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Micromorphological Textures and Pozzolanic Cements in Imperial Age Roman Mortars

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Abstract The highly durable pozzolanic mortars of wall concretes from the Theater of Marcellus and Great Hall of Trajan’s Markets preserve traces of micromorphological textures in altered Pozzolane Rosse volcanic ash. Reaction of hydrated lime with potassic scoriaeous ash, and halloysite, phillipsite, and chabazite surface coatings, as well as Tufo Lionato tuff particles, produced distinct, alkali- and alumina-calcium-silica hydrate cement microstructures, including strätlingite. The assemblage of diverse pozzolanic components in the Trajanic mortar was remarkably effective in combining hydrated lime.

1 Introduction

The volcanic ash-hydrated lime mortars of the extraordinarily durable, composite concretes of Imperial age monuments in Rome contain altered granular, scoriaceous ash aggregate (harenae fossiciae) from the Pozzolane Rosse pyroclastic-flow, erupted at 456±3 ka from Alban Hills volcano (Fig. 1) [1]. The lime is ~95 wt% CaO calcined from the limestone bedrock of the Appennines [2]. The high quality mortars of the walls of the Great Hall of Trajan’s Markets (~96-115 CE), have Pozzolane Rosse from various alteration facies, finely ground Tufo Lionato zeolitic tuff, amorphous alkali- and alumina-rich cement hydrates, and strätlingite (gehlinite hydrate, C2ASH8), which gives modern cements good durability and compressive strength [3]. The mortars of the Theater of Marcellus (~23-11 BCE), constructed 120 years earlier, also have strätlingite cement (Fig. 2), Pozzolane Rosse with mainly argillic alteration, and slightly more coarsely ground Tufo Lionato. The pozzolanic components of Pozzolane Rosse ash are the alkali-rich groundmass of altered scoriae; opal and limpid halloysite surface coatings from a transitional Bt to Bw soil horizon (Fig. 3a); and phillipsite and
chabazite surface coatings from the lowermost C horizon of the deposit, altered in ground water (Fig. 3b,c) [1]. Here, we address questions about the diverse compositions of the altered Pozzolane Rosse ash, their relict, authigenic clay and zeolite textures in the mortars, and the compositions and microstructures of associated pozzolanic cements. We emphasize the importance of micromorphological context [4] in describing the stratigraphic distribution and composition of pozzolanic components of the Pozzolane Rosse pyroclastic-flow deposit: the opaline silica, poorly crystalline clay minerals, and zeolites that activate pozzolanic reactions [5]. Petrographic and backscattered scanning electron microscope images (BSE-SEM) and energy dispersive spectrographic (EDS) analyses provide a foundation for gaining insights into the Pozzolane Rosse and Tufo Lionato ashes, describing the mortar microstructures, and developing durable alkali-rich calcium-aluminum-silica cement gels and strätlingite cements for modern repair mortars.

Fig. 1 Map showing the Roman region and specimen sites

Fig. 2 Theater of Marcellus substructure, SEM-EDS analysis of strätlingite cement
Alteration facies of the Pozzolane Rosse pyroclastic-flow

Pozzolane Rosse is the lowermost of the three Alban Hills mid-Pleistocene granular volcanic ash pyroclastic-flow deposits, which are locally interlayered with epiclastic ash and Monti Sabatini airfall and pyroclastic-flow deposits, as shown for the Cappannacce quarry northeast of Rome (Figs. 1, 3). Recent work [1] identifies three main alteration facies, characterized by different pozzolanic components within the Pozzolane Rosse pyroclastic-flow deposit. Several experimental programs [5, 6] have investigated the characteristics of the ash excavated from modern quarries near Colleferro and Segni, ~50 km east of Rome. The samples come from a loose, incoherent reddened facies of Pozzolane Rosse (A, Figs.1, 3a) or a lithified, coherent dark gray facies [7] (B, C, Figs. 1, 3b, c). The studies report conflicting compositions of primary volcanic crystals and authigenic alteration components [7]. Results range from leucite, pyroxene, and brown mica and clusters of dark gray scoriae cemented with chabazite; primary leucite and diopside crystals, authigenic analcime crystals, and chabazite cements; to analcime crystals, only, with clay mineral cements. Furthermore, SEM images of the Colleferro pozzolan show well-developed phillipsite cements [5]. The chemical and mineralogic compositions of [5, 6] correspond to the least altered facies of [1].

Petrographic studies of Pozzolane Rosse collected near Segni, from Montelanico to Colleferro (Fig. 1), give insights into the stratigraphic distribution of micromorphological textures developed during mid-Pleistocene alteration of the pyroclastic-flow deposit. For example, a well-lithified deeper specimen collected at ~210 msl (C, Figs. 1, 3c, c), has dark gray scoriae and occasional palagonite fragments, and pervasive chabazite cements that have consumed the fine volcanic ash fraction. This resembles the specimen described by Sersale [7] and the least altered facies, altered in ground water at Santa Tecla catacomb in Rome (Fig. 1) [1]. A less lithified specimen collected at ≥210 msl (B, Fig. 1, 3b, b), has dark gray scoriae with euhedral phillipsite surface coatings, and resembles that described by Massazza [5]. Leucite may be intact or replaced by analcime, similar to the higher levels of the least altered facies, altered in ground water at Santa Tecla [1]. However, the void space and phillipsite crystals in the Colleferro ash are partially filled or coated with thin, pale yellow clay, previously shown to be translocated halloysite that developed during hydrolytic weathering and illuviation during mid-Pleistocene pedogenesis [1]. Similar textures occur in dark gray Pozzolane Rosse at the Corcolle quarries northeast of Rome [1]. Higher in the section, outcrops between ~270–260 msl on the Montelanico Road reveal reddened Pozzolane Rosse with leucite replaced by analcime or wholly dissolved (A, Figs. 1, 3a, a) and thick, birefringent, illuvial halloysite coatings, corresponding to the greatest alteration facies of the mid-Pleistocene paleosol [1], as well as a lower, intermediate alteration facies (a’) with partially intact leucite, and opal and pale yellow translocated halloysite coatings corresponding to a Bt to
Bw soil horizon. The approximate stratigraphic locations of the specimens are shown in the context of the Cappannacce quarry, although there is only minimal zeolite in the deeper horizons there. The pronounced zeolite of the lower Segni horizons (c) may reflect interstitial water compositions related to closed hydrologic systems [8], probably where the pyroclastic-flow filled deep valleys, and interstitial groundwater with higher alkalinity favored precipitation of chabazite [9]. Imperial age builders selected only the intermediate and least altered facies (a', b, c) [1] for monumental concrete constructions.

**Fig. 3** Micromorphological textures of Segni ash situated within the stratigraphic context of the mid-Pleistocene paleosol and lower horizons of Pozzolane Rosse at Capannacce quarry.

Authigenic components and pozzolanic cements

The Pozzolane Rosse of the Theater of Marcellus mortars is mainly the intermediate alteration facies from the middle horizons of the pyroclastic-flow (a', Figs. 3, 4). The opal and halloysite occur as surface coatings, and in naturally
cemented ash accretions on the perimeters of larger scoriae, as at Castel di Leva quarry south of Rome [1]. Leucite (lc) is intact, dissolved, or replaced by analcime. Mortar cements in ash accretions (Fig. 4a) occur as lamina of petrographically isotopic cement gel (Cl) and acicular strätlingite (str). Strätlingite also occurs in the cementitious matrix and in irregular voids (Fig. 2). The palagonitic glass and authigenic phillipsite (ph) of Tufo Lionato particles ≥1 mm remain somewhat intact (Fig. 4b). Relict spherical voids, perhaps due to free water in the wet mortar mix, have birefringent, fibrous cement (Cf) fillings. Although the mortars are somewhat poorly compacted, they are highly coherent. The Colosseum foundation mortars, ~70–80 CE, also have strätlingite [10].

Fig. 4 Theater of Marcellus mortar, a) pozzolanic cements in ash accretion, b) binding matrix

Pozzolane Rosse scoriae in the Great Hall mortars (Fig. 5) preserve traces of halloysite, phillipsite, and chabazite. Builders evidently created an aggregate mix from the full range of alteration horizons (Fig. 3), most likely excavated from different quarries. Tufo Lionato particles are mainly 0.1-1 mm (11). Distinct cement microstructures are associated with the diverse reactive components. For example, an ash accretion on a reddened scoria (Fig. 5a) reveals in situ dissolution of microscoriae (ms), diopside (di), and leucite (lc), with coatings of bright, petrographically isotropic, cement lamina (Cl). Pale yellow, illuvial halloysite (hal) coatings on a dusky yellowish brown scoria (Fig. 5b) contain localized, radiating spherulites of acicular crystals (Cs), yet also have incipient alteration to gypsum. Vesicles in a dark gray scoria have apparent phillipsite (ph) (Fig. 5c) in contact with a very fine ~10µm equigranular cement with low first order birefringence (C). Relict chabazite selvages in the vesicles of another dark gray scoria (Fig. 5d) have intergrown, first order birefringent, acicular crystals in radial spherulites (Cs). The palagonitic glass and zeolite of Tufo Lionato particles are strongly dissolved. There are few relict lime clasts.

SEM-BSE images and EDS analyses further illustrate the diverse cement microstructures (Fig. 6). For example, a petrographically isotropic cement in a scoria vesicle that once contained a thin halloysite coating (Fig. 6a), has a potassic silica-calcium-alumina hydrate composition (a-1) and fine, fibrous microstructures with a silica-calcium-alumina hydrate composition (a-2). The vesicles of a large, gray scoria (Fig. 6b), with a potassic groundmass (b-1), have potassic silica-
alumina-calcium hydrate coatings (b-2), with an unusual colorless (PPL), first order gray, rod-and-block microstructure that has begun to dissolve. A Tufo Lionato particle (Fig. 6c) has a calcium-silica-alumina-ferric rind (c-1) that may reflect dissolution of iron-rich palagonitic glass; diopside is finely etched and phillipsite cement is dissolved (12). The calcium-alumina silica fibrous cement (d-1) with second order birefringence, in a spherical void (Fig. 6d), is similar to that in the Theater of Marcellus mortar (Fig. 4b, Cf).

3 Pozzolanic processes in the Imperial age mortars

The Theater of Marcellus mortars (Figs. 2, 4) have Pozzolane Rosse with predominantly opal (SiO₂) and halloysite (Al₂Si₂O₅(OH)₄) coatings. The alkalis released from dissolution of scoriae groundmass and the palagonitic glass and zeolite of Tufo Lionato particles may have lowered lime concentrations and increased silica concentrations in pore fluids, favoring the formation of strätlingite cement [8, 5]. Even so, calcite (relict lime) clasts are common and Tufo Lionato
particles may retain zeolite and glassy matrix (Fig. 4b) suggesting that the volcanic pozzolans could not combine all the lime present; this would have been a 3:1 volumetric proportion if the Vitruvian formulation were followed [2]. In contrast, the Great Hall wall mortar has few relict calcite clasts; Tufo Lionato particles have glass and zeolite nearly wholly dissolved; and distinct cement microstructures and compositions are associated with host pozzolans. Here, pozzolanic reaction apparently proceeded more effectively, more fully consuming free lime and pozzolanic components of the volcanic ash.

The reaction of lime in aqueous suspension and in pastes with a variety of natural pozzolans confirms that a strong relation exists between the compositions of reactants and their pozzolanic products [6, 12, 5]. For example, reaction of chabazite-bearing Pozzolane Rosse from the Segni area with hydrated lime in suspension produced CSH, C₃A·CaCO₃·12H₂O, and C₃AS₃–C₃AH₆ crystalline phases. Significantly, reaction in pastes after five years curing produced CSH, C₃ASH₈ (gehlenite hydrate), and C₅A·CaCO₃·12H₂O (6). Further investigations of
the ancient cement compositions and microstructures, and pozzolanicity tests of Tufo Lionato and Pozzolane Rosse will provide new insights into the chemical processes that activate the durable Imperial Roman cement systems, as well as the evolving expertise of the engineers who developed the mortars over several centuries of experimentation.

4 Conclusions

Pozzolanic reaction of volcanic ash with lime and water to produce enduring calcium silicate and aluminate hydrates is remarkably effective when mortar systems contain activating phases such as volcanic glass, zeolites, amorphous silica, and poorly crystalline clay minerals (5). Pozzolane Rosse volcanic ash has the extraordinary distinction of possessing all these reactive components, in distinct stratigraphic horizons associated alteration in ground and surface water. Trajanic era builders formulated a highly reactive aggregate design mix with these alteration facies and finely ground Tufo Lionato. Diverse pozzolanic cement phases reflect the compositions of specific micromorphological textures.

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6 References

