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ANCIENT ROMAN MORTARS: MIX DESIGN, MINERALOGICAL COMPOSITION AND MINEROGENETIC SECONDARY PROCESSES

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INTRODUCTION

Since ancient times humans prepared mortars, *i.e.*, artificial products deriving from transformed geological materials. Mortars are composite materials, consisting of hydraulic or aerial binding material, aggregates and additives, passive or active, which react with binding material and are modified during their setting (Moropoulou *et al.*, 2004).

Their uses have been various, such as production of bedding mortar for masonry buildings, frescoes and decorations using particularly valuable mortars, concretes production for maritime constructions and many others. Large use of these materials was not simply based on development of their specific functions but also from the historical period and location where they were prepared.

Excellent preservation state of many products, made in Roman age, demonstrates the high technological level achieved by these construction workers.

Although evidences show that Egyptians knew "the way" to produce lime, this geomaterial began to be largely used by Greeks and especially by Romans, that diffused it since the third century B.C. (Collepardi, 2003). Many documents about the acquired knowledge in the construction field have been passed down thanks to these civilizations. Several writers treated the building art of the Roman builders such as: Cato in *De Agricola* (160 B.C.), M. Vitruvius Pollio (I century B.C.) in the ten books of *De Architectura* and Pliny the Elder (23 - 9 A.D.) with its *Naturalis Historia* treaty.

The Roman builders knew that combination of lime with special volcanic deposits (*pozzolana*), conferred hydraulic properties to mortars, allowing underwater hardening and giving greater mechanical strength too (Collepardi, 2003). The use of pozzolana marked a revolutionary progress in construction sectors, due to the ability of mixture to cure also underwater (hydraulic limes) even with higher speed, compared to that required by carbonation processes of slaked lime. Whenever volcanic material was not available, fragments of artificial materials (such as bricks and ceramics, which have the same hydraulic properties of pozzolana) were used.

The aims of this research project were: a) improve knowledge of Roman construction techniques by means of detailed microstructural and compositional examination of *i*) cementitious binding matrix and *ii*) aggregates (to point out both mortars' mix-design and provenance of raw materials) along with b) the study of secondary minerogenetic processes and c) comparing the obtained results with the modern mortars.

Several archaeological sites were chosen for mortars sampling, in particular those related both to ancient Roman structures built in subaerial environment, submerged later by seawater, and structures which had been in contact for long times with "fresh" water (*e.g.*, thermal baths and cisterns). Such Roman structures are located in Phlegrean Fields area (*Piscina Mirabilis* and *Terme di Baia*) and along Sorrento peninsula coast (*Villa del Capo* or *Bagni della Regina Giovanna* at Massa Lubrense and *Villa del Pezzolo* at Seiano), in Campania region.

Sampling was achieved in cooperation with archaeologists and thanks to authorization and the supervision of Archaeological Superintendence of Campania Region (courtesy of Dr. Budetta and Dr. Talamo).

45 samples (13 *Piscina Mirabils*; 9 *Terme di Baia*; 13 *Villa del Capo*; 10 *Villa del Pezzolo*) were obtained with specific criteria, such as little invasiveness, representativeness, limited samples size and visual impact; a photographic campaign before and after sampling was also carried out.

Archive research at Superintendence offices wera also conducted, to find out about areas subjected to previous restoration work.

Studies on these geomaterials could be very interesting to understand "secrets" of such enduring resistance; in fact, cisterns or Villae resisted over two thousand years to the strength of waves and weathering of seawater. They are a tangible example of a transformation product of geological materials (namely geomaterials) that can last so long during the eras. Even today the concept of "durability" is of great interest. The current concrete technologists trying constantly to improve formulations to achieve new special concrete able to resist to the aggressive agents such as seawater and sulphates.

ANALITYCAL TECHNIQUES

Collected samples (bedding, coating and floor mortars) were used for an integrated analytical program using multiple methodologies such as: optical microscopy (OM) on thin sections, X-ray powder diffraction (XRPD), scanning electron microscopy analysis (SEM), energy-dispersion X-ray spectroscopy (EDS), X-ray fluorescence (XRF), thermal analyses (TGA-DTA) and mercury intrusion porosimetry (MIP). This research activity was performed in collaboration with CTG (Group Technical Center) of Italcementi, HeidelbergCement Group at Bergamo (Italy).

RESULTS AND DISCUSSION

Mineralogical, petrographical, chemical and physical-mechanical analyses were performed on mortars samples according to their different mix designs.

Bedding mortars resulted constituted by a mixture of slaked lime, water, fine grained volcanic materials and aggregates of volcanic and carbonate rocks origin, whereas, coating and floor mortars, may be considered as a mixture of slaked lime, water, fine grained volcanic and ceramic materials with volcanic, ceramic and carbonatic aggregates.

The mix-design of coating and floor mortars is also called *Cocciopesto* or *Opus signinum*. Vitruvius, in fact, describes this mix design, calling it "signinum", as the mix that was used to waterproof tanks containing water, thermal pools and caverns of aqueducts (*Sin autem loca dura erunt aut nimium venae penitus fuerint, tunc signinis operibus ex tectis aut superioribus locis excipiendae sunt copiae. In signinis autem operibus haec sunt facienda. Uti harena primum purissima asperrimaque paretur, caementum de silice frangatur ne gravius quam librarium, calx quam vehementissima mortario mixta, ita ut quinque partes harenae ad duas respondeant. Eorum fossa ad libramentum altitudinis, quod est futurum, calcetur vectibus ligneis ferratis, De Architectura*, *Liber* VIII).

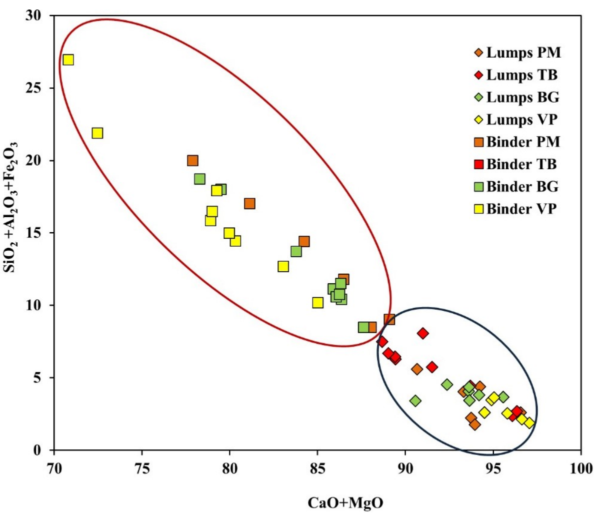
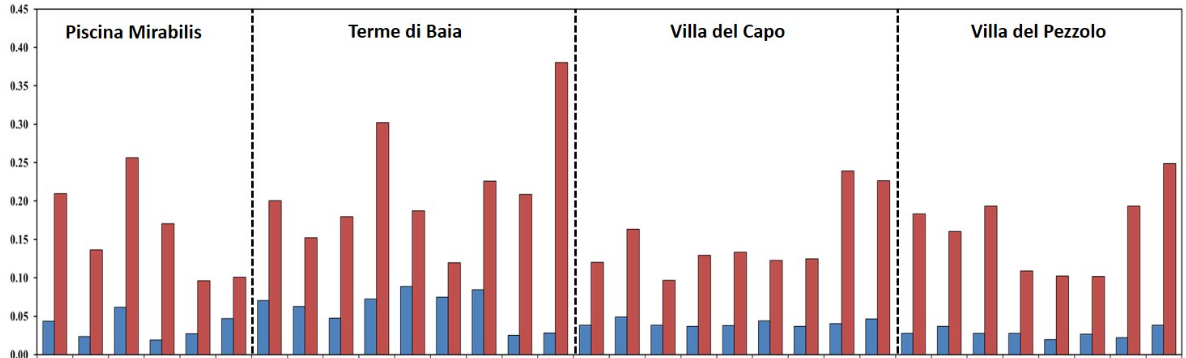


Fig. 1 - CaO + MgO *vs*. SiO_2 diagram (EDS), lumps (blu circle) and binder (red circle), PM: Piscina Mirabilis, TB: Terme di Baia; BG: Villa del Capo; VP: Villa del Pezzolo.

Hydraulicity of examined mortars was verified by SEM-EDS and thermal analyses.

EDS microanalyses were performed on binder and lime lumps, which consist of unreacted lime (Bakolas *et al.*, 1995; Barba *et al.*, 2009). The results showed that lime lumps are composed mainly of CaO, with very high CaO + MgO values, between 89% and 96%, whereas higher concentrations of $SiO_2 + Al_2O_3 + Fe_2O_3$ (9 - 20%) were retrieved in the binder, with respect to the lime lumps (1 - 6%), and lower contents of CaO + MgO (75 - 86%; Fig. 1).

Hydraulicity Index (HI, Fig. 2), calculated according to Boynton's formula (HI = SiO_2 + Al_2O_3 + Fe_2O_3)/(CaO + MgO); Boynton, 1966), for lime mps of the mortars showed very low values (HI < 0.10, quicklime; Zawawi, 2006), while binders' HI ranges between 0.10 and 0.38 (weakly-moderately hydraulic). Thus, results of HI analysis allowed to state that hydraulicity of mortars is associated to the abundant presence of materials with "pozzolanic" activity (ceramic and volcanic fragments), which increases considerably since the reactive silica contained in the "pozzolana" reacts with calcium hydroxide, leading to formation of calcium aluminum silicate hydrates: the so-called C-A-S-H phases (De Luca *et al.*, 2015).



	MM2	MM4	MM5	ZM8	M3	M7	VA1	SV1	SV2	PT1	PT2	TM1	TM2	TM3	V1
Lumps	0.04	0.02	0.06	0.02	0.03	0.05	0.07	0.06	0.05	0.07	0.09	0.08	0.08	0.02	0.03
Binder	0.21	0.14	0.26	0.17	0.10	0.10	0.20	0.15	0.18	0.30	0.19	0.12	0.23	0.21	0.38

	BG1	BG3	BG4	BG5	BG9	BG10	BG11	BG12	BG13	VP1 L	VP2 L	VP3 L	VP4 L	VP5 L	VP7 L	VP9 L	VP10 L
Lumps	0.04	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.05	0.03	0.04	0.03	0.03	0.02	0.03	0.02	0.04
Binder	0.12	0.16	0.10	0.13	0.13	0.12	0.12	0.24	0.23	0.18	0.16	0.19	0.11	0.10	0.10	0.19	0.25

Fig. 2 - Hydraulicity Index (HI), lime lumps (blue) and binder (red) for all analyzed mortars.

Thermal analyses were also performed to evaluate total (binder plus aggregates) hydraulic features of these materials. This technique was used by many authors to study and classify ancient and modern mortars on the basis of their relative contents of gypsum, carbonates and hydraulic compounds (Moropoulou *et al.* 1995; 2005; Bonazza *et al.*, 2013). Investigated mortars (fraction < 63 µm) showed a progressive loss of mass in the range 20-1000 °C. In agreement with literature data, particular attention was paid in the 200-600 °C range, where the percentage of mass losses may be entirely attributed to the water fraction (SBW) chemically bound to hydraulic phases (C-A-S-H), whereas at temperature higher than 600 °C, mass loss is essentially due to the decomposition of carbonates.

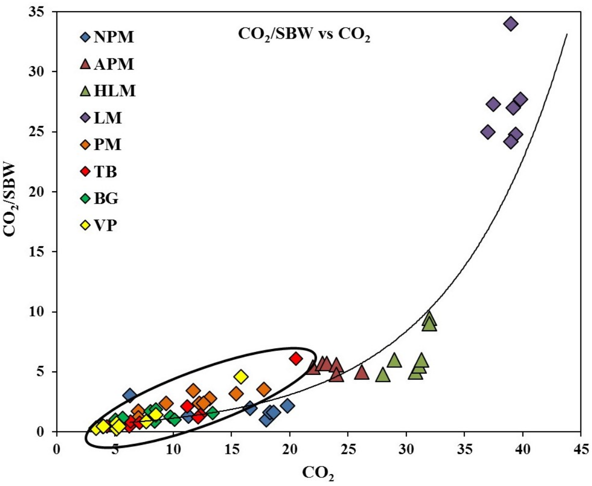


Fig. 3 - CO_2/SBW *vs*. CO_2 diagram, comparing data from analyzed Roman mortars (black circle) and from Moropoulou *et al.*, 2005. (NPM: natural pozzolanic mortars; APM: artificial pozzolanic mortars; HLM: Hydraulic lime mortars; LM: lime mortars; PM: Piscina Mirabilis; TB: Terme di Baia; BG: Villa del Capo; VP: Villa del Pezzolo).

Using the obtained data, CO_2/SBW ratio was calculated, and according to Moropoulou *et al.* (2005), all analyzed mortars can be classified as highly hydraulic. In particular, examined mortars fall in the field of of natural pozzolanic mortars (Fig. 3).

As regards raw materials, provenance of lime and carbonatic fragments is still unknown, even if it is highly reasonable to think that they were produced on site using locally available materials. The Geological Map of the Bay of Naples shows that Campania Plain is completely bordered by carbonatic deposits of Mesozoic age.

Concerning volcanic fragments, a local provenance was confirmed. Origin of volcanic aggregates retrieved in the mortar samples from

Piscina Mirabilis, *Terme di Baia* and *Villa del Capo*, was ascribed to the Neapolitan Yellow Tuff formation (NYT), deriving from the volcanic activity of Phlegrean Fields, dated back to 15,000 y.b.p. (de' Gennaro *et al.*, 1999, 2000), due to mineralogical-petrographic compositions and, especially, the peculiar association of phillipsite > chabazite > analcime, as revealed by XRPD and SEM-EDS analyses. This information was furtherly confirmed by chemical analyses of pumice fragments that, according to TAS diagram, follow the compositional trend of NYT.

In some samples from *Villa del Capo* site, the presence of volcanic fragments (as aggregates), characterized by leucite-bearing scoriae and crystal fragments of garnets in the binder matrix, led to hypothesize that such particular aggregates could be associated to eruptive deposits from Somma-Vesuvius complex. In fact, EDS analyses of garnets showed a solid solution composition between andradite (48.98 - 58.38 mol.%) and grossular (25.91 - 30.46 mol.%), very close to the garnets from Somma-Vesuvius (andradite 46 - 70 mol.% and grossularia 16 - 45 mol.% (Scheibner *et al.*, 2007; Melluso, pers. comm.).

Volcanic aggregates of *Villa del Pezzolo* samples should be treated separately, considering the different age of building phases that characterize this *Villa*. Tuff fragments found in the first building phase are probably associated to the Campanian Ignimbrite formation, cropping out in the same geographical area; this hypothesis was also confirmed by the presence of zeolitic phases (chabazite and analcime; CI-LYT, Langella *et al.*, 2013) and, mainly, by the glassy shards aspects, which are partially devitrified and replaced by authigenic feldspar as the welded gray Campanian Ignimbrite lithofacies (CI-WGI - Langella *et al.*, 2013). Samples belonging to second and third building phases (after A.D. 79 eruption of Mt. Somma-Vesuvius), showed differences in mineralogical composition and aggregates shapes (from angular to sub-rounded). The presence of volcanic scoriae, containing abundant leucite and garnet fragments, both in pumice and binder, allow us to consider that these materials come from deposits of Somma-Vesuvius. SEM-EDS chemical analyses, performed on pumice and garnet fragments, confirmed the use of Somma-Vesuvius materials. Chemical compositions of pumice, plotted in the TAS diagram, follow the compositional trend of pumice belonging to A.D. 79 Somma-Vesuvius eruption, whereas chemical composition of garnets (solid solution between andradite 52.99 - 57.29 mol.% and grossular 25.64 - 28.65 mol.%) is compatible with Somma-Vesuvius garnets (see above). Samples from third building phase (coating and floor mortars) showed presence of ceramic fragments, completely lacking in the other building phases. However, it was almost impossible to define their provenance, due to the extreme heterogeneity of samples, likely suggesting recycling of building materials. Actually, the great role played by such ceramic fragments was to confer hydraulicity to the mortars, as pointed out by the HI estimation.

As regards secondary minerogenetic processes, composition of the cementiceous binding matrix of analyzed mortars is extremely interesting. In detail, ubiquitous presence of gel-like C-A-S-H, calcite, gypsum, halite and Al-tobermorite was retrieved in the *Piscina Mirabilis* mortar samples, whereas hydrocalumite occurs in *Villa del Capo* mortars. Gel C-A-S-H derived from the following reaction between lime and pozzolanic material (volcanic and ceramic materials): $Ca(OH)_2 + SiO_2 + Al_2O_3 + H_2O \rightarrow$ C–S–H + C–A–H.

Usually, the presence of calcite is related to not-completely reacted clasts of under-burned lime. Further, since mortars have been stored in subaerial environment, carbonation processes from residual portlandite could have occurred. Gypsum, the most widespread neoformation mineral, is related to calcite sulphation as a consequence of decrease in pH value, caused by dissolution of atmospheric SO_2 (de' Gennaro *et al.*, 1993), but interaction with thermal waters (especially in *Terme di Baia* samples) could not be disregarded. The presence of halite can be definitely related to interaction of the materials with seawater or marine aerosol (Rispoli *et al.*, 2015).

Tobermorite $\{[Ca_4(Si_{5.5}Al_{0.5}O_{17}H_2)]\ Ca_{0.2}\ Na_{0.1}\ H_2O\}$, an unusual hydrotermal, calcium-silicate hydrate mineral with cation exchange properties (Jackson *et al.*, 2017), was unexpectedly retrieved in relict voids of *Piscina Mirabili*s mortars. Formation of such mineral should not occur in conventional concretes, but its presence was found in Roman marine concretes (Stanislao *et al.*, 2011; Jackson *et al.*, 2013, 2017), occasionally in hydrothermally altered volcanic rocks (such as palagonitic tuff of Surtsey volcano, Iceland (Jackson *et al.*,

2017) and as an alteration product at the cement-rock interface in toxic and nuclear waste repositories (Jackson *et al.*, 2017). Generally, tobermorite synthesizes at 120-240 °C (Jackson *et al.*, 2017), but these temperatures are uncompatible with those of lime-based materials. Moreover, it is well known that heat of hydration in hydraulic mortars is definitely lower than ordinary cements (Collepardi *et al.*, 2009; Rispoli *et al.*, 2015). According to Jackson *et al.* (2017), it is possible to consider tobermorite crystallization in Roman concrete at lower temperatures, strictly referred to Phlegraean Fields deposits; in this site, post-eruptive hydrolysis and dissolution of trachytic glass generated alkaline fluids from which zeolites originated. Lime mortars mixed with zeolitized materials and seawater, a typical recipe of Roman engineers, created highly alkaline, but relatively short-lived, pozzolanic system buffered by calcium hydroxide, which produced C-A-S-H phase and tobermorite at < 95 °C (Jackson *et al.*, 2017). Presence of tobermorite allows us to identify more precisely the mix design of *Piscina Mirabilis* mortars, suggesting use of sea-water during their production.

Occurrence of hydrocalumite (Ca, Cl, and Al hydroxide), identified in relict pores of *Villa del Capo* mortars, may be associated to migration of Cl^{-}, from seawater-saturated portlandite to aluminium-rich sites. Crystalline hydrocalumite microstructures have apparently sequestered Cl^{-} anions, thus producing deleterious reactions, unwanted expansions, and corrosion of steel reinforcements in modern Portland cement concretes (Brandon *et al.*, 2014). By contrast, the presence of this phase in the relict pores of ancient Roman mortars, which do not present steel reinforcements, contribute to the long- term chemical durability of the mortars.

Then, comparing analyzed Roman mortars and standard modern hydraulic mortar (SHM) through thermal analyses, highlighted the fact that a fairy connection between the two-different kinds of mortars exists, whereas mercury intrusion porosimetry (MIP) analyses revealed a difference. The results of thermal analyses, according to Moropoulou *et al*. (1995, 2005), suggest an overall high hydraulicity of ancient and modern mortars. MIP analysis highlighted different values of both pore radii and total porosity between ancient mortars and SHM. As far as MIP data are concerned, ancient roman mortars showed a maximum in porosimetric distribution between 4 and 120 nm and total porosity between 38-52%, whereas in SHM main distribution of pore radii ranges between 100 and 1000 nm and total porosity is around 28% (Fig. 4).

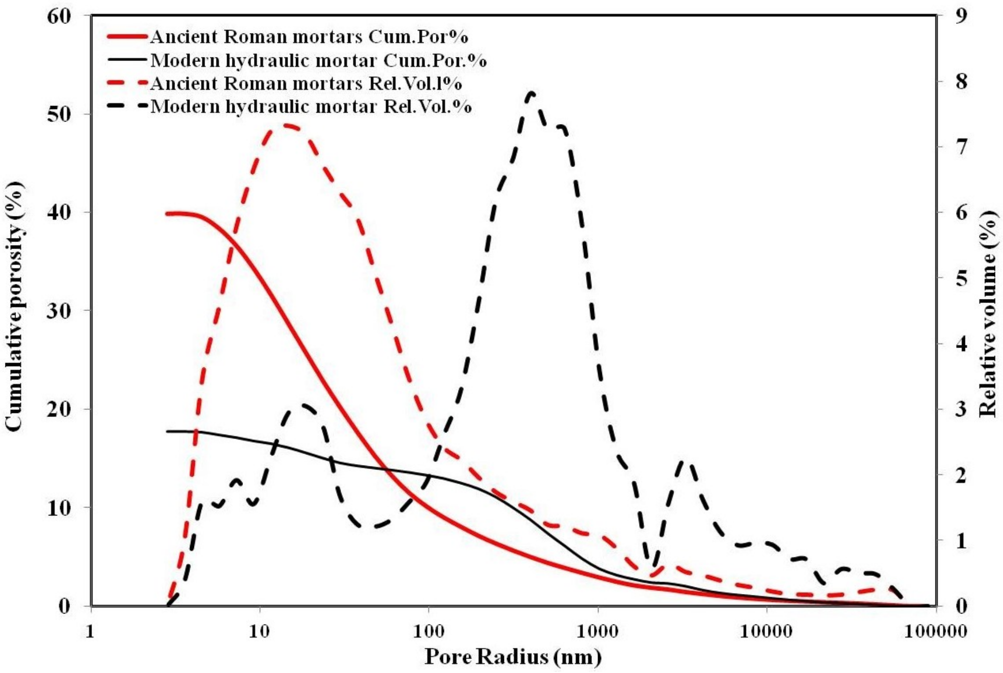


Fig. 4 - Cumulative and relative pore size distribution in Roman mortars compared with SHM (Standard Hysdraulic Mortar).

Thus, average pore size in ancient Roman mortars suggested a definitely small dimension of pore radii, about one order of magnitude smaller than modern conventional mortars.

Porosity tests, along with with microstructural observations, suggested that in ancient Roman mortars the vesicular structure of pozzolanic materials (*i.e.*, pumice) represents a fundamental feature of the complex pore structures of the cementitious matrix. Mineral phases related to secondary minerogenetic processes (such as gel C-A-S-H, tobermorite and hydrocalumite) settling in pores of pozzolanic materials make mortars more resistant and ductile (Brandon *et al.*, 2014).

It was confirmed that the, peculiar vesicular nature of pumice-bearing pozzolanic materials, led to low permeability (Brandon *et al*., 2014), and slowed fluids diffusion through mortars over time, leading to a relatively stable chemical system. On the contrary, higher pore size in modern mortars could account for their poor durability, thus making crucial to understand the reasons of such unusual pore structure of the ancient mortars, providing their extraordinary longevity.

CONCLUSIONS

This research permitted not only a first minero-petrographic characterization of raw materials used to produce mortars from important archaeological sites (such as, *Piscina Mirabilabis, Terme di Baia, Villa del Capo* and *Villa del Pezzolo*) but also shed some light on the provenance and gave further information on the technology used for preparation of different geomaterials used by ancient Romans.

Building materials used in the studied archaeological sites had a local provenance, and are very well consistent with the surrounding geological setting. In fact, both pozzolanic materials such as volcanic fragments, scoriae, pumice, and crystal fragments (*i.e.*, clinopyroxene, feldspar, and garnet) derive from pyroclastic rocks of the Phlegraean Fields district and from rocks of Somma-Vesuvius complex, as inferred by mineralogical and chemical composition.

In coating and floor mortars there is an addition of ceramic fragments that improve the pozzolanic aptitude of the mortar. It was not possible to define their provenance (due to extreme heterogeneity) and this likely suggests a recycle of building materials.

A common feature of investigated mortars is their high hydraulicity, as shown by reaction rims of pozzolanic materials (volcanic and ceramic fragments). Such high hydraulicity is the result of an accurate selection, preparation and mixing of raw geomaterials, supplied by the geological availability of the area surrounding the different archeological sites.

Composition of cementitious binding matrix is definitely peculiar; it shows various products of reaction, including amorphous gel C-A-S-H, calcite, tobermorite (*Piscina Mirabilis* samples) and hydrocalumite (*Villa del Capo* samples). In particular, these two latter secondary minerogenetic products fill pore space and enhance bonding in pumice clasts (Jackson *et al.*, 2017). In addition, formation of tobermorite and hydrocalumite is also related to specific chemical elements (*i.e*., alkali cations and chloride), that in modern mortars and concretes generally produce unwanted expansion and corrosion of steel reinforcements, while in Roman mortars increase ductility and mechanical resistance (Jackson *et al.*, 2017).

The main difference between ancient Roman mortars and modern hydraulic mortars it is related to porosity. The size distribution and cumulative volume of pores in the ancient mortars has the potential to strongly influence chemical and mechanical durability of structures, especially along beaches and intertidal environments. In these two settings, a continuous cycling of subaerial drying and moisture, and repetitive penetration of seawater salts into the mortars fabric took place (Brandon *et al.*, 2014). The volume and connectivity of pores in modern cementitious materials have important influences on fluids pathways through mortar and/or concrete, so comparisons of pore characteristics of ancient materials with conventional mortars may be a key factor to understand the exceptional resistance to decay of ancient Roman mortars.

This research contributes to the knowledge and understanding of the technical skills achieved during Roman times. It may represent a valuable reference for the future restoration projects of investigated archaeological sites.

Moreover, this research project is a further demonstration that manufacturing technology of the ancient Romans was really oriented to innovation, quality, sustainability, durability and beauty. In particular, i) mix-design, performance: quality; ii) origin of pozzolanic material: sustainability; iii) porosity of mortars: durability.

If the teachings of ancient Romans are applied to nowadays construction materials, we can state that "innovation in ancient Rome is the state-of-the-art of today".

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