with Pozzolane Rosse ash. Modern alkali-rich cements, however, are highly susceptible to internal expansion, cracking, and failure (Fournier & Bérubé, 2000). We provide preliminary insights as to why the alkali- and alumina-rich cements associated with the Pozzolane Rosse aggregate of some important examples of concrete monumental construction in Rome have remained resistant to decay for 2000 years.

## HISTORICAL PERSPECTIVES

Pozzolans, derived from the Latin *pulvis puteolanus*, or "powdery ash" from *Puteoli*, now modern Pozzuoli in the Campi Flegrei caldera (de'Gennaro et al., 1999; Oleson et al., 2004), are inorganic materials that contain reactive constituents, generally aluminates and silicates, which combine with lime in the presence of moisture to form stable binding hydrates.

Romans used Campi Flegrei pumiceous ash from the Bay of Naples for maritime concretes (Oleson et al., 2004; Goldsworthy & Min, 2008). In contrast, mortars of Roman imperial age monuments generally contain altered scoriae with authigenic surface coatings from the Pozzolane Rosse ignimbrite (Jackson et al., 2007). When combined with hydrated lime calcined from limestone bedrock, Campi Flegrei ash (*pulvis puteolanus*) and Roman excavated volcanic sands (*harenae fossiciae*) produce pozzolanic reactions, as described by Vitruvius in *De Architectura* (27-31 BC). Although Vitruvius described the "reactive capacity" of *harenae fossiciae* with hydrated lime, there is a general absence of data regarding the components of Pozzolane Rosse that provided the pozzolanic reactivity with hydrated lime, and the stable, binding, alkali- and alumina-rich calcium-silica-hydrate cements (Roy & Langton, 1989) of Roman mortars.

Vitruvius' highly accurate empirical descriptions of the material characteristics of Roman tuff and travertine building stones and the judicious use of these rocks in the existing Roman monuments (Jackson et al., 2005) indicate that by first century BC, Roman builders had a good understanding of the bedrock geology of the Roman region (Figure 2). Vitruvius also recorded the diverse characteristics of the various volcaniclastic deposits with which builders formulated the republican era pozzolanic mortars of Rome. He wrote *De Architectura* for Octavian, who became Emperor Augustus in 27 BC, at the initiation of the imperial age. Augustus' extensive building program in Rome coincided with a period when Roman builders were making significant advances in concrete technologies (Van Deman, 1912a; b; Lechtman & Hobbs, 1987). In previous work, we resolved discrepancies among Latin transcriptions of *De Architectura* dating to AD 900; made new, literal, translations of Vitruvius' empirical observations of the raw materials of Roman mortars and concretes; and identified the provenance of volcaniclastic aggregates in several republican era concrete monuments constructed between

121 and 30 BC (Jackson et al., 2007). Geologic maps showing ancient quarries for these building materials in Rome and its surroundings appear in Jackson & Marra (2006).

Republican era concrete monuments in the Roman Forum, such as the early constructions of the Temple of Concord (121 BC) and the Temple of Castor and Pollux (117 BC), are composed of tuff cut stone masonry and concretes with friable pozzolanic mortars (Table I). These mortars contain aggregate from the reworked volcanic and sedimentary sands of the San Paolo and Aurelia Formations (Jackson et al., 2007) deposited by the Tiber River and its tributaries at the base of the Capitoline Hill (Marra & Rosa, 1995; Alvarez et al., 1996; Corazza, Lombardi, & Marra, 2004). Vitruvius described such light gray (*cana*) excavated sands as earthy (*terrosa*) and not rough enough for durable mortars. Ideal excavated sands make a "harsh, grating, rasping noise when rubbed vigorously in the hand" (*De Architectura* 2.4.1) and correspond to the dark gray (*nigra*) and reddened (*rubra*), non-dispersive, scoriaceous sands of the Pozzolane Rosse ignimbrite (Jackson et al., 2007). Vitruvius based his remarks on the previous experiences of builders and attempted to explain physical processes of pozzolanic reaction and curing in terms of the theory of the four elements (*De Architectura* 2.8.1-4; 2.6.1-6). In this paper, we use petrographic and chemical data to explain the "suitability" (*idonea*) of Pozzolane Rosse sands for mortar aggregate.

The construction of the Forum of Julius Caesar in 46 to 44 BC, about 15 to 20 years before Vitruvius wrote *De Architectura*, coincided with an important transition in concrete construction when builders began to systematically select Pozzolane Rosse as mortar aggregate (Jackson et al., in press). Furthermore, Augustan age concrete renovations to the Temple of Castor and Pollux (AD 6) and the Temple of Concord (AD 10) and the very durable mortars of the imperial age contain specific alteration facies of Pozzolane Rosse aggregate (Figure 1) (Jackson et al., 2007; Bianchi et al., in press). The closest outcrops of

Pozzolane Rosse occur about 2.5 km south of the Forum in the Caffarella Valley (Figure 2), which has a distorted topography, enlarged by excavations for ash over the past 2000 years. As described by the Roman archaeologist, E. B. Van Deman (1912a): "The data derived from this *pozzolana-arena*, the varieties of which used in the various periods differ widely, are often of great importance. A most striking example of this is found in the Augustan period, in which one of the distinctive characteristics of the construction, the dusky red color of the mortar, arises from the use in it of a special variety of pozzolana (the *arena rubra* of Vitruvius (2.4.1)), the introduction of which by Augustus, or by his predecessor Julius Caesar, marks an epoch in the history of concrete construction." Table 1 summarizes Van Deman's precise descriptions of Roman pozzolanic mortars, which have not been properly recognized, and her perceptive interpretations of the evolution of Roman builders' expertise.

**MID-PLEISTOCENE VOLCANIC ASH IN ROMAN MORTARS**

In Rome, interfingered mid-Pleistocene tephras of the Monti Sabatini and Alban Hills volcanic districts are interbedded with Paleo-Tiber River sedimentary deposits in a complex depositional pattern resulting from interplay between glacial eustacy and sedimentation (Marra & Rosa, 1995; Karner & Marra, 1998; Karner, Marra, & Renne, 2001; Marra, Florindo, & Boschi, 2008). Alban Hills products have highly potassic, silica-depleted, K-foidite compositions, with the feldspathoid mineral leucite, clinopyroxene, and several accessory phases (Trigila et al., 1995). The ignimbrites and subordinate airfalls of Pozzolane Rosse (456±3 ka), Pozzolane Nere (407±2 ka), and Pozzolanelle (366±7 ka) (Marra et al., 2008) dated by $^{40}Ar/^{39}Ar$ ages on leucite crystals (Karner, Marra, & Renne, 2001), represent the three final eruptive cycles of the Tuscolano-Artemisio explosive phase (De Rita, Funiciello, & Parotto, 1988; De Rita et al., 1995). These eruptions filled depressions in the paleolandscape, depositing ash up to several tens of meters thick.

Pozzolane Rosse is the historical name (Karner, Marra, & Renne, 2001; and references therein) for the pyroclastic flow deposit, or ignimbrite, erupted during marine isotope stage 12 of the deep-sea $\delta^{18}O$ record (Figure 3). During the stage 12 low stand phase, bracketed by ages of volcanic layers spanning 456 to 437 ka (Marra, Florindo, & Boschi, 2008) its upper surface was partially eroded. Subsequent to glacial termination V, bracketed by Roman tephra ages of ~437 to 407 ka, the San Paolo Formation filled stage 12 paleoincisions with eroded ash that were fluvially reworked with airfall tephra erupted from Monti Sabatini vents during the stage 11 aggradational phase (Marra & Rosa, 1995). The Pozzolane Nere ignimbrite buried these deposits during the stage 11 high stand. The Tufo Lionato and Pozzolanelle ignimbrites were coincident with the low stand of stage 10 at the onset of glacial termination IV (Marra, Florindo, & Boschi 2008). During the stage 9 high stand, fluvial and lacustrine deposits of the Aurelia Formation filled paleovalleys incised during stage 10 sea level fall (Karner & Marra, 1998).

Areas corresponding to flat lying, Pleistocene pyroclastic plateaus and geomorphic highs preserve the original, horizontally layered stratigraphy of the pyroclastic flow deposits. These are separated by paleosols and accumulations of airfall and colluvial, re-worked, or re-deposited ash that developed during nearly absolute volcanic dormancies of ~50 kyr (Marra et al., 2008). The 15 meter high cuts of a modern quarry at Castèl di Leva, ~11 km south of Rome and ~20 km west of the Tuscolo-Artemisio crater vent source provide thorough and representative exposures of this volcanic stratigraphy (Figure 4). The weathering of the ash illustrates pedogenic processes on a tectonically stable topographic plateau during stage 12 to stage 10; Pozzolane Rosse exhibits predominantly argillic alteration (Figure 5). In contrast, Pozzolane Rosse at the Santa Tecla Catacomb quarry (Figure 6) exhibits predominantly zeolitic alteration. There, the ignimbrite filled a valley incised by the Tiber River during marine isotope stage 12. The ash was intermittently inundated by floodwaters that may have produced interstitial fluid compositions that encouraged the precipitation of zeolitic surface coatings and cements (Hay & Iijima, 1964; Hay, 2003). The Pozzolane Rosse aggregate of imperial age mortars retains traces of both argillic and zeolitic alteration (Figure 1).

Clear petrographic and textural differences exist among Pozzolane Rosse, Pozzolanelle, and Pozzolane Nere. Variations in their mineralogical, textural, and alteration characteristics are sufficiently distinct so as to be identified through thin section petrography (Jackson et al., 2007). Pozzolanelle typically contains altered, almost pumiceous, light brown (5YR 5/6 Munsell color) to moderate reddish orange (10R 6/6) palagonite (iron-rich glass) fragments with little resistance to crushing when pressed between the fingers. Pozzolane Nere contains a large proportion of sand–sized, darkly opaque, altered glass fragments (5YR 2/1), which retain shades of orange palagonite and are usually less vesicular than those in Pozzolanelle. The dull, altered palagonite fragments may not breakdown completely when pressed between the fingers, but they do leave a fine, earthy residue. Pozzolane Rosse has altered fine gravel- and sand-sized dusky yellow brown (10YR 4/4) to dusky red (10R 2/2 to 5R 3/4) to dark gray (N2) scoriae that are largely resistant to crushing and disintegration. The ash is poorly sorted, but sand-sized tephra, 0.05 to 2.0 mm in diameter, form about 40 to 60 weight percent of the deposit (Jackson et al., 2007). Although yellowish orange (10YR 6/6), altered palagonite fragments may form up to 25 frequency percent of some Pozzolane Rosse samples, scoriae are always the predominate type of tephra (Table III).

**METHODS AND TECHNIQUES**

During 2006 to 2008, we measured and sampled vertical sections of the mid-Pleistocene ash at the Castèl di Leva, Fosso di Tor Marancia, Tenuta di Capannacce, and Santa Tecla quarries and the Istituto Nazionale di Geofisica e Vulcanologia and Santa Maria della Mole boreholes (Figure 2), documenting the transitions from one compositional or alteration layer to the next, taking samples at 20 to 50 cm vertical intervals, and investigating lateral variations in the ash deposits. Using petrographic and micromorphological techniques (Hay, 1959; Birkeland, 1984; Retallack, 2001) we describe the 1) the primary textures and compositions of primary volcanic components such as scoriae, glass (palagonite) fragments, lava lithic fragments, and phenocrysts, and 2) the secondary micromorphological features and alteration, or authigenic, components and surface coatings of the pyroclasts.

We sampled the Roman concretes with the assistance of the archaeologist in charge of each site, collecting specimens from a variety of structural elements, such as foundations, podiums, walls, staircases, and/or vaults, from each epoch of construction within a given monument (Table II). Using thin section petrography, we identified the textures of the pozzolanic cements and the lithological provenance of the pozzolanic aggregates. From the traces of unreacted authigenic components that remained in the volcaniclastic clasts, we identified the alteration provenance of the pozzolanic aggregate, as described below.

We augmented the petrographic studies of the ash and mortars with x-ray diffraction analyses, carried out using an INEL x-ray diffractometer with a position-sensitive detector using Co radiation, operating at 30kv and 30mA, and x-ray fluorescence spectroscopy of fused glass beads for whole rock, major element compositions at Michigan State University. (Laser-ablation inductively coupled plasma mass spectrometry of the same beads for trace and rare earth element compositions appear in Deocampo, Jackson, & Marra, in review). Preliminary SEM/EDS studies of certain Pozzolane Rosse ash and mortar samples, integrated with petrographic, x-ray diffraction, and geochemical analyses provide insights into the importance of pozzolanic reactions on the compositions and durability of the mortar cements. Analyses from ongoing research (Jackson et al., in press; Bianchi et al., in press) and additional data from Roy & Langton (1989) and Jackson et al. (2007) provide an analytical framework for observations summarized here.

**Thin Section Petrography**

Point counts, based on 550 or more sites per thin section to record the heterogeneous textures of the ash, rely on methods developed for study of the Roman volcanic tuff building stones (Jackson et al., 2005). They describe the frequency of primary volcanic components, authigenic components, and void space in a roughly 2 x 3 $cm^2$ area, and are reproducible to about 5%, based on repeat counts of several sections. For loose, incoherent Pozzolane Rosse samples, we made immersion oil mounts of the powdered ash to identify leucite alteration and the compositions of authigenic surface coatings.

Scoriae compose about 55% to 75% percent of Pozzolane Rosse; light brown (5YR 5/6), palagonite (iron rich glass) fragments form up to 25% of some samples; and fragments of leucititic melilite lava, italite, and leucite (or analcime replacement), clinopyroxene, biotite form about 5% to 17% (Table III). Authigenic surface coatings, composed of poorly crystalline clay, opal, illuvial and translocated halloysite, as well as zeolite, mainly phillipsite and chabazite, form about 23% to 37% of the whole rock (Figures 5, 6). Here, the term "illuvial" refers to halloysite deposited by significant downward movement of soil water containing colloidal clay (Courty, Goldberg, & MacPhail, 1989:151; Ashley & Driese, 2000). The petrographic studies indicate that scoria groundmass is ubiquitously opaque, and that it was weathered to predominantly poorly crystalline, non-dispersive halloysite, based on x-ray diffraction analyses (Jackson et al., 2007). There is no fresh glass. Instead, the edges of scoriae exhibit very fine grained, generally < 5μ, high relief ovoids or tubes with refractive index $1.46 \leq n \geq 1.529$, which appear to be poorly crystalline clay (Lowe, 1986), possibly incipient halloysite (Fornaseri, Scherillo, & Ventriglia, 1963; Jackson et al., 2007).

## CASTÈL DI LEVA QUARRY

### Stratigraphy and Alteration of Volcanic Ash

The Castèl di Leva quarry provides good vertical and lateral exposures of the mid-Pleistocene ignimbrites (Figures 2, 3, 4), and the sequences of mineralogic changes produced by weathering of these ash between the eruption of Pozzolane Rosse at 456±3 ka, Pozzolane Nere at 407±2 ka, and Pozzolanelle at 366±7 ka (Marra, Florindo, & Boschi, 2008). The >5.5 m thick Pozzolane Rosse ignimbrite has primary volcanic components of fine gravel- to sand-sized scoriae, 45-55%; crystal fragments, mainly leucite, clinopyroxene, and biotite, 5-10%; and lava fragments, <5%, based on point counts (Table III).

Pedogenic zone 1, the lower 4 m of the ignimbrite, defines a least altered facies of weathering with leucite mainly intact (Figure 5a). Dark gray (N2) to dark dusky red (10R 2/2 to 5R 3/4), non-dispersive, altered scoriae have groundmass altered to poorly crystalline clay mineral and intermittent thin rims of opal. Patches of 10Å halloysite with “petal” textures occasionally occupy grain interstices. Major element chemistry shows low $Al_2O_3$ and negligible loss of base cations (Figure 4), and weakly developed soil structures suggest alteration in paleogroundwater (Retallack, 2001; Deocampo, Jackson, & Marra, in review).

Pedogenic zone 2 records an intermediate facies of weathering. Fine leucites ($KAlSi_2O_3$) in reddened (5R 3/4 to 10R 2/2) scoriae are replaced by analcime ($Na[AlSi_2O_6]\cdot H_2O$) or dissolved; larger leucite crystals persist. Opal and opal-clay mixtures coat tephra surfaces and cement fine ash accretions at scoriae perimeters. Translocated, pale yellow to colorless, 10Å halloysite coatings overlay these textures (Figure 5b). Major element chemistry shows intermediate $Al_2O_3$, $K_2O:SiO_2$, and alkali concentrations (Figure 4). This is the “dusky-red” ash of Van Deman (1912a) (Table I). It corresponds to a loose and often unconsolidated transitional Bt to Bw horizon below the zone 3 paleosol (Birkeland, 1999). Imperial age Romans systematically employed this facies, and the less altered ash of zone 1 as mixtures in durable pozzolanic mortars. The ternary diagram of Figure 7, demonstrates that the intermediate and least altered facies of zones 1 and 2 contain the greatest abundance of alkalis, 20 to 25%. It is curious that Roman builders preferred this alkali-rich ash, because the modern concrete industry generally avoids aggregates with > 0.6 weight percent $Na_2O$ (or $K_2O$) (Mindess, Young, & Darwin, 2003:144), because of the risk of producing damaging alkali-aggregate reactions, as discussed below.

In contrast, intense pedogenic weathering occurred within pedogenic zone 3, the 1.3 m thick Pozzolane Rosse co-ignimbritic ash cloud and upper ignimbrite. Reddish brown (10R 3/6 to 4/6) scoriae show weathering to poorly crystalline clay mineral and birefringent clay cutans. Downward movement of silt-sized scoriae and petrographically isotropic, yellow illuvial clay cements, pale yellow clay alone, and lastly, colorless clay surface coatings, all mainly 10Å halloysite, then formed cutans around scoriae and molds around once intact leucite crystals that later dissolved (Figure 5c). (Note that the petrographically isotropic halloysite overlays the thin, intermittent, birefringent clay cutans on altered scoriae, suggesting changing pedogenic conditions.) Very low $K_2O/SiO_2$ records near complete leucite dissolution. A peak in $Al_2O_3$ indicates abundant clay (Figure 4). Redoximorphic mottles in hand samples, and microscopic root traces with Fe-oxide glaebules and illuvial clay cutans with record strong pedogenesis, which correspond to the Bt horizon of a hydrolytically weathered paleosol with ultisolic properties (Birkeland, 1999; Retallack, 2001). Significantly, the pozzolanic cements of Roman mortars do not penetrate thick, yellow, illuvial clay coatings of clasts from the alkali-depleted paleosol, as illustrated by republican era mortars at the Forum of Julius Caesar, which preserve traces of roots surrounded by Fe-glaebules and illuvial clay (Figure 8).

Overlying colluvial deposits of zone 4, stratigraphically equivalent to reworked ash of Conglomerato Giallo coincident with glacial termination V (Figure 3) (Marra & Rosa, 1995), incorporate sub-rounded, highly altered clasts of the Pozzolane Rosse paleosol with moderate brown (5YR 5/6) Monti Sabatini fallout ash containing sanidine, leucite, and etched clinopyroxene; coarse diopside from Pozzolane Rosse is etched or dissolved (Figure 5d). Significantly, extensive macroscopic and petrographic observations of mortars of the existing Roman monuments (Tables I, II) indicate that Roman builders did not apparently employ this type of fine sideromelane ash as pozzolanic aggregate.

The 2.5 m thick, lower horizon of the Pozzolane Nere ignimbrite is a least altered facies with stable values of $Al_2O_3$ and negligible loss of base cations (Figure 4), and leucite mainly intact. Perhaps subsequent burial placed this horizon at groundwater level. The overlying co-ignimbritic ash cloud and upper ignimbrite, however, have characteristics indicative of marine isotope stage 11 pedogenic alteration: leucite is nearly completely dissolved; clinopyroxene is strongly etched; and authigenic opal forms intermittent surface coatings over altered palagonite fragments. $K_2O/SiO_2$ shows a small increase in this incipient paleosol, indicating leaching and loss of base cations. Pedogenesis may have terminated abruptly with burial by a ~1 m thick layer of partially reworked air fall and colluvial ash. Prismatic structures indicative of dessication form the upper surface of this horizon. A ~25 cm thick, laminated ash deposit unconformably overlies this weathered ash, followed by a ~50 cm thick, roughly graded, volcaniclastic layer, which is in turn overlain by the Pozzolanelle ignimbrite.

**Pedogenic History**

An understanding of the pedogenic history of the mid-Pleistocene, Roman aggradational ash (Figure 3), as exposed at Castèl di Leva, provides a valuable context in which to situate the lithological and alteration provenance of the pozzolanic ash aggregate of Roman mortars as well as the stratigraphic characteristics of ancient excavation localities in the Roman region.

During the relatively colder and drier conditions of marine isotope stage12 (457 to 437 ka), weathering of Pozzolane Rosse and hydrolysis of scoria groundmass to poorly crystalline clay may have progressed rapidly (Lowe, 1986) but leucite remained largely intact. Intensive hydrolytic pedogenic weathering, with strong leaching (zone 3, Figure 4), low base cation saturation, and no calcareous horizon (Birkeland, 1999) occurred within the warm humid period from 437 to 407 ka. Leucite dissolved but clinopyroxene remained largely intact (Deocampo et al., 2008). The lower horizons of the Pozzolane Rosse ignimbrite corresponding to the least altered facies of the ash apparently underwent alteration in ground water with little influence of surficial pedogenic processes. Subsequently, during this same period, Monti Sabatini airfall ash buried the highly altered Pozzolane Rosse paleosol and the two deposits colluvially intermingled (zone 4, Figure 4). Monti Sabatini leucite remained intact but clinopyroxene dissolved, reflecting paleowaters with compositions unrelated to the Pozzolane Rosse paleosol. This deposit was buried by the Pozzolane Nere ignimbrite at 407 ka.

During the marine isotope stage 11 high stand, a paleosol with etched leucite and clinopyroxene developed on the Pozzolane Nere ignimbrite, indicating yet a different alteration regime (Deocampo et al., 2008). Finally, the polygonal, prismatic structures at the top of the later airfall and colluvial ash suggest well-drained or arid conditions preceding emplacement of the volcaniclastic deposits of the “Conglomerato di Leva”, and eruption of Pozzolane during MIS 10.

Most significantly, Romans did not apparently employ any of the highly pedogenically altered Pozzolane Rosse, Pozzolane Nere, and Pozzolanelle ash in high quality imperial age mortars. However, republican era mortars and those of certain concretes of Nero’s Golden House

(AD 64-68) contain reworked ash of the San Paolo and Aurelia Formations, which contain ubiquitous fragments of Pozzolane Nere and Pozzolane Rosse with leucite replaced by analcime and/or illuvial clay coatings (Figure 9). These clasts were apparently eroded from the upper surfaces of the ignimbrites during the marine isotope stage 12 and 10 sea level low stands (Figure 3) and deposited by tributaries of the Tiber River in the valley of the Roman Forum. For mortars of the Forum of Julius Caesar (46 to 44 BC), builders selected Pozzolane Rosse aggregate with strong pedogenic alteration indicative of the greatest alteration facies, with illuvial clay coatings, root traces, and leucite replaced by analcime (Figure 8).

## PETROGRAPHIC CHARACTERISTICS OF ALTERATION FACIES

Using stratigraphic, petrographic and chemical techniques, such as those described for the Castèl di Leva quarry, we define three general alteration facies (Jackson et al., 2007) within vertical sections of Pozzolane Rosse (Figure 2). Point counts of thin sections (Table III), identify the primary volcanic components of scoriae, palagonite, and lava and crystal fragments and the secondary authigenic components of poorly crystalline clay and opal; translocated, "illuvial" halloysite or in situ "petal" halloysite; and phillipsite and chabazite surface coatings or cements. Figure 10 shows the abundances of the authigenic minerals relative to the total proportion of authigenic components in samples from several Pozzolane Rosse quarries. It provides a framework for evaluating the relative abundances of the alteration components of Pozzolane Rosse ash sampled from quarries through the Roman region (Figure 2); for further investigation of pedogenic processes influencing the alteration of the ash; and the composition and relative abundances of potentially reactive pozzolanic components within vertical quarry sections. The data show a rather consistent pattern through the Roman region, which archeologists can use to identify the alteration provenance of the Pozzolane Rosse that builders selected for imperial age mortars.

**Greatest Alteration Facies**

The intense pedogenic weathering of Pozzolane Rosse during marine isotope stage 11, as at the uppermost horizons of the Castèl di Leva (Figure 5c), Fosso di Tor Marancia, and Tenuta di Capannacce quarries produced thick, yellow, illuvial halloysite surface coatings and cements (zone 3, Figure 4, Figure 5c). These form about 20 frequency percent of the whole rock (Table III) and about 70 to 75 frequency percent of the alteration components in the Castèl di Leva and Tenuta di Capannacce paleosol (Figure 10). The paleosol at Fosso di Tor Marancia may have been partially eroded away. At the INGV borehole, a lava flow directly overlies Pozzolane Rosse and a palagonite-rich interval above the more scoriaceous intermediate alteration facies, so the paleosol may also have been eroded away.

Within the greatest alteration facies, leucite within scoria groundmass and as crystal fragments is dissolved or wholly replaced by analcime; scoriae are generally dark yellowish brown (10 YR 4/2) to moderate grayish brown (10R 4/6); thick, yellow (in plan polarized light) clay cutans, mainly halloysite in composition, form pervasive surface coatings and cements; and scoria clay is largely dispersive and remains suspended in water, giving a dark–brown opacity. At the Castèl di Leva and the Fosso di Tor Marancia quarries, leucite is dissolved but at the Tenuta di Capannacce quarry, leucite is almost wholly replaced by analcime. There is little or no zeolite surface coating, and a lesser degree of scoriae decomposition to poorly crystalline clay and opal.

**Intermediate alteration facies**

The transitional Bt to Bw horizon of the Pozzolane Rosse marine isotope stage 11 paleosol produced an intermediate facies of alteration, as at the middle horizons of the Castèl di Leva (zone 2, Figure 4; Figure 5b). The Fosso di Tor Marancia, and Tenuta di Capannacce quarries, and intermediate INGV borehole contain this horizon. The ash commonly has a loose, incoherent texture, and is easily excavated. Because it is difficult to obtain thin sections of the poorly consolidated ash, the point count data from Fosso di Tor Marancia (Figure 10; Table III; samples 08-TC2-PR-A; 04-TC-PR-06) and INGV (Figure 10; Table III; sample INGV-PR-06) were augmented with immersion oil studies of the intermediate facies ash at Castèl di Leva and Tenuta di Capannacce.

Within the intermediate alteration facies, large, discrete leucite crystal fragments remain fresh but smaller crystals are replaced by analcime or dissolved; scoriae are dark reddish brown to moderate reddish brown (10R 3/4 to 10R 4/6), corresponding to the "dusky red" ash described by Van Deman (1912a, b) (Table I); surface coatings are predominantly of thin rims of opal, $n < 1.46$, or interlayered opal and clay, with variable $n$, which are overlain by thin colorless or very pale yellow halloysite cutans, $1.53 \leq n \geq 1.54$; scoriae are non dispersive, but a light-colored layer of fine, dispersive white to pale yellow clay mineral and opal resettles over the darker tephra. Dissolution and/or decomposition of scoria groundmass to poorly crystalline clay mineral is more pronounced than in the overlying greatest alteration facies. Translocated halloysite surface coatings form about 30 frequency percent of authigenic components (Figure 10). There is little or no zeolite surface coating.

**Least altered facies**

In horizons where alteration in groundwater apparently predominated (Deocampo, Jackson, & Marra, in review), illustrated by the lower horizons of the Pozzolane Rosse ignimbrite at Castèl di Leva, Fosso di Tor Marancia, and Tenuta di Capannacce (zone 1, Figure 4), fresh leucite is common throughout, although there is dissolution of fine leucite. Scoriae are dark red brown (10R 3/4) to moderate grayish brown (5YR 4/2) and show textures indicative of groundmass dissolution and/or decomposition to poorly crystalline clay in the form of high relief ovoids and tubes; thin opal rims form intermittent surface coatings on scoriae; and these textures may be overlain by petal-like halloysite textures (Figure 5a). The tephra are strongly non-dispersive and resettle quickly in water. The poorly crystalline clay and opal associated with altered scoriae form > 90 frequency percent of the authigenic components (Figure 10).

In comparison, the Pozzolane Rosse of the Santa Tecla catacomb quarry and the Santa Maria delle Mole borehole contains a predominance of zeolitic surface coatings and cements, in which patchy to continuous phillipsite rosettes formed first and were then followed by blocky chabazite (Figure 6). Altered scoriae form about 25 to 40 frequency percent of the volcanic components, and there is also a significant percentage, up to 20 frequency percent, of altered palagonite fragments (Table III). Scoria and palagonite groundmass are pervasively altered to poorly crystalline clay or dissolved, and zeolite forms about 35 to 50 frequency percent of the alteration components (Figure 10). The Santa Tecla samples have the overall characteristics of the least altered facies; leucite is generally intact, but may occasionally be replaced by analcime or dissolved. The overlying intermediate and greatest alteration facies may have been quarried away or, conversely, eroded away subsequent to glacial termination V (Marra & Rosa, 1995). The ignimbrite filled a tributary valley to the Tiber River and was, most likely, intermittently saturated by floodwaters. The zeolite cements may have developed in response to alkaline interstitial water compositions, and/or dissolution of palagonite (Hay & Iijima, 1963; Leggo et al., 2001).

The Istituto Nazionale di Geofisica e Vulcanologia borehole presents a juxtaposition of zeolitic and argillic alteration of Pozzolane Rosse (Jackson et al., 2007). The ignimbrite occupied a topographic plateau during marine isotope stage 12 and 11, but was buried by a leucititic melilite lava flow. The upper horizons of the ignimbrite, which contain a substantial proportion of altered palagonite fragments, up to 25 frequency percent, have relatively well developed chabazite cements and a lesser degree of groundmass decomposition to poorly crystalline clay and opal (INGV-2, -3; Figure 9, Table III). These palagonite-rich zones, which also occur in the upper Fosso di Tor Marancia section and the lower Santa Tecla and Santa Maria delle Mole sections, may be related to variations in the composition of eruptive pulses of the ignimbrite. The lower horizons, which contain a greater proportion of altered scoriae, 45 to 60 frequency percent of the whole rock, show a typical progression from the argillic intermediate altered facies (INGV-4, -5) to the least altered facies (INGV-8, -9, -10, -11) (Figure 10, Table III).

## ROMAN PREFERENCES

When integrated with new stratigraphic, petrographic, and chemical data for the mid-Pleistocene volcaniclastic deposits (Tables II; III; IV), the observations of the "color, composition, and cohesion" of Roman mortars and the macroscopic descriptions of their pozzolanic sands recorded by E. B. Van Deman (Table I) provide a firm basis for assessing Roman builders selections of mortar aggregates for republican and imperial age concrete construction in Rome. For example, Van Deman (1912a: 239) states that the mortar of republican era concrete constructions of the Roman Forum "is of an ashy-gray type and is very friable" and "the *arena* [sand] varies much in color, gray and brown predominating, while red is almost wholly lacking." Builders excavated this aggregate, which corresponds to the *cana* excavated sand of Vitruvius (*De Architectura*, 2.4.1), from the San Paolo and Aurelia Formations at the base of the Capitoline Hill (Jackson et al., 2007). It contains an abundance of grayish-brown, pedogenically-altered granular ash with waxy clays and earthy textures, as well as zeolitic tuff fragments and sedimentary sands, mainly quartz and sanidine. The San Paolo Formation was deposited subsequent to glacial termination V (Figure 3), so it contains ash erupted prior to about 437 ka (Marra, Florindo, & Boschi, 2008), including Pozzolane Rosse. The Aurelia Formation was deposited subsequent to marine isotope stage 10 (Figure 3), so it contains ash erupted prior to 337 ka, including Pozzolanelle and Tufo Lionato (Marra, Florindo, & Boschi, 2008). The mortars of the original construction of the Temple of Saturn (380 to 360 BC) also contain aggregate from the Aurelia Formation. Note, however, that Van Deman's descriptions of the Temple of Saturn mortar (1912b: 393) refer to a younger, 43 BC reconstruction of the podium, which contains Pozzolane Rosse (Table II).

Van Deman (1912a: 250) describes the mortar of the Forum of Julius Caesar (46 to 44 BC) as "grayish-red and almost entirely free from the friability of the earlier type. The *arena* is a true *pozzolana*, consisting of sharp angled particles, which vary much in size and are often very large. It is but slightly *terrosa*." Mortar from the concrete steps, walls, and vaults of the Forum of Julius Caesar indicate that builders selected Pozzolane Rosse of the greatest alteration facies, quarried from the upper levels of the ignimbrite (Figure 8). In addition, they included a significant proportion of pumice and (Amici, 1991) excavated directly from the San Paolo Formation along north flank of the Capitoline Hill at the building site (Jackson et al., in press). Here, the San Paolo Formation consists of quartz and feldspar sand grains as well as yellow gray (5Y 8/1), sanidine-bearing, airfall pumices erupted from Monti Sabatini volcano (Marra & Rosa, 1995). The closest outcrops of Pozzolane Rosse occur 2.5 km away, so builders evidently made a deliberate effort to transport this aggregate to the worksite. In many respects, the Forum of Julius Caesar records the innovative and experimental expertise of Roman builders of mid-first century BC in selecting diverse volcanic building materials for integrated cut stone and concrete masonry (Jackson et al., 2005; in press; Jackson & Marra, 2006).

During the Augustan age, builders produced a mortar that Van Deman (1912b: 392-393) describes as "without exception, of the dusky red type found only in this general period. It is far finer in quality and less friable than the mortar of the republican period, though lacking the rock-like hardness of a century later. The *arena* consists of red or reddish brown *pozzolana*, with which a little gray and white are occasionally mixed". The mortars of the Tomb of Caecilia Metella (~30 BC) and reconstructions of the Temple of Castor and Pollux (AD 6) and Temple of Concord (AD 10) are good examples (Van Deman 1912b: 392-393). Petrographic and x-ray diffraction studies of these mortars (Jackson et al., 2007) indicate that they contain reddened Pozzolane Rosse of the intermediate alteration facies, similar to the loose, unconsolidated ash of the Castèl di Leva and Fosso di Tor Marancia quarries and INGV borehole, along with less abundant dark gray scoriae of the least altered facies. The white particles described by Van Deman are calcite derived from lime calcined the limestone bedrock of the Appennines.

The reworked sediments of the Aurelia Formation used as aggregate in mortars from Nero's Golden House (AD 64-68) (figure 9b), may come from deposits on top of the Esquiline Hill (Marra & Rosa, 1995), through which builders would have had to excavate to create the Golden House construction site. Van Deman (1912b: 404) describes this mortar as a "dark gray or reddish gray type, coarse in its composition and, at times, somewhat friable. The *arena* consists of an inferior quality of *pozzolana*, coarsely sifted and slightly *terrosa*". Mortars of the Vespasian era (AD 69 to 70), which include those of the Flavian Amphitheater, or Colosseum (AD 70 to 78), reintroduced "the earlier clean, red pozzolana in place of the poorer grayish variety used in the buildings of Nero" (Van Deman, 1912b: 407), which had been constructed in haste after the great fire of AD 64.

In the Trajan era (AD 98-117) monuments, Van Deman (1912b: 415) states, "the mortar is of a clean-white and red type, very compact, and of flint-like hardness. The *arena* is composed of a clean red *pozzolana*, with a slight admixture of reddish brown and gray particles. It is very "sharp," finely sifted, and free from any earthy quality." Petrographic and chemical studies of the steps, walls, and vault concretes of the Basilica Argentaria (AD 113), and the Forum and Markets of Trajan (AD 96 to 115) indicate that the mortars of these structures all contain

Pozzolane Rosse of the least and intermediate altered facies, with both argillic and zeolitic alteration (Figure 1; Table II). Furthermore, the mortars of vaulted ceilings contain various proportions of light-colored, sanidine-bearing pumices of diverse origin (Bianchi et al., in press).

**POZZOLANIC CEMENTS**

The microstructures of the durable Trajanic era mortars, such as those at the Basilica Argentaria (AD 113) (Figure 11), are composed of a skeleton-like framework of blade-like cementitious gel, which penetrates ash accretions; pervades scoria vesicles; and securely bonds volcanic clasts within a cementitious matrix. Later calcite, possibly resulting from alteration of pozzolanic cements, fills the interstices of the blade-like framework, as shown in mortar from the Baths of Caracalla (AD 217) (Figure 11). The predominate reactive components of Pozzolane Rosse appear to be authigenic constituents (Figure 10) produced by a) pedogenic processes, giving the clay groundmass of scoriae, poorly crystalline clay and opal surface coatings, and translocated, halloysite surface coatings, or b) alteration generally in ground water, giving altered scoria groundmass, poorly crystalline clay and opal surface coatings, "petal" halloysite, and zeolite cements.

Experimental mortars developed by Sersale & Orsini (1969) document the pozzolanic reactivity of Pozzolane Rosse. Furthermore, the cementitious gels of Roman mortars analyzed by Roy & Langton (1989) reflect strong pozzolanic reaction of hydrated lime with volcanic ash aggregates. They have low Ca:Si, at about 0.3 to 1.0, alumina-enriched compositions, with Si:Al at about 2.5 to 3, and substantial alkali concentrations, with $K_2O$+$Na_2O$ at 2.5 to 4 weight percent giving potassic-, sodic-, calcic-, alumina-, ferric-silicate-hydrate, or KNCAFSH cement gel compositions. Roman lime is nearly pure CaO, with < 5 weight percent auxiliary oxides (Jackson et al., 2007), so the alumina- and alkali-rich cement gel compositions reflect the pozzolanic contribution of components of Pozzolane Rosse ash. The major element compositions of the cementitious matrix (Table IV) of three mortars of "flint-like hardness" (Van Deman 1912b: 415) from Trajanic age walls with Pozzolane Rosse aggregate from the least and intermediate alteration facies are similar: Ca:Si is low, 0.46 to 0.59; Si:Al is high, 2.7 to 3.0; and $K_2O$+$Na_2O$ is very high, 4.3 to 5.5 weight percent. In particular, the pervasive blade-like cement gels observed in many imperial age mortars (Figure 11) have KNACSH compositions with very low Ca:Si ratios.

These alkali-rich compositions differ substantially from the standard calcium-silica-hydrate (CSH) of modern Portland cements, which have much higher Ca:Si, at 1.5 to 3, and <1 weight percent $K_2O$+$Na_2O$ (Van Oss, 2005). The modern concrete industry prefers cement aggregates with very low alkali concentrations, because expansions produced by reaction between alkalis in the cement paste and reactive silica in the aggregates frequently lead to fracture and failure (Fournier & Bérubé, 2000). In contrast, the imperial age builders preferred the alkali-rich Pozzolane Rosse ash of alteration zones 1 and 2 (Figure 4) for their highest quality mortars. Indeed, the intermediate and least altered facies of Pozzolane Rosse at Castèl di Leva have ~20–23 wt % alkalis (Figure 7). Enigmatically, the strength and durability of these concretes have remained intact and robust (Table 1) in Rome's humid climate, exposed to high relative humidity (Jackson et al., 2005), a high ground water table (Corazza & Lombardi, 1995), and regularly inundations by Tiber River floodwaters (Bencivenga et al., 1995).

The heightened durability of the alkali-rich, hydrated lime-Pozzolane Rosse cements (Figure 11) of imperial Rome as compared with modern, alkali-rich, Portland-type cements may be the result of certain unique qualities of the alumina-rich Pozzolane Rosse pozzolan (Figure 7). Reaction of hydrated lime with alumina-rich components of Pozzolane Rosse ash may have increased sorption and binding of alkalis into very low Ca:Si calcium-aluminate-silicate hydrate (CASH) (Hong & Glasser, 2002). Sersale & Orsini (1969) record the high uptake of lime by

Pozzolane Rosse in lime-water suspensions, and the role of the release of large amounts of alkalis by zeolitic authigenic components in producing various calcium-alumina cementitious phases. The chemical and textural characteristics of the poorly crystalline clay groundmass of scoriae, fine rims of opal, thin halloysite cutans, as well as zeolitic cements may generate high reactivity with lime, producing these early pore fluids with high alkali concentrations. The alkaline pore fluids may have reduced calcium solubility, which in turn increased the potential for further alumina and alkali sorption into cementitious gels (Hong & Glasser, 2002). Experimental data (Hong & Glasser, 2002) indicate that desorption from an alkali-rich solid phase (with a lower Ca:Si limit of 0.85) in alkali free water is reduced. This suggests a somewhat irreversible process of alkali sorption into the Roman high alumina and low Ca:Si cementitious gels (Figure 11). Our ongoing research addresses these topics, which may help explain the high durability of ancient concrete constructions within the humid environment of Rome.

**CONCLUSIONS**

Pyroclastic flows, airfall deposits, and reworked volcaniclastic deposits of the Roman region (Karner et al., 2001) have distinctive primary compositions and textures, as well as secondary, authigenic components, which are recognizable in Roman mortars. These deposits and their alteration characteristics record episodes of mid-Pleistocene climate change in the Roman region (Figure 3), determined by stratigraphic investigations and radioisotopic dating (Karner and Marra, 1998; Marra et al., 2008). The geochemical compositions, sequences of mineral changes, and authigenic components of volcanic ash deposits at Castèl di Leva and other quarries through the Roman region record diverse alteration regimes that developed in response to changing paleowater compositions and paleoclimate conditions accompanying glacial eustatic variations from marine isotope stage 12 through 10 (Figure 4). Micromorphological descriptions of the pedogenic textures and authigenic surface coatings of samples collected from representative exposures of Pozzolane Rosse in modern quarries (Figures 5, 6) and from ancient mortars (Figure 1, 8, 9) give insights into the reactive components of the volcanic ash with hydrated lime and the provenance of the ash selected by Roman builders as pozzolans.

The textures and compositions of these volcanic aggregates in Roman mortars give new information about the development of Roman builders' expertise during late first century BC, and their eventual selection of specific alteration facies of Pozzolane Rosse ash for high quality imperial age concrete work (Van Deman, 1912a; b). Friable republican era mortars commonly contain primary and reworked volcaniclastic sediments (Figure 9) deposited by complex surficial processes involving erosion and fluvial deposition resulting from mid-Pleistocene climate change coupled with aggradational pyroclastic eruptions (Karner & Marra, 1995). These are the *cana* excavated sands, which Vitruvius described as unsuitable for durable mortars (*De Architectura*, 2.4.1). In contrast, robust imperial era mortars contain geochemically altered ash from the least and intermediate altered horizons of the Pozzolane Rosse ignimbrite (Tables I, II), where altered volcanic glass and crystals are slightly dissolved and/or further altered to form argillic and zeolitic authigenic components (Figures 5, 6) that apparently enhanced pozzolanic activity, producing highly durable alkali- and alumina-rich cements (Figure 11). These are the *rubra* and *nigra* sands excavated sands, which Vitruvius described as ideal for mortars (*De Architectura*, 2.4.1). Strong, hydrolytic, pedogenesis evidently produced this uniquely reactive and mechanically resistant pozzolan, with which Roman builders developed their extraordinarily durable concretes. The petrographic characteristics of Pozzolane Rosse (Figure 10) indicate that these mineral changes and the alteration components show a rather consistent pattern through the Roman region.

Petrographic and chemical investigations of the Roman ash and mortars validate the macroscopic observations made by E. B. Van Deman (1912a; b) nearly 100 years ago, without the benefit of modern analytical techniques (Table I). These observations show the value of careful, objective, empirical descriptions of archaeological materials, and they provide a historical framework with which modern archaeologists may evaluate the mortars of many republican and imperial age monuments in Rome. Archaeologists can use the analytical data presented in this paper to identify the "alteration provenance" of the Pozzolane Rosse ash in the mortars of Rome, and evaluate the preferences of Roman builders for pozzolanic aggregates in imperial age monumental concrete construction. Further investigation of the petrographic and chemical characteristics of the aggregates and cementitious matrix of ancient mortars will clarify the role of volcanic ash in the potential development of extraordinarily durable alkali- and alumina-rich pozzolanic cementitious complexes within ancient Roman concretes throughout the Mediterranean area.

**FIGURE CAPTIONS**

Figure 1. Imperial age Roman concretes showing textures of pozzolanic mortars containing Pozzolane Rosse granular volcanic ash. a) slice through a 7 cm thick section of a drill core from the eastern wall of the Great Hall, Markets of Trajan (AD 96 to 115). Coarse aggregate (*caementa*) clasts are brick, TGdVT: Tufo Giallo della Via Tiberina, TL: Tufo Lionato, and lava from Pozzolane Rosse; b) photomicrograph of vesicles of Pozzolane Rosse scoria aggregate of the Baths of Caracalla (AD 217) wall mortar. Traces of authigenic opal rims with cog-like forms are overgrown by blade-like pozzolanic cements; and c) photomicrograph of vesicles of Pozzolane Rosse scoriae of the Great Hall wall mortar. Traces of authigenic chabazite surface coatings are partially overgrown by fibrous pozzolanic cements.

Figure 2. Generalized geologic map of the Roman region, showing the locations of quarries and boreholes in mid-Pleistocene Pozzolane Rosse volcanic ash. (after Jackson et al., 2007).

Figure 3. Chronology of volcanic layers based on $^{40}Ar/^{39}Ar$ dating and paleopedological processes from marine isotope stage 12 to 9, with respect to glacial terminations determined by mild summer insolation minima (grey shaded areas) compared with those predicted by orbital tuning of the deep-sea $\delta^{18}O$ curve (dashed lines) from Lisiecki & Raymo (2005) (after Marra, Florindo, & Boschi, 2008).

Figure 4. Castèl di Leva quarry, volcanic stratigraphy, geochemical variations, and paleopedological zones. **1, 2, 3, 4** of the stratigraphic section refer to paleopedological zones described in the text. The italic numbers on the right side, *1* through *7*, of the diagram refer to the chronology of volcanic layers and pedological processes that occurred between marine isotope stages 12 to 10, described in Figure 3. Major element chemistry from Deocampo, Jackson, and Marra (in review).

Figure 5. Photomicrographs of ash, Castèl di Leva quarry. a) the least altered facies of the Pozzolane Rosse ignimbrite (zone 1) has leucite mainly intact, decomposition of scoria groundmass to poorly crystalline clay and opal, and halloysite with "petal" textures; b) the intermediate alteration facies of the Pozzolane Rosse ignimbrite (zone 2) has leucite commonly dissolved or replaced by analcime, opal rims around scoriae with poorly crystalline clay groundmass, and thin colorless cutans of translocated halloysite; c) the greatest alteration facies of Pozzolane Rosse, shown here in the co-ignimbritic ash cloud (zone 3), has leucite wholly dissolved or replaced by analcime, but clinopyroxene mainly intact, lesser decomposition of scoria groundmass, and thick cutans of illuvial clay and silt-sized scoria (see also Figure 8); and d) the reworked, colluvial ash (zone 4) has an altered sanidine-bearing, sideromelane ash matrix of Monti Sabatini airfall tephra and Pozzolane

Rosse scoriae with yellow, illuvial clay cutans, leucite is mainly intact but clinopyroxene is partially to wholly dissolved.

Figure 6. Photomicrographs of Pozzolane Rosse ash, Santa Tecla catacomb quarry. a) an early stage of phillipsite precipitation produced intergranular rosettes; and b) pervasive chabazite cements with blocky textures filled grain interstices and scoriae vesicles.

Figure 7. Ternary diagram showing the $SiO_2$, $Al_2O_3$, and alkali ($Na_2O + K_2O + CaO + MgO$) compositions of Pozzolane Rosse, Castèl di Leva quarry.

Figure 8. Photomicrographs of pozzolanic mortars, Forum of Julius Caesar (46 to 44 BC). a) steps mortar has aggregate of the Pozzolane Rosse greatest alteration facies and sand-sized, sanidine-bearing pumices of the San Paolo Formation, excavated from the building site. A rim of silt-sized scoriae and illuvial yellow clay around an altered scoria makes a sharp contact with the cementitious matrix, indicating little reactivity with hydrated lime; b) vaulted ceiling mortar shows root traces from the Pozzolane Rosse greatest alteration facies. Rims of weathered Fe-glaebules are surrounded by thick, yellow illuvial clay; and c) vaulted ceiling mortar shows a cross-sectional form of a rounded pumice and ubiquitous analcime replacement of leucite within Pozzolane Rosse scoriae of the greatest alteration facies.

Figure 9. Photomicrographs of Roman mortars with Aurelia and San Paolo Formation aggregates. a) the Temple of Concord (121 BC) mortar shows pedogenically altered Pozzolane Rosse (PR) clasts with leucite replacement of analcime similar to those of the Tenuta di Capannacce zone 3 paleosol (Figure 10), pedogenically altered clasts of Pozzolane Nere (PN) similar to those of the incipient paleosol at Castel di Leva quarry, and fragments of reworked Tufo Lionato (366±7ka, Marra et al., 2008); and b) the Golden House (AD 64 to 68) mortar shows strongly pedogenically altered clasts of Pozzolane Rosse (PR) with thick, illuvial clay filling vesicles, clasts of pedogenically altered Pozzolane Nere (PN), and

fragments of Tufo Lionato and Tufo Rosso a Scoriae Nere from Monti Sabatini ( 449±1ka, Marra et al., 2008). The Temple of Concord mortar aggregate was probably excavated at the building site and records a period of republican era experimentation with various aggregates excavated from the Capitoline Hill. The Golden House mortar aggregate was probably excavated at the building site on the Esquiline Hill and records a period of hasty building after the AD 64 fire.

Figure 10. Ternary diagram showing abundances (frequency percentages) of authigenic components relative to the total percentage of authigenic components determined through point counts of Pozzolane Rosse samples from quarries and boreholes (Table III). The components include the poorly crystalline clay and opal of altered tephra, "illuvial" or "petal" halloysite cutans, and phillipsite and chabazite zeolite cements. **1**, **2**, and **3** refer to samples from the paleopedogenic zones of Figure 4 with predominantly argillic alteration. **Z** refers to samples with predominantly zeolitic alteration.

Figure 11. Blade-like cementitious gels of imperial age Roman wall mortars with alkali- and alumina-rich compositions. a) Basilica Argentaria (AD 113), backscattered SEM image and representative EDX analysis; and b) Baths of Caracalla (AD 217), secondary electron (SE) image, representative EDX analysis. The blade gel forms a skeleton like framework that securely bonds scoriae to a cementitious matrix. Later calcite, possibly resulting from alteration of pozzolanic cements, fills the interstices of cement framework.

**TABLE CAPTIONS**

Table I. Historical context of Roman concrete construction and pozzolanic mortars, based on verbatim descriptions of Roman concretes by E. B. Van Deman (1912a, b). These observations form the basis of our sampling and petrographic and chemical investigations. [1]Jackson et al., 2007; [2]Marra and Rosa 1995; [3] For geological nomenclature of tuff masonry, see Jackson and Marra, 2006. ("Cappellaccio" is Tufo di Palatino or Grottarossa Pyroclastic Sequence Tuff; "grayish yellow tuff" is Tufo Giallo della Via Tiberina; "brownish red tuff" is Tufo Lionato; "selce" is lava.) The geologically correct "tuff" is substituted for Van Deman's use of "tufa". [4]Jackson et al., in press; [5]Lancaster, 2005; [6]Bianchi et al., in press.

Table II. List of the Roman mortars studied with petrographic analyses in this study. For dates and descriptions of the ancient monuments, see the *Lexicon Topographicum Urbis Roma* (Steinby, 1993-1999). 1 is the least altered facies of Pozzolane Rosse; 2 is the intermediate alteration facies; and 3 is the greatest alteration facies indicating strong ultisolic pedogenesis. All samples were collected with the permission and collaboration of the Sovraintendenza ai Beni Culturali del Comune di Roma and the Soprintendenza Archeologica di Roma.

Table III. Point counts of Roman mortars. Castèl di Leva quarry (CASTEL), Santa Tecla Catacomb quarry (STECLA), Istituto Nazionale di Geofisica e Vulcanologia borehole (INGV), Fosso di Tor Marancia quarry (TC), and Tenuta di Capannacce quarry (CAPANN); n is the number of points counted per thin section; a is thick, yellow, pedogenic illuvial clay cutans; b is colorless to pale yellow, translocated halloysite in upper horizons or "petal" halloysite in lower horizons; 1 is least altered facies; 2 is intermediate altered facies; 3 is greatest altered facies; [1]52% altered fine sideromelane airfall ash from Monti Sabatini volcanic district.

Table IV. Major element chemical compositions of the cementitious matrix of wall mortars from the Forum and Markets of Trajan, containing the least and intermediate altered facies of Pozzolane Rosse ash aggregate. The cementitious matrix is the binding phase of the pozzolanic mortar; it includes tephra <2 mm diameter and alkali- and alumina-rich pozzolanic cements (Figure 11).

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**Table I.** Descriptions of Roman concretes from the republican and imperial eras by Esther B. Van Deman (1912a, b)

| Period | Monument | Mortar | Excavated Sands (*harenae fossiciae*) | Lithological & Alteration Provenance[1] | Coarse Aggregate (*caementa*) |
|---|---|---|---|---|---|
| Later republican: 210 BC to 82 BC | Temple of Concord, 121 BC; Temple of Castor and Pollux, 117 BC | "ashy gray color and very friable"; "due to admixture of earthy material in the sand in the *arena* [sand], called by Vitruvius *terrosa* (*De Arch*. 2.4.1) | "varies much in color with brown and gray predom-inating"; "red almost wholly lacking"; "large amount of earthy material" | Reworked volcaniclastic and sedimentary sands of the San Paolo and Aurelia Formations[2] | "cappellaccio and grayish yellow tuff"[3]; "broken and rejected materials of earlier periods" |
| Summary: "Monuments of *opus caementicium* show but little change either in materials or methods of construction" | | | | | |
| Sulla: 82 to 79 BC | Tabularium, 70s BC | "ashy gray but slightly less friable than preceding period" | "darker in color and a little less *terrosa* than earlier"; "no change in lime is perceptible" | Reworked sands of the Aurelia Formation | "almost wholly brownish red tuff with little admixture of older materials" |
| Summary: "ashy color and friability of mortar"; "early types of *caementa* materials and technique." | | | | | |
| Julius Caesar: 48 to 27 BC | Forum of Julius Caesar, 44-46 BC | "ashy gray of earlier monuments, though a little darker"; "of superior quality, finer texture and hardness" | "of the same general type as earlier, but less *terrosa"*; *"*lime is of a slightly better grade" | Mixtures of Pozzolane Rosse, greatest altered facies, and San Paolo Formation[4] sediments and pumice | "grayish brown tuff and peperino, with travertine for points of special pressure" |
| | Theater of Marcellus, initiated 40s BC, inaugurated 13 BC | "grayish red"; "approaching Augustan mortar"; "almost entirely free of friability of earlier type" | "true pozzolana"; "reddish brown and dark gray predominate, but there is also much red"; "sharp angled particles"; "it is but slightly *terrosa*" | Pozzolane Rosse, inter-mediate altered facies, some friable mortars contain Pozzolane Rosse and roughly crushed Tufo Lionato | "varies, according to nature of the structure"; "reddish brown tuff, travertine and selce" |
| Summary: "darker gray or reddish gray mortar"; "free from friability", "introduction of a special red pozzolane by Julius Caesar?" | | | | | |
| Augustus to Claudius: 27 BC to AD 41 | Tomb of Caecelia Metella, ~30 BC; Temple of Castor and Pollux, AD 6; Temple of Concord, AD 10 | "dusky red type found, without exception, during this period" | "a clean, red variety…to which is due the strength of Roman concrete", "red or red-brown, with gray"; "fine red dust" | Tomb of C. Metella: Pozzolane Rosse, upper least altered facies; Temples of Concord, Castor and Pollux: Pozzolane Rosse, inter-mediate altered facies | "reddish brown tuff," "grayish yellow tuff in vaults" |
| Summary: "mortar is finer and less friable than that of republican period, though lacking the rock-like hardness of that of a century later"; "introduction of a special variety of pozzolana"; "clearer recognition of values of various materials and methods of construction"; a recognized, though imperfect, canon of construction (Vitruvius, *De Arch.* 2.8.17; Suetonius, *Augustus*, 89)." | | | | | |
| Claudius to Domitian: AD 41 to 96 | Golden House (Nero), AD 64-68; Colosseum (Vespasian), AD 79 | Nero: "dark gray or reddish gray, coarse, somewhat friable"; Flavians: "dirty white and red, firmly tenacious" | Vespasian: "reintroduction of clean red pozzolana in place of poorer, friable grayish [*terrosa*] variety, used in buildings of Nero" | Golden House: Aurelia Formation; Colosseum: Pozzolane Rosse, intermediate altered facies, vault mortars may also contain light-colored pumice[5] | Nero: "refuse of buildings destroyed by fire"; Flavians: "foundations of selce"; "vaults of yellowish gray tuff" |
| Summary: Nero: "new building regulations…so [Rome] would not be so easily swept away by another conflagration"; Vespasian: "intelligent, economical use, skillful combination of already existing materials and methods"; Domitian: "little contribution to the art of construction." | | | | | |
| Trajan to Marcus Aurelius: AD 98 to 180 | Baths of Trajan AD 104-109; Forum and Markets of Trajan AD 105-112 | "clean-white and red type, very compact and almost flint-like in hardness"; "fineness and homogeneous quality" | "clean red pozzolana, slight admixture of reddish-brown and gray particles"; "sharp, finely sifted, free from any earthy quality" | walls: Pozzolane Rosse intermediate and least altered facies and 2-3% finely ground Tufo Lionato; vaults also contain 20-30% light-colored pumices[6] | foundations: "selce and a little travertine"; walls: "broken bricks of all kinds"; "regularity and beauty in facings" |
| Summary: "fineness and homogeneous quality of the mortar used in various parts of the structures"; "marvelous adaptation not only of different materials but of the different grades of the same material to the structural demands of various buildings or parts of a single building." | | | | | |

**Table II.** List of the ancient mortars considered with petrographic analysis in this study.

| Monument | Samples | Date | Structural Element | Pozzolanic Aggregate |
|---|---|---|---|---|
| Temple of Saturn | 06-SATURN-C3, C4 | 380-360 BC | podium | Aurelia Formation |
| | 06-SATURN-C1, C2 | 43 BC | podium | Pozzolane Rosse (3) |
| Navalia (Porticus Aemilia) | 04-PA-C1, C2 | 192-174(?) BC | walls | Pozzolanelle |
| Temple of Castor and Pollux | 06-CASTOR-C1 to C3 | 117 BC | podium, walls | Aurelia & San Paolo Formations |
| | 06-CASTOR-C4 to C5 | AD 6 | walls | Pozzolane Rosse (2) |
| Temple of Concord | 06-CONCORD-C5 | 121 BC | podium | San Paolo Formation |
| | 06-CONCORD-C3 to C4 | AD 10 | walls | Pozzolane Rosse (2) |
| Tabularium | 06-TABULAR-C1, C2 | 70s BC | walls | Aurelia & San Paolo Formations |
| Rostra | 07-ROSTRA-C1 | republican | podium | Aurelia & San Paolo Formations |
| | 07-ROSTRA-C2 | Augustan | walls | Pozzolane Rosse (2) |
| Forum of Caesar | 04-FC-C1 to C4<br>07-FC-C1-C5 | 46-44 BC | steps, walls, vaults | Pozzolane Rosse (3) and San Paolo Formation |
| Tomb of Caecilia Metella | 06-METELL-C1 to C7 | ~ 30 BC | walls, vaults | Pozzolane Rosse (1 & 2) |
| Portico d'Ottavia | 07-OTTAVIA-C1 | 27-25 BC | podium | Pozzolane Rosse (1, 2, 3) |
| Theater of Marcellus | 06-MARCELL-C1 to C7 | ~13 BC | walls | Pozzolane Rosse (2) & occasional crushed tuff |
| Golden House | 04-DA-C1, C4 | AD 64-68 | walls | Aurelia Formation |
| Colosseum | 05-COLOSS-C1 to C9 | AD 70 – 79 | walls, vaults | Pozzolane Rosse (2 & 1) |
| Baths of Trajan | 04-DA-C2 | AD 104-109 | walls | Pozzolane Rosse (2 & 1) |
| Markets of Trajan | 07-MTRAI-C1 to C3<br>08-GRAULA-C1 to C4 | AD 100-110 | walls, vaults | Pozzolane Rosse (2 & 1) |
| Forum of Trajan | 07-FTRAI-C1 to C26 | AD 105-112 | steps, walls, vaults | Pozzolane Rosse (2 & 1) |
| Basilica Argentaria | 04-FC-C4 | AD 113 | walls | Pozzolane Rosse (2 & 1) |
| Temple of Hadrian | 08-ADRIANO-C1-C4 | ~ AD 145 | steps, walls, vault | Pozzolane Rosse (1) |
| Baths of Caracalla | 04-CARAC-C1 | AD 217 | walls | Pozzolane Rosse (2 & 1) |

**Table III.** Frequency percentages of primary volcanic components and secondary authigenic components within Pozzolane Rosse ash from quarries and boreholes in the Roman region

| Sample | n | Depth (meters) | Scoriae | Palagonite | Lava and Crystals | Voids | Halloysite | | Poorly Crystalline Clay | Opal | Phillipsite | Chabazite | Alteration Facies |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | a | b | | | | | |
| 06-CASTEL-01 | 546 | 0 | 3 | 5 | 16 +52[1] | 3 | 4 | 8 | 7 | 2 | / | / | colluvial ash |
| 06-CASTEL-05 | 535 | 0.1 | 55 | 1 | 7 | 7 | 20 | / | 7 | 2 | / | / | 3; paleosol |
| 06-CASTEL-07 | 638 | 0.75 | 49 | 1 | 4 | 11 | 20 | 6 | 7 | 2 | / | / | 3; paleosol |
| 06-CASTEL-08 and -09 (1.35 to 1.85 meters depth) are loose incoherent ash | | | | | | | | | | | | | 2; argillic |
| 06-CASTEL-13 | 538 | 3.85 | 45 | / | 10 | 13 | / | 2 | 26 | 3 | / | 1 | 1; argillic |
| 06-CASTEL-15 | 505 | 4 | 44 | 1 | 8 | 15 | / | 4 | 23 | 5 | / | / | 1; argillic |
| 08-TC2-PR-A | 625 | 0.1 | 37 | 20 | 7 | 8 | / | 10 | 14 | 4 | / | / | 2; argillic |
| 04-TC-PR-06 | 626 | 0.8 | 36 | 7 | 13 | 10 | / | 15 | 12 | 4 | / | / | 2; argillic |
| 97-CAPANN-10 | 613 | 0 | 50 | 2 | 7 | 5 | 20 | 4 | 11 | 1 | / | / | 3; paleosol |
| 07-CAPANN-01 to -10 (0 to 4.5 m depth) are loose incoherent ash | | | | | | | | | | | | | 2; argillic |
| 07-CAPANN-14 | 602 | 6.5 | 39 | 2 | 11 | 7 | / | 4 | 34 | 2 | / | 1 | 1; argillic |
| 07-STECLA-03 | 605 | 1.5 | 31 | 12 | 12 | 8 | / | 2 | 17 | 6 | 6 | 6 | 1; zeolitic |
| 07-STECLA-06 | 502 | 3 | 35 | 14 | 8 | 4 | / | 1 | 15 | 3 | 2 | 18 | 1; zeolitic |
| 07-STECLA-09 | 616 | 4.5 | 41 | 7 | 9 | 5 | / | 2 | 17 | 3 | 3 | 13 | 1; zeolitic |
| 07-STECLA-11 | 664 | 5.5 | 24 | 21 | 7 | 3 | / | 1 | 21 | 3 | 2 | 18 | 1; zeolitic |
| INGV-PR-01 | 579 | 0 | 23 | 25 | 11 | 4 | / | / | 3 | 2 | / | 32 | 3; zeolitic |
| INGV-PR-02 | 560 | 0.5 | 31 | 17 | 13 | 13 | / | / | 8 | 2 | / | 16 | 2; zeolitic |
| INGV-PR-03 | 532 | 1.5 | 45 | 10 | 9 | 11 | / | / | 16 | 2 | / | 7 | 2; zeolitic |
| INGV-PR-04 | 562 | 2.7 | 55 | 1 | 10 | 11 | / | 2 | 8 | 5 | / | 8 | 2; zeolitic |
| INGV-PR-05 | 508 | 4.5 | 62 | / | 8 | 6 | / | 2 | 9 | 6 | / | 7 | 2; argillic |
| INGV-PR-06 | 527 | 5.5 | 46 | / | 15 | 12 | / | 8 | 6 | 13 | / | / | 2; argillic |
| INGV-PR-07 (7.5 meters depth) is loose incoherent ash | | | | | | | | | | | | | 2; argillic |
| INGV-PR-08 | 553 | 10 | 50 | / | 12 | 10 | / | 3 | 24 | 1 | / | / | 1; argillic |
| INGV-PR-09 | 527 | 13 | 47 | 2 | 13 | 9 | / | 2 | 22 | 5 | / | / | 1; argillic |
| INGV-PR-10 | 515 | 14.5 | 45 | 11 | 11 | 6 | / | 2 | 14 | 9 | 1 | 1 | 1; argillic |
| INGV-PR-11 | 604 | 15.7 | 48 | 3 | 17 | 10 | / | 3 | 13 | 6 | 0 | 1 | 1; argillic |

**Table V**. Chemical Compositions of Cementitious Matrix of Wall Mortars, Forum and Markets of Trajan

| Sample | $SiO_2$ wt% | $TiO_2$ wt% | $Al_2O_3$ wt% | $Fe_2O_3$ wt% | MnO wt% | MgO wt% | CaO wt% | $Na_2O$ wt% | $K_2O$ wt% | $P_2O_5$ wt% | LOI wt% | Total wt% | Ca:Si |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Great Hall, Markets of Trajan, eastern wall core | | | | | | | | | | | | | |
| GRAULA 20a-C1 | 34.12 | 0.65 | 12.61 | 6.98 | 0.14 | 3.26 | 20.29 | 0.84 | 3.46 | 0.48 | 82.83 | 100.00 | 0.59 |
| Basilica Ulpia, Forum of Trajan, wall core of staircase C | | | | | | | | | | | | | |
| FTRAI-C14 | 34.19 | 0.66 | 11.74 | 7.35 | 0.14 | 3.32 | 19.71 | 0.48 | 4.19 | 0.60 | 82.38 | 100.00 | 0.58 |
| Basilica Ulpia, Forum of Trajan, wall core of staircase A | | | | | | | | | | | | | |
| FTRAI-C16 | 34.77 | 0.64 | 11.48 | 7.09 | 0.14 | 3.06 | 16.13 | 1.16 | 4.35 | 1.28 | 82.10 | 100.00 | 0.46 |

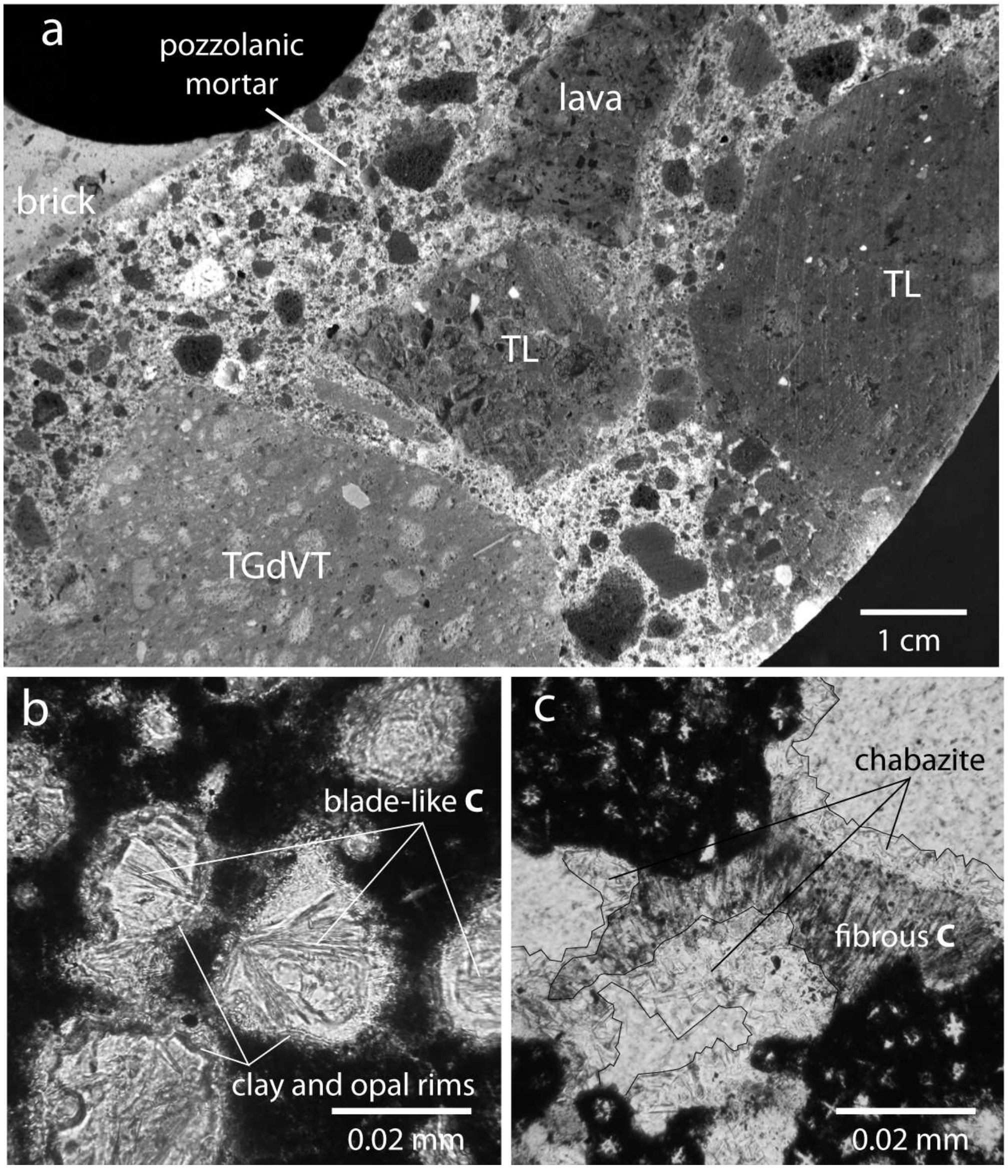



Figure 1. Imperial age Roman concretes showing textures of pozzolanic mortars containing Pozzolane Rosse granular volcanic ash. a) slice through a 7 cm thick section of a drill core from the eastern wall of the Great Hall, Markets of Trajan (AD 96 to 115). Coarse aggregate (caementa) clasts are brick, TGdVT: Tufo Giallo della Via Tiberina, TL: Tufo Lionato, and lava from Pozzolane Rosse; b) photomicrograph of vesicles of Pozzolane Rosse scoria aggregate of the Baths of Caracalla (AD 217) wall mortar. Traces of authigenic opal rims with cog-like forms are overgrown by blade-like pozzolanic cements; and c) photomicrograph of vesicles of Pozzolane Rosse scoriae of the Great Hall wall mortar. Traces of authigenic chabazite surface coatings are partially overgrown by fibrous pozzolanic cements.
108x126mm (300 x 300 DPI)

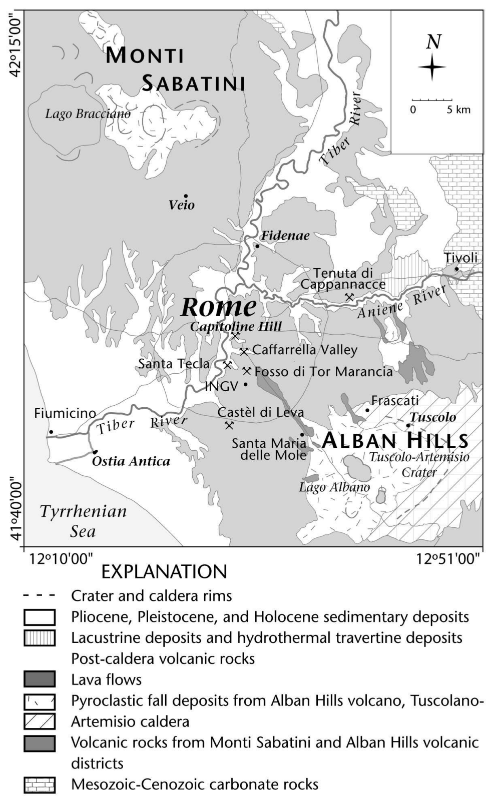
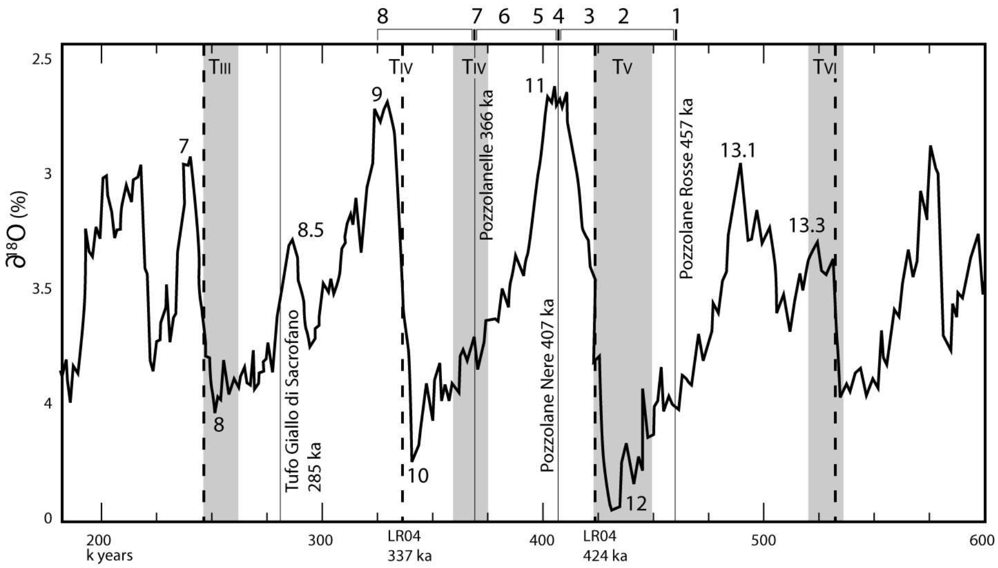



Figure 2. Generalized geologic map of the Roman region, showing the locations of quarries and boreholes in mid-Pleistocene Pozzolane Rosse volcanic ash. (after Jackson et al., 2007).
177x250mm (300 x 300 DPI)




1 Eruption of Pozzolane Rosse ignimbrite, development of weak andisol
2 Strong hydrolytically altered paleosol develops on Pozzolane Rosse
3 Colluvial redeposition of paleosol with Monti Sabatini airfall ash
4 Eruption of Pozzolane Nere ignimbrite, development of weak andisol
5 Incipient paleosol forms on Pozzolane Nere ignimbrite
6 Airfall and colluvial ashes bury paleosol, polygonal joints form on surface
7 Eruption of Tufo Lionato and Pozzolanelle ignimbrites (Villa Senni eruption cycle)
8 Aurelia Formation fills paleovalleys

Figure 3. Chronology of volcanic layers based on 40Ar/39Ar dating and paleopedological processes from marine isotope stage 12 to 9, with respect to glacial terminations determined by mild summer insolation minima (grey shaded areas) compared with those predicted by orbital tuning of the deep-sea δ18O curve (dashed lines) from Lisiecki & Raymo (2005) (after Marra, Florindo, & Boschi, 2008).
122x96mm (300 x 300 DPI)

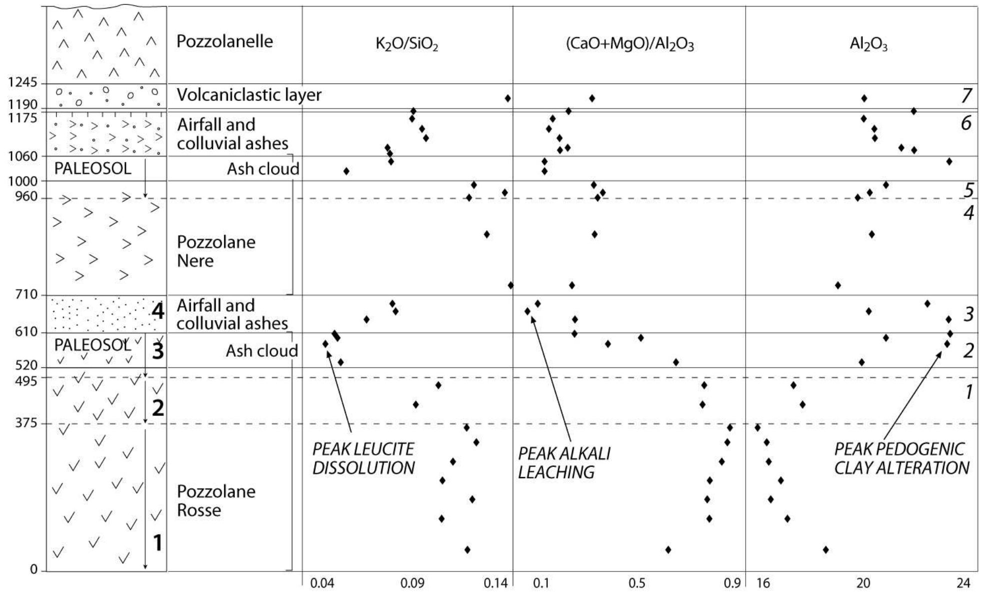



Figure 4. Castèl di Leva quarry, volcanic stratigraphy, geochemical variations, and paleopedological zones. 1, 2, 3, 4 of the stratigraphic section refer to paleopedological zones described in the text. The italic numbers on the right side, 1 through 7, of the diagram refer to the chronology of volcanic layers and pedological processes that occurred between marine isotope stages 12 to 10, described in Figure 3. Major element chemistry from Deocampo, Jackson, and Marra (in review).
125x73mm (300 x 300 DPI)

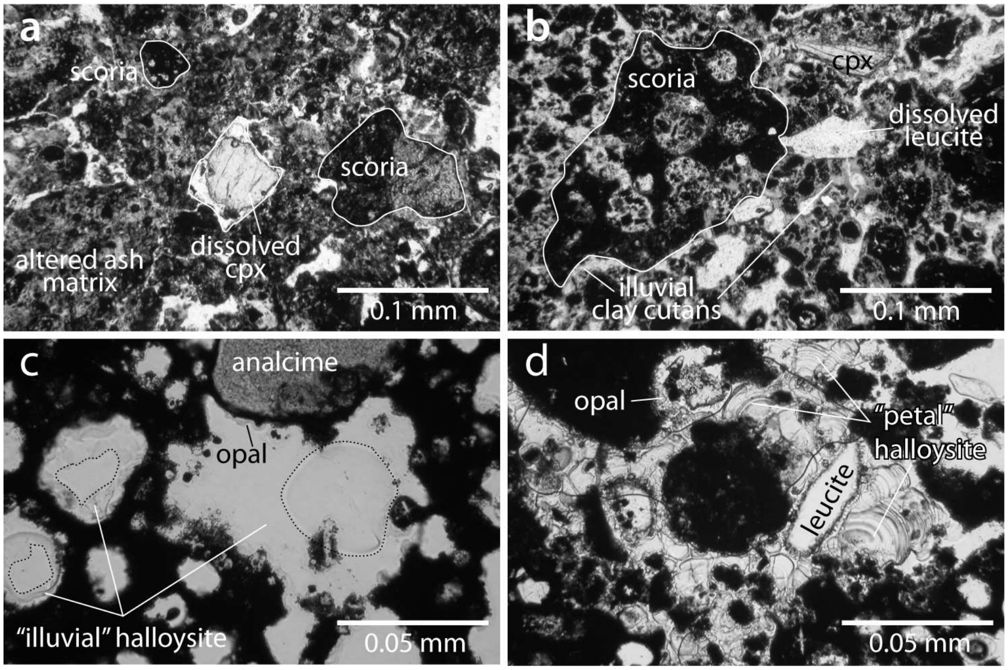



Figure 5. Photomicrographs of ash, Castèl di Leva quarry. a) the least altered facies of the Pozzolane Rosse ignimbrite (zone 1) has leucite mainly intact, decomposition of scoria groundmass to poorly crystalline clay and opal, and halloysite with "petal" textures; b) the intermediate alteration facies of the Pozzolane Rosse ignimbrite (zone 2) has leucite commonly dissolved or replaced by analcime, opal rims around scoriae with poorly crystalline clay groundmass, and thin colorless cutans of translocated halloysite; c) the greatest alteration facies of Pozzolane Rosse, shown here in the co-ignimbritic ash cloud (zone 3), has leucite wholly dissolved or replaced by analcime, but clinopyroxene mainly intact, lesser decomposition of scoria groundmass, and thick cutans of illuvial clay and silt-sized scoria (see also Figure 8); and d) the reworked, colluvial ash (zone 4) has an altered sanidine-bearing, sideromelane ash matrix of Monti Sabatini airfall tephra and Pozzolane Rosse scoriae with yellow, illuvial clay cutans, leucite is mainly intact but clinopyroxene is partially to wholly dissolved.
124x82mm (300 x 300 DPI)

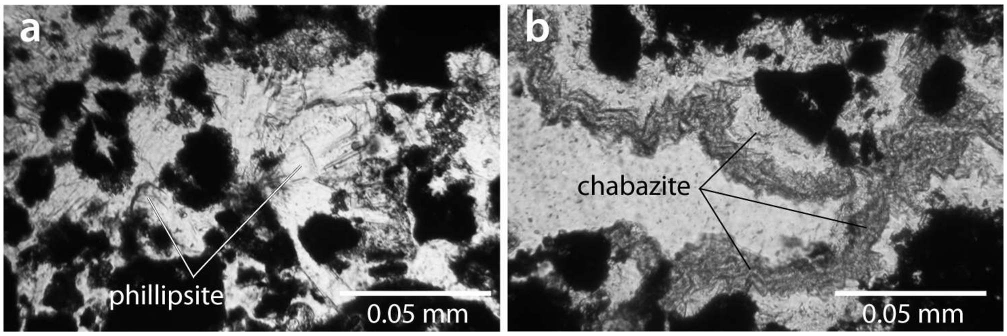



Figure 6. Photomicrographs of Pozzolane Rosse ash, Santa Tecla catacomb quarry. a) an early stage of phillipsite precipitation produced intergranular rosettes; and b) pervasive chabazite cements with blocky textures filled grain interstices and scoriae vesicles.
124x40mm (300 x 300 DPI)

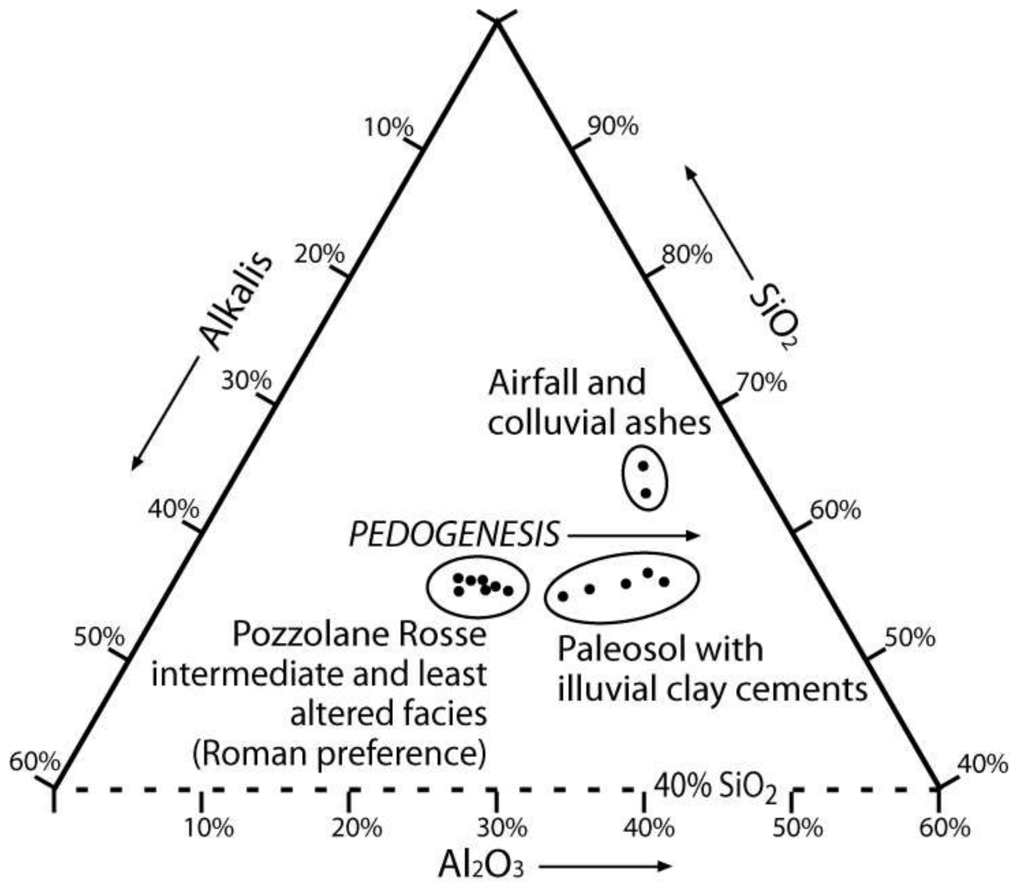



Figure 7. Ternary diagram showing the SiO2, Al2O3, and alkali (Na2O + K2O + CaO + MgO) compositions of Pozzolane Rosse, Castèl di Leva quarry.
62x54mm (300 x 300 DPI)

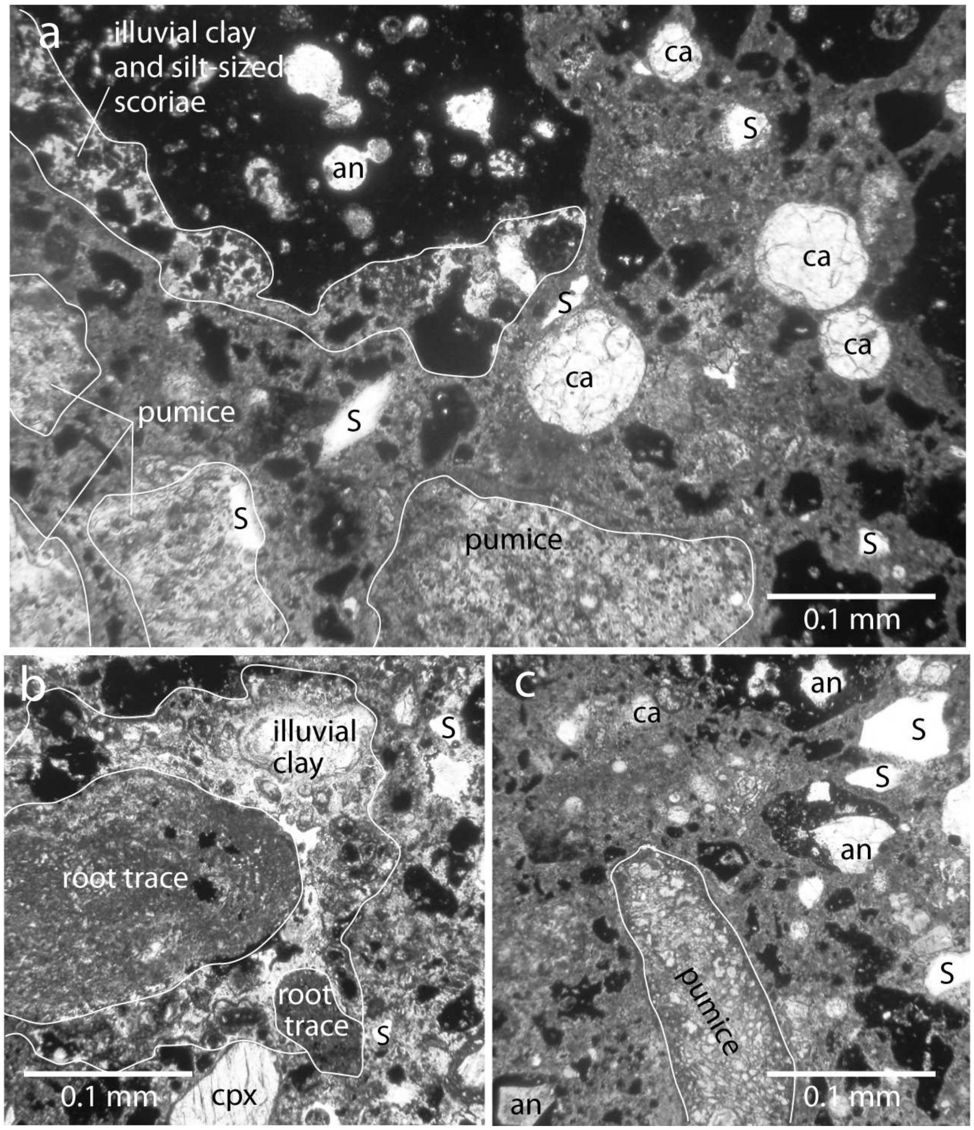



Figure 8. Photomicrographs of pozzolanic mortars, Forum of Julius Caesar (46 to 44 BC). a) steps mortar has aggregate of the Pozzolane Rosse greatest alteration facies and sand-sized, sanidine-bearing pumices of the San Paolo Formation, excavated from the building site. A rim of silt-sized scoriae and illuvial yellow clay around an altered scoria makes a sharp contact with the cementitious matrix, indicating little reactivity with hydrated lime; b) vaulted ceiling mortar shows root traces from the Pozzolane Rosse greatest alteration facies. Rims of weathered Fe-glaebules are surrounded by thick, yellow illuvial clay; and c) vaulted ceiling mortar shows a cross-sectional form of a rounded pumice and ubiquitous analcime replacement of leucite within Pozzolane Rosse scoriae of the greatest alteration facies.
108x134mm (300 x 300 DPI)

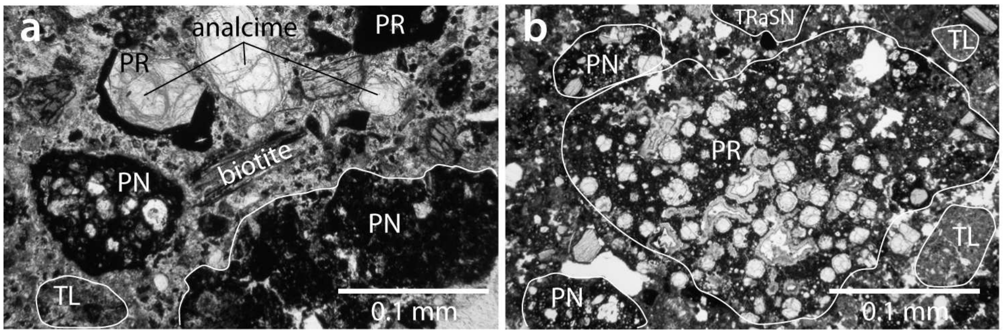



Figure 9. Photomicrographs of Roman mortars with Aurelia and San Paolo Formation aggregates. a) the Temple of Concord (121 BC) mortar shows pedogenically altered Pozzolane Rosse (PR) clasts with leucite replacement of analcime similar to those of the Tenuta di Capannacce zone 3 paleosol (Figure 10), pedogenically altered clasts of Pozzolane Nere (PN) similar to those of the incipient paleosol at Castel di Leva quarry, and fragments of reworked Tufo Lionato (366±7ka, Marra et al., 2008); and b) the Golden House (AD 64 to 68) mortar shows strongly pedogenically altered clasts of Pozzolane Rosse (PR) with thick, illuvial clay filling vesicles, clasts of pedogenically altered Pozzolane Nere (PN), and fragments of Tufo Lionato and Tufo Rosso a Scoriae Nere from Monti Sabatini ( 449±1ka, Marra et al., 2008). The Temple of Concord mortar aggregate was probably excavated at the building site and records a period of republican era experimentation with various aggregates excavated from the Capitoline Hill. The Golden House mortar aggregate was probably excavated at the building site on the Esquiline Hill and records a period of hasty building after the AD 64 fire.
125x40mm (300 x 300 DPI)

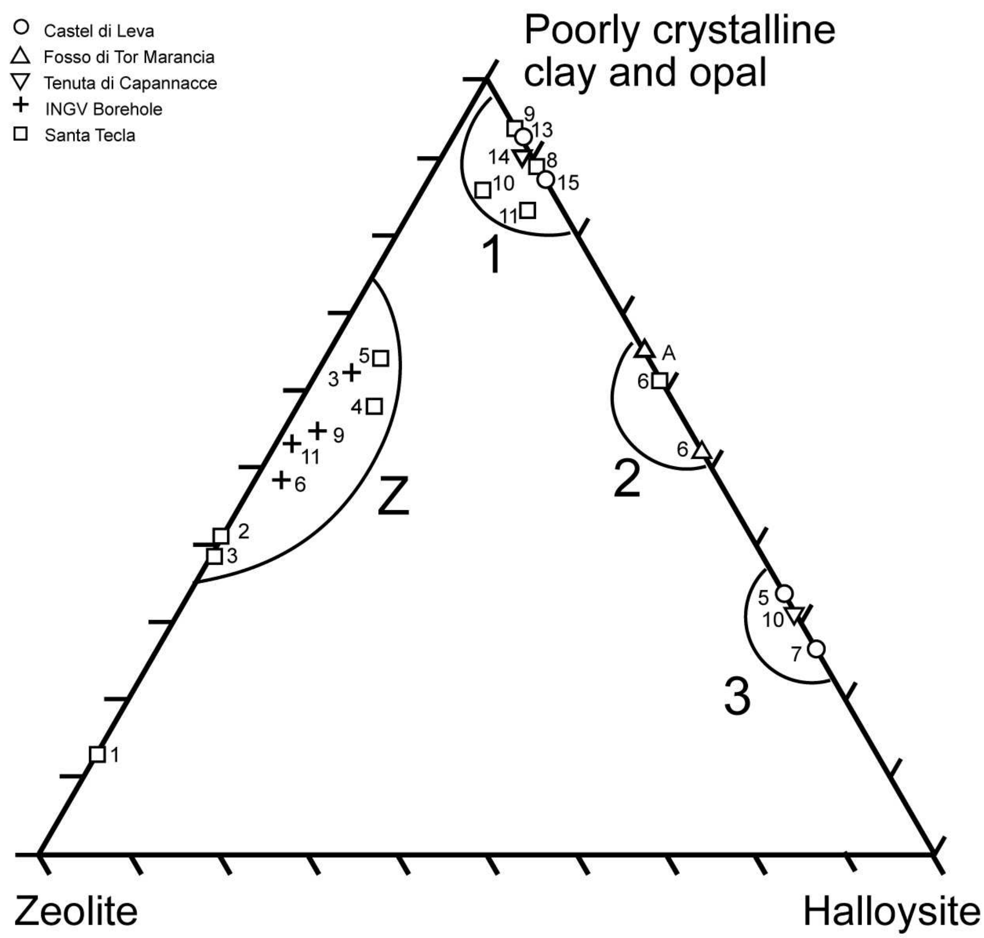



Figure 10. Ternary diagram showing abundances (frequency percentages) of authigenic components relative to the total percentage of authigenic components determined through point counts of Pozzolane Rosse samples from quarries and boreholes (Table III). The components include the poorly crystalline clay and opal of altered tephra, "illuvial" or "petal" halloysite cutans, and phillipsite and chabazite zeolite cements. 1, 2, and 3 refer to samples from the paleopedogenic zones of Figure 4 with predominantly argillic alteration. Z refers to samples with predominantly zeolitic alteration.
107x108mm (300 x 300 DPI)

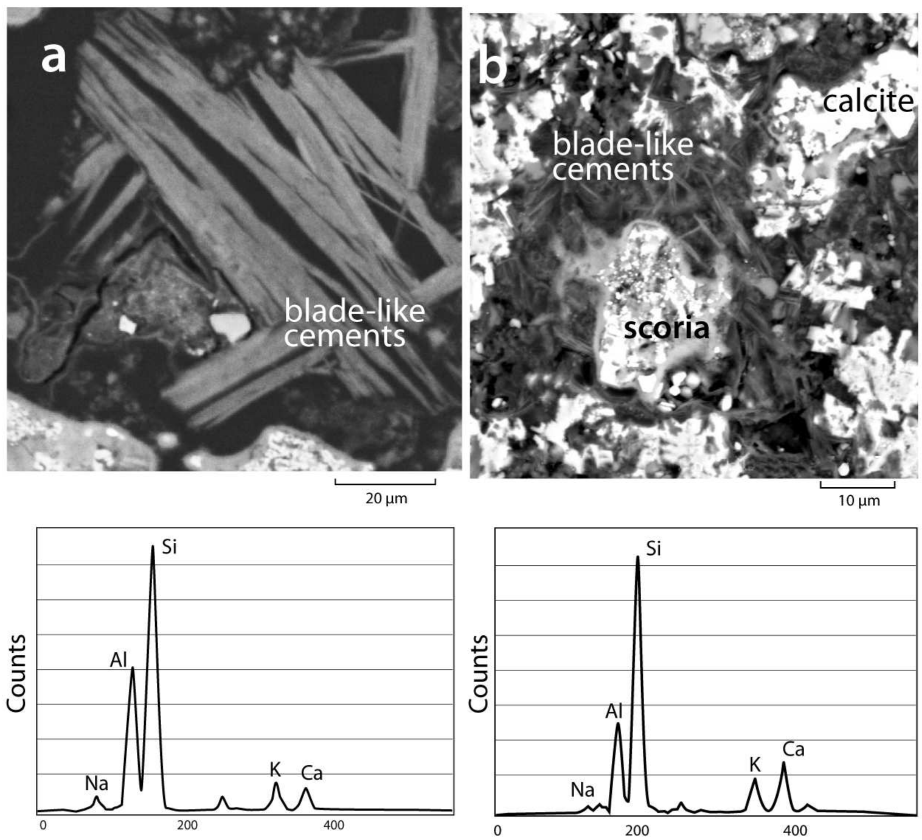



Figure 11. Blade-like cementitious gels of imperial age Roman wall mortars with alkali- and alumina-rich compositions. a) Basilica Argentaria (AD 113), backscattered SEM image and representative EDX analysis; and b) Baths of Caracalla (AD 217), secondary electron (SE) image, representative EDX analysis. The blade gel forms a skeleton like framework that securely bonds scoriae to a cementitious matrix. Later calcite, possibly resulting from alteration of pozzolanic cements, fills the interstices of cement framework.
114x108mm (300 x 300 DPI)