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Characterization of ancient mortars: preliminary results from *Villa del Pezzolo*, Sorrento Peninsula, Italy

Rispoli C.[(1)], Graziano S.F.[(1)], Guarino V. [(1)], De Bonis A.[(1)], Di Benedetto C. [(1)], Esposito R.[(2)], Budetta T. [(3)], Morra V. [(1)] & Cappelletti P. [(1)]

[(1)]*DiSTAR, Università degli Studi di Napoli Federico II, 80134 Napoli, Italia*
[(2)] *Dipartimento di Studi Umanistici,Università degli Studi di Napoli Federico II, 80134 Napoli, Italia*
[(3)] *Soprintendenza Archeologica, Belle Arti e Paesaggio per l'area metropolitana di Napoli*

***Abstract* – This study deals with the characterization of ancient mortars from *Villa del Pezzolo*, a Roman villa located in Seiano (Napoli - Campania, Italy), dated from 1st century B.C. to 3rd century A.D. During the A.D. 79 Vesuvius eruption, the villa was destroyed and then rebuilt twice, in the second and third centuries A.D. (Aucelli et al., 2015).**

The goal of this work is to improve the knowledge of Roman construction techniques by means of detailed microstructural and compositional examination of a) cementitious binding matrix and b) aggregates, to point out: provenance of raw materials, secondary minerogenetic processes, mortars' mix-design.

This research was conducted in collaboration with the Superintendence of Archeological Heritage of Campania. The first results confirmed that Roman engineers extensively used local geomaterials such as volcanic and sedimentary aggregates mixed with lime. The presence of leucite and garnet let us hypothesize the provenance of the volcanic aggregate from the Somma-Vesuvius complex.

I. INTRODUCTION

The patrician Roman *Villa del Pezzolo* (Mingazzini, 1946) is very interesting for both geologists and archaeologists (Aucelli et al., 2015) because it is one of only few sites, along the Sorrento Peninsula coast, where the consequences of the A.D. 79 eruption of Mt. Vesuvius are clearly visible, despite the great distance from the eruptive center.

Geomaterials from the *Villa*, in particular mortars, are here studied in order to improve knowledge on raw materials used to produce mortars, as well as their alteration products. Non-invasive, but representative, samples (a statistically valid number of samples for each of three building phases) were obtained thanks to Superintendence of Archeological Heritage of Campania. Literature data research allowed collecting all existing information about the geological and archaeological history of the site.

II. GEOLOGICAL SETTING

The archaeological site is set in the Sorrento Peninsula, in the northern flank of the Lattari Mountains, constituting the southern margin of the Campanian Plain. The geological evidences of such plain are mostly related to tectonic extensional movements and volcanoclastic events (Cinque et al., 2000). The Lattari Mountains are set 20 km south of the Somma-Vesuvius volcano and 40 km south of Naples (Italy). This mountain ridge is composed by Mesozoic limestone facies covered by late Quaternary ashfall deposits belonging to the A.D. 79 eruption of Mt. Vesuvius (Cinque & Robustelli, 2009).

In particular, the roman villa is placed in a pocket beach (40°39'42''N, 14°25'13'' E) along the shore of Pezzolo Beach in Marina di Equa Bay (Seiano), (Fig. 1).

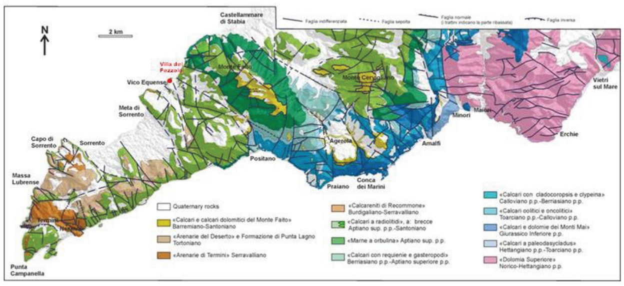

Fig. 1: geological map of the Sorrento Peninsula and archeological site location (modified after Vitale et al., 2012).

The impact of A.D. 79 Vesuvius eruption is strongly recognizable in the villa. In particular, this geographical area was affected by two different phases of deposit: firstly the sedimentary records retrieved under the stairs of the villa are related to base surge events which caused the formation of pyroclastic deposits with variable thickness to the southeast of the eruptive center (Cinque, 2007); alluvial events consecutive to the volcanic eruption produced the erosion of the volcanic deposits and, subsequently, debris and mud flow (Senatore, Ciarallo, & Stanley, 2014) which covered the villa, forming an alluvial delta called “Durece deposition” by the local population in order to define a lithofacies characterized by ashfall products (Cinque & Robustelli, 2009). Later, the alluvial delta was broke down creating a 6–8 m high Durece Cliff still present on the beach (Cinque & Robustelli, 2009).

III. THE HISTORY OF *VILLA DEL PEZZOLO*

Ruins of a Roman villa, as previously mentioned, are visible near the eastern side of the Marina di Equa Bay, at the foot of the promontory of Vico Equense, in the Sorrento peninsula.

The marine erosion processes have seriously damaged the rooms making it impossible to recognize the original construction plan. However, thanks to the analysis of a) geological stratigraphy and b) building techniques, three building phases can be identified (Aucelli et al., 2015).

The villa was certainly damaged by the A.D. 79 Vesuvius eruption, whose products covered the stairs of access to the residence by the sea. In the 2nd century A.D., after a series of flood events, some rooms, on the north-eastern side of the Bay, were restructured with the creation of new environments in *opus reticulatum*, different in form and orientation respect to the original core structures.

During the last building phase (3rd century A.D.) a new access to the sea was built in the space between the first access staircase and the gallery. Probably a further Middle Ages building activity is retrieved in the traces of some walls foundations.

The decoration of the Roman villa is documented by some sporadic marble findings, now kept at the National Archaeological Museum of Naples.

IV. ANALYTICAL METHODS

Knowledge of mineralogical composition, and microstructural properties of cement-based mortars is very important for the understanding of their chemical and physical properties. In order to obtain these information, the following analyses were carried out:

- mortars sampling for thin sections realization;
- optical and stereoscopic studies on thin sections;
- Mechanical separation of the different constituent phases (matrix, *ceramic fragments* aggregate), according to the UNI 11305;
- X-ray powder diffraction (XRPD);
- scanning electron microscopy (SEM);
- microanalyses (SEM-EDS).

The main mineralogical features were obtained by polarized light microscopy (Leica Laborlux 12 pol) on thin sections. XRPD samples were prepared by dry crushing samples by hand in agate mortar. Operative conditions of XRPD analyses were the following: CuKα radiation, 40 kV, 40 mA, 2θ range from 4° to 70°, equivalent step size 0,017° 2θ, 30 s per step counting time on a modular Panalytical X’Pert Pro diffractometer equipped with a RTMS X’Celerator detector. Scanning electron microscopy (SEM) observations were performed on a JEOL JSM5310 instrument. Chemical analyses were carried out by energy dispersive spectrometry (EDS) on an Oxford INCAx microanalyser.

V. MATERIALS AND RESULTS

Ten different samples were collected on several walls of the archaeological site (Fig. 2), supervised by the archaeologists and the Superintendence of Archeological Heritage of Campania in order to collect representative materials of the building. The sampling followed specific criteria, as type of mortar, good state of aggregation, availability and representativeness.

Nine bedding mortars and one floor mortar were collected : three corresponding to the first building phase, three to the second one and four to the third.

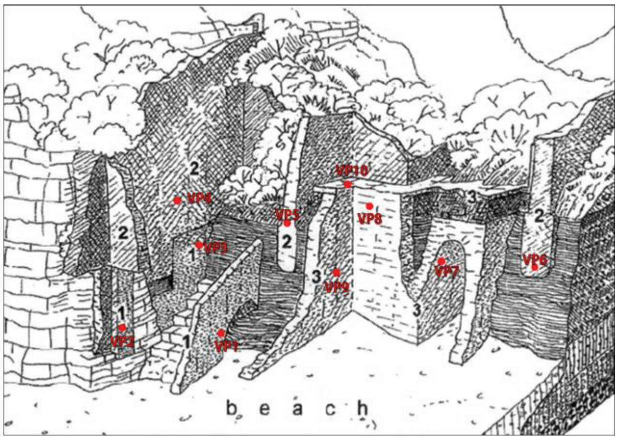

Fig. 2: Sketch maps of the *Villa del Pezzolo* with sampling site (modified after Cinque et al., 2000).

Macroscopic observations of the samples show light yellow-dark brown colors with coarse aggregates ranging in diameter from 3 mm up to 3 cm. The aggregates are made of volcanic grey tuff and carbonatic fragments along with few amounts of ceramic fragments.

The mortars show lime lumps (2-4 mm) which origin is to be sought in the properties of the slaked lime (calcium hydroxide) and in the water/quicklime ratio (Bakolas et al. 1995; Barba et al., 2009). Their formation occurred during the slaking process of the lime and it is due to an insufficient seasoning of the calcium hydroxide and a low water/ lime ratio. Therefore, the lime lumps composition is mainly carbonatic ($CaCO_3$), and generally consists of pure binder (without aggregates) with the same composition of the limestone used to make the lime.

Mineralogical and petrographical observation

Thin section observations of the mortars allowed to recognize three groups (A, B, C) (Fig. 3). All mortars show poor homogeneity and compactness of the binder. Moreover, secondary calcite was observed in all samples, such as in the binder, on the pore rims and in the pumice vesicles.

The A Group (VP1, VP2, VP3, first building phase) is characterized by a yellowish-light brown cryptocrystalline binder. The aggregates are constituted mainly by carbonate fragments, scoriae, pumice, volcanic fragments, one ceramic fragment (VP3) and crystal fragments of plagioclase, clinopyroxene and sanidine. Volcanic fragments are characterized by glassy shards partially devitrified and replaced by authigenic feldspar (Langella et al., 2013). Small and fractured lumps with not well-defined edges were observed. The mortars of group A appear poorly sorted.

The B group (VP4, VP5, VP6, second building phase) includes mortars with binder variable in color from light-grey to brown, and cryptocrystalline texture. The aggregate shape varies from sub-angular to sub-rounded and the size distribution is moderately sorted. The aggregate fraction is mostly characterized by carbonatic, marble and volcanic fragments, scoriae, leucite-bearing scoriae, deeply altered pumice (with garnet and leucite fragments) and crystal fragments of plagioclase, clinopyroxene, sanidine, garnet and leucite. The lime lumps are small, fractured, and poorly compacted with not well defined edges. In VP5 sample lumps are present as relicts.

The C group (VP7, VP8, VP9, third building phase) has a cryptocrystalline to micritic binder, poorly homogeneous and moderately compact. The color varies between grey and dark-brownish. The aggregate fraction appears moderately sorted and sub-rounded, composed by volcanic (porphyric to aphyric texture), carbonatic and ceramic (VP8 and VP9) fragments, pumice with clinopyroxene, amphibole, garnet and leucite as crystal fragments. In these samples we note the presence of mineral aggregates formed by clinopyroxene, leucite, analcime and, sometimes, calcite.

The lime lumps show undefined and irregular edges with poorly compactness.

VP9 sample is slightly different from the other samples, due to the presence of sparite grains in the binder. Its origin can be related to a residual limestone, not completely calcinated.

VP10 sample is different from the previous groups. It is a floor mortar characterized by light grey color and cryptocrystalline/micritic binder.

The main aggregate is *cocciopesto*, characterized by a mixture of lime, volcanic material and aggregates formed by shattered tiles, bricks and pottery. Other constituents are carbonatic and volcanic fragments, pumice, scoriae and some sanidine and clinopyroxene fragments. Furthermore, the presence of lime lumps is identified also in this sample.

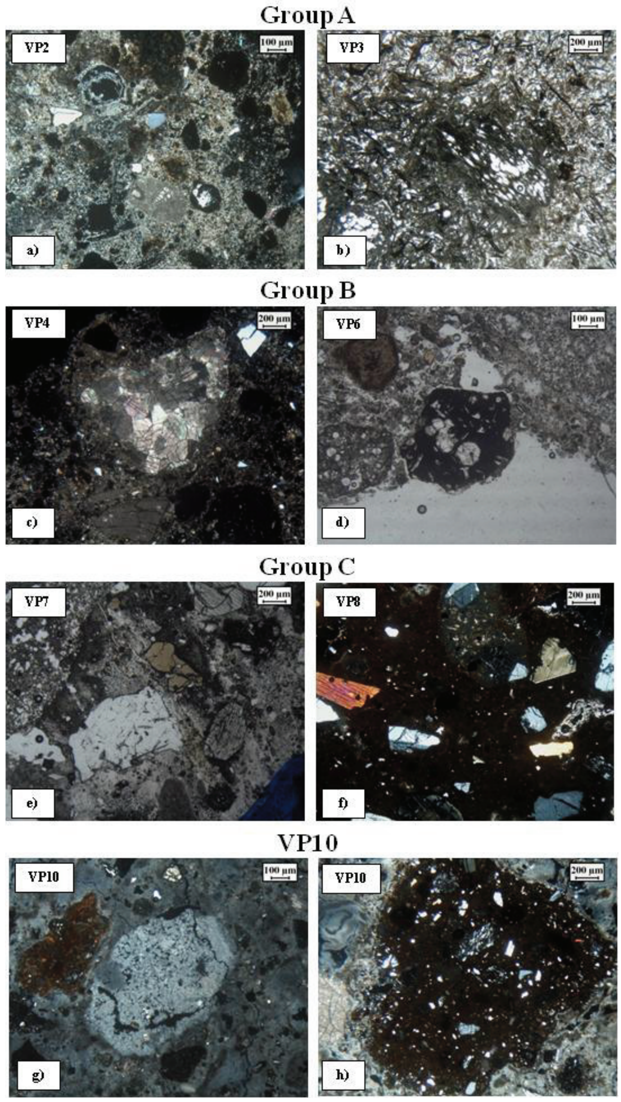

Fig. 3: Microphotographs of different petrographic groups identified in mortars.
a-b) Group A: a) carbonatic fragments in the cryptocystalline matrix (CPL); b) devitrified glassy shards (PPL). c-d) Group B: c) Marble fragment (CPL); d) leucitic scoria and pumice (PPL). e-f) Group C: e) garnet, clinopyroxene and pumice (PPL); f) ceramic fragment (CPL). g-h) VP10: g) white lump and ceramic fragment in micritic binder (CPL); h) ceramic fragments (CPL).

XRPD analysis

The samples were divided in binder, aggregates, and ceramic fragments, according to the UNI Normal 11305 document (mortar characterization) and then analyzed by XRPD. Results are showed in the tables 1, 2 and 3.

The XRPD results show calcite as the main mineral in mortar-based materials along with alkali feldspar (sanidine), plagioclase, analcime, mica and clinopyroxene as mineral phases of the aggregate (tables 1, 2); few amounts of leucite, garnet and chabazite are also present (table 2).

table 1: XRPD analysis of binder

	Binder								
VP1m	Cal	Hl		Anl		Cpx	Afs	Pl	Mca
VP2m	Cal	Hl	Gp	Anl		Cpx		Pl	Mca
VP3m	Cal	Hl	Gp	Anl		Cpx		Pl	Mca
VP4m	Cal	Hl		Anl	Lct	Cpx	Afs	Pl	Mca
VP5m	Cal	Hl		Anl	Lct	Cpx	Afs	Pl	Mca
VP6m	Cal	Hl		Anl		Cpx	Afs	Pl	Mca
VP7m	Cal	Hl		Anl	Lct	Cpx	Afs	Pl	Mca
VP8m	Cal	Hl		Anl		Cpx	Afs	Pl	Mca
VP9m	Cal	Hl	Gp	Anl		Cpx	Afs	Pl	Mca
VP10m	Cal	Hl		Anl		Cpx		Pl	Mca

table 2: XRPD analysis of aggregates

	Aggregates										
VP1i	Anl	Cbz		Cpx	Afs	Pl		Mca	Cal	Hl	
VP2i	Anl	Cbz		Cpx	Afs	Pl		Mca	Cal	Hl	Gp
VP3i	Anl	Cbz		Cpx	Afs	Pl		Mca	Cal	Hl	
VP4i	Anl		Lct	Cpx	Afs	Pl	Grt	Mca	Cal	Hl	
VP5i	Anl		Lct	Cpx	Afs	Pl		Mca	Cal	Hl	
VP6i	Anl		Lct	Cpx	Afs	Pl	Grt	Mca	Cal	Hl	
VP7i	Anl	Cbz		Cpx	Afs	Pl		Mca	Cal	Hl	
VP8i	Anl		Lct	Cpx	Afs	Pl	Grt	Mca	Cal	Hl	
VP9i	Anl	Cbz	Lct	Cpx	Afs	Pl		Mca	Cal	Hl	Gp
VP10	Anl			Cpx	Afs	Pl		Mca	Cal	Hl	

table 3: XRPD analysis of ceramic fragments

	Ceramic fragments								
VP8c	Cal	Qtz	Hl	Hem	Anl	Cpx	Afs	Pl	Mca
VP9c	Cal	Qtz	Hl	Hem		Cpx	Afs	Pl	Mca
VP10c	Cal	Qtz	Hl	Hem	Anl	Cpx	Afs	Pl	

Cal: calcite, Hl: halite, Gp: gypsum, Anl: analcime, Cbz: Chabazite, Lct: leucite, Cpx: clinopyroxene, Pl: plagioclase, Grt: garnet, Afs: alkali feldspar, Mca: mica, Qtz: quartz, Hem: hematite

In ceramic fragments, occurrences of calcite, quartz, mica and hematite were observe (table 3).
XRPD analyses allowed to reveal also presence of an amorphous phase, probably related to the volcanic glass component (pumice and scoriae) and the C-S-H and C-A-H phases; the latter formed after pozzolanic reactions between lime and volcanic glasses or ceramic fragments.
All analyzed fractions show the presence of halite.

Micro-morphology and chemical analysis of mortars (SEM-EDS)

In order to support and integrate XRPD results, SEM observations were carried out on polished thin sections. SEM-EDS analysis allowed to obtain detailed chemical compositional profiles. As regards binder, results show, in some cases, presence of newly formed hydraulic phases (C-S-H e C-A-H), and confirmed gypsum [$CaSO_4 \cdot 2(H_2O)$] presence, as XRPD suggested.
Occurence of leucite and garnet, along with leucite-bearing scoria suggests the use of volcanic products from Somma-Vesuvius (Fig. 3a). In addition, use of a grey Phlegraean tuffs was identified, due to the presence of analcime, chabazite and glass shards. Furthermore, along pumice rims, authigenic feldspars were also analyzed (Fig. 3b).

The EDS analysis of ceramic fragments confirmed the presence of quartz, calcite, Na- and K-feldspars, mica and hematite.

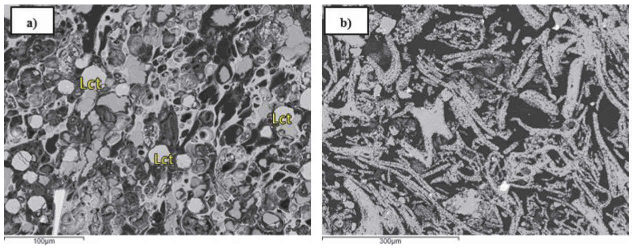

Fig. 3: BSE–SEM images, a) leucitc scoria in samples VP7; b) glass shards partially coated by a thin layer of micrometric feldspars in sample VP3,

VI. DISCUSSION AND CONCLUSION

Mineralogical and petrographical examination, performed on mortars from *Villa del Pezzolo,* showed that raw materials were mixed with lime for casting the mortars.
Volcanic aggregates in the samples of the first building phase were represented by some grey tuff fragments, pumice and scoriae.
The grey tuff fragments are probably associated to Campanian Ignimbrite formation, cropping out in the same geographical area (Fig. 4); confirmation of this hypothesis is given by mineralogical and petrographic analysis too. Presence of zeolitic phases (chabazite and analcime), revealed by XRPD, could be ascribed to the zeolitic facies of the Campanian Ignimbrite (LYT - Langella et al., 2013).

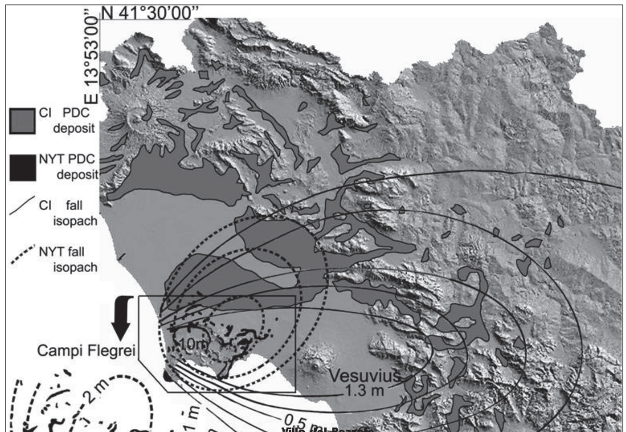

Fig. 4: Distribution of Campanian Ignimbrite (CI) and Neapolitan Yellow Tuff (NYT) pyroclastic density current (PDC) deposits and fall deposits (modified after Scarpati, and Perrotta, 2012). Inset (left) shows their source area (Campi Flegrei) and presumed vent locations (black star—NYT vent; gray star—CI vent).

In addition, thin section observations and SEM-EDS analysis have shown glassy shards, partially devitrified and replaced by authigenic feldspar, typical again of the

Campanian Ignimbrite (WGI - Langella et al. 2013 - Fig. 5 a, b).

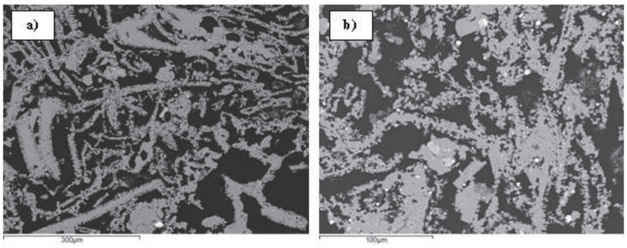

Fig. 5: SEM images, a) glass shards coated by thin layer of micrometric feldspars in VP3; b) glass shards coated by thin layer of micrometric feldspars in representative sample of Campanian Ingnimbrite from the archaeological site of Cuma.

The samples belonging to the second building phase (after A.D. 79 eruption of Mt. Vesuvius), have shown differences in their mineralogical composition and aggregate shapes (from angular to sub-rounded). The presence of volcanic scoriae, containing abundant leucite, and garnet, both in pumice and binder, allow us to assess that these materials belonging to the eruptive products of Mt. Somma-Vesuvius (Fig. 6 a, b).

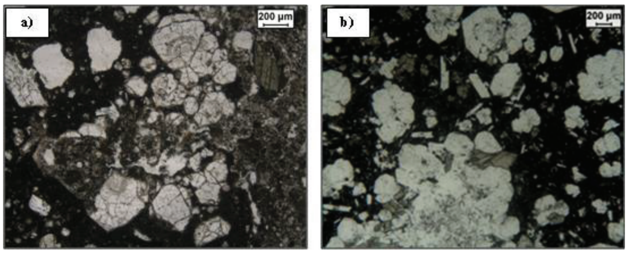

Fig 6: Microphotographs, a) leucite-bearing scoriae in VP4; b) leucite-bearing scoria in Somma-Vesuvius products (Melluso L, pers. comm.).

Furthermore, samples with a sub-rounded shape of aggregates allow us to hypothesize the use of “Durece”, the alluvial delta lithofacies formed by the products of the debris- and mud-flows emplaced after strong rainfalls following the volcanic eruption.
Analysis of the third phase samples have shown the presence of ceramic fragments, totally lacking in the other building phases. Minero-petrographic and chemical analysis have demonstrated that such ceramic fragments are different to each other.

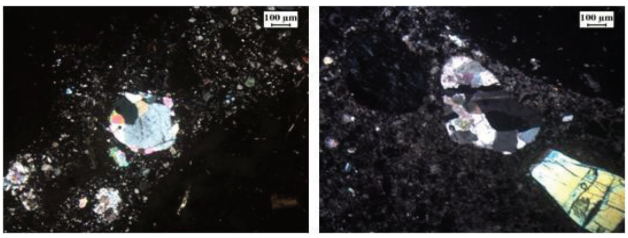

Fig. 7: Microphotographs of particular crystal aggregates in VP9.

Furthermore, presence of peculiar crystal aggregates (Fig.7) could be associated to a sandstone-like facies, made up of volcanoclastic debris with limestone fragments, as reported by Cinque et al. (2000).
As VP10 sample is regarded, presence of *cocciopesto*, was reported; this is a typical material of floor mortars of Roman age. C*occiopesto* components (shattered tiles, bricks and pottery) produce a pozzolanic reaction with free lime, forming hydraulic compounds.
Lime utilized in cementiceous binding matrix and carbonatic fragments could be considered as material of local provenance, due to the geographical position of the villa, close to northern flank of the Lattari Mountains, composed primarily of Mesozoic carbonatic rocks.
Composition of cementiceous binding matrix, in some samples, shows contemporary presence of -like calcite, gypsum and gel-like C-A-S-H. The last one derived from the previously reported reaction between lime and *cocciopesto* or volcanic aggregates. Calcite presence is likely connected to the not-well reacted clasts of underburned lime, although it is not possible to exclude that carbonation processes took place subsequently from residual portlandite, since mortars have been stored in subaerial environment. Gypsum [$CaSO_4 \cdot 2(H_2O)$] can be ascribed to late sulphation of calcite or even reaction between sulfate and hydrolysis lime (Rispoli et al., 2015).
Finally, halite in all samples can be easily related to interaction with seawater, due to the site location.
This preliminary study provides useful information about provenance of raw materials and mix-design of mortars from the archaeological site of *Villa del Pezzolo*.
The identified mix-design is characterized by a mixture of lime, fine volcanic material, both volcanic and sedimentary aggregates and water.
As origin of raw materials is concerned, minero-petrographic and chemical analysis, along with surrounding geological setting, allow to identify a very probable local provenance.

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