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# Archaeometric approach for the study of mortars from the underwater archaeological site of Baia (Naples) Italy: Preliminary results

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#### Abstract

This work was aimed to evaluate the features of mortar samples taken from the underwater archaeological area of Baia (Naples, Italy), an important site, where the remains of the ancient Roman city of Baiae and Portus Iulius are submerged after bradyseism events, started from 4<sup>th</sup> century AD. Several architectural structures are still preserved into the submerged environment, such as: luxurious maritime villas, imperial buildings, private houses, thermae, *tabernae* and warehouses. In particular, some samples were collected from the masonry walls belonging to a building of the underwater area called Villa a Protiro. A first archaeometric approach has been applied to analyse twelve archaeological mortars samples in order to define: textural features, chemical composition and raw materials used for their production. For this purpose different analytical methods were used, such as, polarizing optical microscope (POM) and scanning electron microscopy (SEM-EDS).

Key words: Mortars; SEM-EDS; underwater archaeological site; cocciopesto.

#### Introduction

Mortars represent one of the most important artificial stone materials due to the many applications in the construction field. Their use in the masonry structures (e.g. bedding mortars,

coating mortars, plasters and supporting material for pavements and mosaics) is widespread in Italy since the Roman times (Collepardi et al., 2003; Fratini and Cantisani, 2008; Pecchioni et al., 2008; Miriello et al., 2010a; Fichera et al., 2012; 2015; Belfiore et al., 2015).

Mortars are composite materials, consisting of hydraulic or aerial binding material, aggregates and additives, passive or active, which react with the binding material and are modified during their setting (Moropoulou et al., 2000). Historical evidence showed that for millennia have been used mortars to meet several needs, in fact, have been the most basic and common binding material used in the construction of buildings from the ancient Greek, Roman and the succeeding periods (Moropoulou et al., 2000; Özkaya and Böke, 2009; Miriello et al., 2011).

Many papers focused their attention on the mineralogical and petrographic features of mortar components aiming at determining the old production techniques used by Roman builders (Silva et al., 2005; Sànchez-Moral et al., 2005; Giavarini et al., 2006; Jackson and Marra, 2006; Jackson et al., 2006; 2009; 2010; Pavia and Caro, 2008; Miriello et al., 2010a; Fichera et al., 2012; 2015; Belfiore et al., 2015).

There is a growing interest in diagnostic analysis and conservation strategies applied to submerged Cultural Heritage (Crisci et al., 2010). In particular, this work represents a contribution to the first archaeometric study of mortars from the underwater archaeological park of Baia (Naples, Italy) (Figure 1). The submerged archaeological area of Baia includes remains of the ancient cities of Baiae and Portus Iulius, which, since the 4th century AD, started to be submerged due to the bradyseism phenomenon. The latter is a slow morphological change in which the surface of the earth undergoes raisings (positive bradyseism) or subsidences (negative bradyseism) due to a deep magma chamber below the surface of the earth (Bodnar et al., 2007). Several architectural structures (with decorations) are still preserved in the site: luxurious maritime villas, imperial buildings, private houses, thermae, tabernae, and warehouses. In particular mortars specimens taken from different walls of the "Villa a Protiro"

a beautiful example of the Roman period ruins, located near Punta Epitaffio.

All samples underwent an integrated analytic program that allowed their complete characterization with a main goal: characterisation of different types of mortars and identify the raw materials used for their preparation. In particular, polarized optical microscopy and scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS) were used.

#### Archaeological site and sampling

The archaeological site of Villa a Protiro is located at 5 m depth; the rooms composing the Villa extend for 40 m along the road, flanked by thermae, tabernae and other villas; however, its real size must have been larger. The name "prothyrum" is derived from the presence of two stuccoed column shafts, no longer in existence, that were placed on two short partition walls built in front of the threshold (Di Fraia, 1993; Ricci et al., 2009; Aloise et al., 2013; Ricca et al., 2014). Floors and walls are largely decorated with marbles; almost all the surveyed rooms have marble-covered walls, and mosaic floors are mostly made of white tesserae. The Villa underwent a second construction phase represented by the building of a wide apsidal room south of the hall. This room had two floor levels, built from large white marble sheets that were also used as coverings for the walls. The Villa is also composed of other service rooms, such as an area identified as a kitchen in the northwestern section, and a rectangular courtyard. Additionally, a garden was located behind these areas (Di Fraia, 1993).

Sampling (12 mortars) was performed on several walls of the archaeological complex (Figure 2), i.e. with the assistance of archaeologists of the Soprintendenza Speciale per i Beni archaeologici di Napoli e Pompei in order to take samples that were representative of the construction. The sampling was carried out



Figure 1. Location of Baia in the Campanian region, Italy, and underwater photos of the archaeological site.

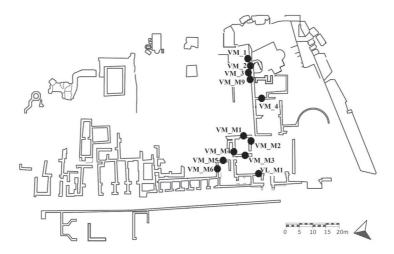


Figure 2. Plan of the Villa showing the location of sampling sites within the different residential rooms.

by hammer and following criteria such as the type of mortar, the good state of aggregation, the available quantities and the representativeness. The samples taken out from the above mentioned edifices consist of bedding, mortars. Most of them appear to be macroscopically intact and quite hard (Figure 3). From a macroscopic point of view, mortar samples show a sand size from a coarse to very coarse dimensions (Wentworth, 1922). In some samples where "cocciopesto" is present, it reaches also dimensions of about 3 cm

A list of the examined mortars with main macroscopic features is reported in Table 1.

#### Materials and methods

All mortar samples underwent petrographic analyses through polarized optical microscopy. Thin-section observations were performed using a Zeiss AxioLab microscope, equipped with a digital camera to capture images. The characteristics observed were: grain size and shape of the aggregate fraction, mineralogical composition and textural features of both

aggregate and binder and percentage ratio between the two components.

Scanning electron microscopy with energydispersive spectrometry (SEM-EDS) analysis was applied to examine the microstructures and the major element compositions of the mortar. The analyses were performed using a scanning electron microscope (SEM36 Cambridge Instruments Stereoscan) equipped with an Edax Philips microanalysis working in energy dispersive spectrometry EDS, operating conditions were set at 20 kV accelerating voltage and 0.2 nA beam current for the analysis of major element abundances; The measurements were performed on polished thin sections, and a raster mode analysis was used to investigate the cementitious binding matrix. Furthermore, SEM/EDS were used to evaluate the hydraulic properties of the lime determining the hydraulicity index (HI) according to the Boynton formula (Boynton, 1980):

HI=(%SiO<sub>2</sub>+%Al<sub>2</sub>O<sub>3</sub>+%Fe<sub>2</sub>O<sub>3</sub>)/(%CaO+%MgO)

High values of HI indicate a more hydraulic

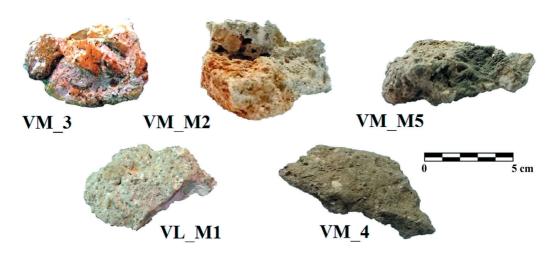


Figure 3. Some representative mortars fragments from underwater archaeological site.

Table 1. Macroscopic description of the bedding mortar samples coming from Villa a Protiro.

Sample	Binder colour	Aggregate abundance	Size	Cohesion
VL-M1	light grey	++	Up to 2 mm	++
VM-1	whitish	++	Up To 3 cm	++
VM-2	whitish	++	Up To 3 cm	++
VM-3	whitish	++	Up To 3 cm	++
VM-4	light grey	+++	Up To 1 cm	+++
VM-M1	whitish	+++	Up to 2 mm	+++
VM-M2	whitish	+++	Up to 2 mm	+++
VM-M3	whitish	+++	Up to 2 mm	+++
VM-M4	whitish	+++	Up to 2 mm	+++
VM-M5	grey	+++	Up to 2 mm	+++
VM-M6	grey	+++	Up to 2 mm	+++
VM-M9	whitish	++	Up To 3 cm	++

Aggregate abundance: +++, very abundant; ++, abundant; +, scarce. Cohesion: +++, high; ++, medium.+ scarse

character of the lime as well as the ability of the mortar to grip and harden and to preserve its strength properties in humid or submerged environments (Pecchioni et al., 2008).

#### Results and discussion

#### Petrographic analysis

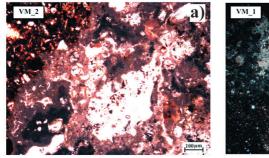
Thin section observations of the mortars from *Villa a Protiro* allowed to recognize three distinct groups (A, B, C) (Figure 4). All mortars show poor homogeneity and compactness in the binder. Moreover, in all samples secondary calcite was observed such as in the binder, on the pores rims and in the pumices vesicles. Table 2 shows the main features of the each group.

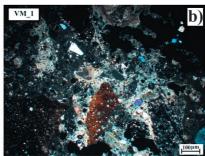
The group A (VM\_1; VM\_2; VM\_3; VM\_M9) is characterized by a yellowish - dark brownish cryptocrystalline binder; the porosity reaches

30% (just secondary voids). Fractured lumps with not well defined edges were observed. Cocciopesto, marble and volcanic rock fragments (pozzolans) and single crystals of plagioclase, pyroxene and K-feldspar constitute the aggregate fraction. It appears poorly sorted.

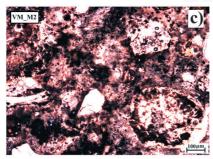
Cocciopesto fragments exhibit sub rounded shape and course size until to 2 cm. The aggregate is well sorted and composed of rounded volcanic fragments and monocrystalline phases as quartz, pyroxene, biotite and plagioclase. The volcanic fragments of the mortars exhibit sub rounded shape, reach also 5 mm in diameter and consist of pumices with a porphyric to aphyric structure; fragments with intersertal texture. Plagioclase and pyroxene represent the more common phenocrysts; moreover, frequent reaction rims can be observed around the volcanic fragments. VM\_3 is partly different from the other samples

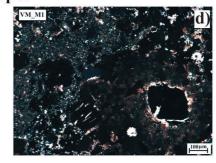
### Group A



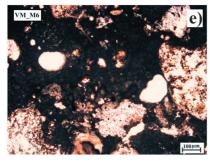


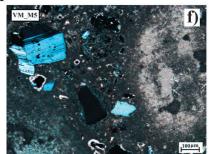
### **Group B**



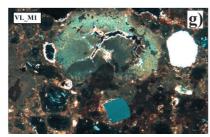


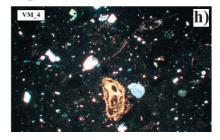
### Group C





### No Group





because binder is brown, micritic and porosity slightly lower. The binder/aggregate ratio achieves 60/40% (Whitbread, 1995).

The group B (VM M1; VM M2; VM M3; VM M4) includes mortars with binder whose colour varies from light-grey to beige and the texture is cryptocrystalline. The lumps appear fractured, scarcely compact with not well defined edges. The porosity (both primary and secondary) varies between 30-40%. The aggregate is mainly constituted by pozzolan fragments with clear reaction rims and constituted by porphyric to aphyric pumices where pyroxene and plagioclase represent the main phenocrysts; by K-feldspar, plagioclase, pyroxene, biotite, opaque minerals. The particle shape of the aggregate varies from sub-angular to sub-rounded and the particle size distribution is moderately sorted. The binder/aggregate ratio reaches 70/30% (Aloise et al., 2013; Belfiore et al., 2010; 2015).

The group C is constituted by VM\_M5, VM\_M6. The binder appears scarcely homogeneous and moderately compact, from cryptocrystalline to micritic, the colour varies between grey and brownish. The lumps show undefined and ragged edges and scarce compactness. The aggregate fraction appears moderately sorted and composed by volcanic fragments with a sub-rounded shape, porphyric to aphyric texture and plagioclase and amphibole as phenocrysts. Reaction rims are frequent in all fragments. The aggregate includes also minerals namely

K-feldspar, plagioclase, pyroxene, biotite and marble fragments. The binder/aggregate ratio is about 70/30%, whereas the porosity (mainly secondary) is ~30% (Belfiore et al., 2010; 2015).

The following samples (VL\_M1; VM\_4) do not belong to any previous group.

VL\_M1 shows a moderately compact binder, a brown colour and a micritic texture. The lumps appear fractured, poorly compact with well defined rims. The porosity (both primary and secondary) is estimated at 30%. The aggregate fraction is poorly sorted, is composed by pozzolan sub-rounded fragments with reaction rims and constituted by aphyric to porphyric pumices where pyroxene and plagioclase represent the main phenocrysts; by minerals with sub-angular shape such as K-feldspar, plagioclase, pyroxene, biotite, opaque minerals. The binder/aggregate ratio is assessed to 50/50%.

VM\_4 shows brown and micritic binder; fractured lumps with well defined edges were observed. The aggregate is poorly sorted with sub rounded – sub angular shape. The pumices show coarse size, reaction rims and porphyric to aphyric structure; K-feldspar, plagioclase, pyroxene, and biotite are present both as phenocrysts in pumices and monocrystalline phases; marble fragments were identified in the aggregate. The binder/aggregate ratio is 70/30%. Porosity is 10% primary and 20% secondary respectively.

The petrographic results obtained have

Figure 4. Microphotographs of the different petrographic groups identified among the examined mortars. a-b) Group A: a) the yellowish - dark brownish binder and a pozzolan fragment in PPL; b) the cryptocrystalline binder and the poor sorting of the aggregate constituted by cocciopesto, pozzolans, plagioclase, pyroxene and K-feldspar in CPL. c-d) Group B: c) the heterogeneous colour of binder varying from light-grey to beige in PPL; d) the cryptocrystalline aspect of the binder, the recrystallization rims in the voids and pozzolans fragments in CPL. e-f) Group C: two areas of the samples characterized by a moderate compactness and a micritic binder in PPL (e) and CPL (f). e) Pozzolans and primary voids in PPL; f) plagioclase, K-feldspar, lump and recrystallized calcite on pores. g-h) VL\_M1 and VM\_4 samples. These latter ones do not belong to any previous group. The images were taken in CPL.

Table 2. Main	netrographic	features	described	in mortars	thin sections
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		Ratio Binder/	nder/ Aggregate			
Group	Samples	aggregate	Mineralogical phases	Cocciopesto	Rock fragments	Sorting
A	VM_1, VM_2, VM_3, VM_M9	1.5	Pl, K-Fld,Px	X	Volcanic rocks, marble	P.S.
В	VM_M1, VM_M2, VM_M3, VM_M4	2.3	Pl, K-Fld,Px , Bt, Om	/	Volcanic rocks	M.S.
C	VM_M5, VM_M6	2.3	Pl, K-Fld, Px , Bt,	/	Volcanic rocks, marble	M.S.
-	VL_M1	1.0	Pl, K-Fld, Px, Bt, Om	/	Volcanic rocks,	P.S.
	VM_4	2.3	Pl, K-Fld, Px, Bt	/	Volcanic rocks, marble	P.S.

Bt: biotite, Om: opaque minerals, K-Fld: K-feldspar, Pl: plagioclase, Px: pyroxene, P.S: poorly sorted, M.S.: moderately sorted, W.S: well sorted, x: present.

allowed us to correlate the textural features of each sample with the sampling site. Probably the various portions of the walls were built, or at different times or with different construction techniques.

Petrographic description of cocciopesto fragments

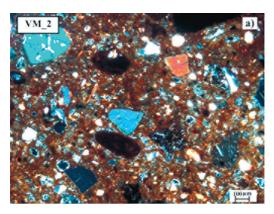
The samples VM\_1, VM\_2, VM\_3, and VM\_M9 have aggregates which are prevalently made of cocciopesto. This group of fragments was described in more details in order to highlight the different types of cocciopesto and to define probable correlations with other materials employed in the archaeological site. The size of these fragments raging from 25 mm to 0.2 mm. The petrographic analysis was performed using the descriptive scheme proposed by Whitbread (1995). Petrographic observations revealed variability in the paste types of ceramic fragments. In particular, there are two typologies of mixtures (Figure 5).

The first type including VM\_2 and VM\_M9, is characterized by a microstructure with meso and micro vughs and vesicles. In some voids, we can detect secondary calcite. The

groundmass is rather heterogeneous. Its colour in PPL (plane polarized light) varies from light brown to dark brown. The optical activity is medium. Amorphous concentration features (Acf), mainly given by pure nodules and some moderately impregnant portions can be observed. Inclusions sub-rounded to sub-angular, display a homogeneous distribution with a medium-coarse size. The inclusions consist of monocrystalline quartz, feldspar, clinopyroxene, biotite, muscovite, amphibole, oxides and fragments of volcanic rocks (Figure 5a).

The second type (VM\_1 and VM\_3) shows a microstructure with vughs, vesicles with a smooth surface and linear voids filled by secondary calcite. Its colour in PPL varies from light brown to dark brown. The optical activity is medium. Amorphous concentration features (Acf) are given by pure nodules. Inclusions are rounded to sub-angular, with a medium sphericity. The inclusions mainly consist of quartz and plagioclase, subordinately oxides and biotite. In some cases, the inclusions show a weak preferred orientation (Figure 5b).

From the petrographic observations, the two typologies of cocciopesto are comparable to



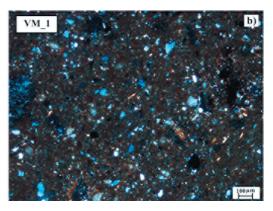


Figure 5. Photomicrographs at crossed polars, representative of the two typologies of cocciopesto.

a) Related to the first type and shows the medium coarse size of inclusions and some of the most abundant phases such as monocrystalline quartz, feldspar, clinopyroxene, biotite, amphibole, oxides and fragments of volcanic rocks. b) Related to the second type, highlights the finer size of inclusions constituted mainly by quartz, plagioclase and subordinately oxides and biotite. A weak preferred orientation is visible in the image.

the bricks coming from the walls of the Villa a Protiro characterized in Aloise et al., 2014. In particular, the aspect of groundmass, the size and the types of inclusions allow to associate VM\_2 and VM\_M9 at the first group identified in Aloise et al., 2014, whereas VM\_1 and VM\_3 at the second one.

This suggest a probable recycle of the building materials, as bricks, in the preparation of the mortars coherently with the common old Roman practises (Ausiello and Maione, 2014).

Micro-morphology and chemical analysis on mortars by SEM-EDS

SEM EDS analysis were carried out in order to obtained information about the type of lime used for the production of the mortars, define the Hydraulic Index (H.I.) and the degree of hydraulicity of the binder finally analyze pumices used such as aggregate to try the identification of their provenance area. The morphological analysis in BSE carried out on the samples showed the presence of many lumps having a shape from sub-spherical to subangular, with diameter ranging from 500 µm to

1 mm and contours not always well defined. Frequently, fractures are observed in the central area and, in some cases, the lumps appear almost dissolved (Figure 6).

The presence of many lumps in the samples is most likely due to the fact that the mortar was not extensively worked, so that complete mixing of lime and aggregate could not occur (Miriello et al., 2010b). In addition, technologies based on the non-seasoning of lime, which produce mixtures with low plasticity, were probably used (Bakolas et al., 1995).

SEM-EDS analysis to determine the chemical composition of lumps, referring to the major elements was carried out. The obtained data have also allowed calculating the Vicat's Index (Amoroso, 2002) also referred to as Hydraulicity Index and expressed as the ratio  $(Al_2O_3+SiO_2+Fe_2O_3)/(CaO+MgO)$ .

The analyses on lumps were performed in their central portion, to reduce the level of contamination. In order to determine their chemical composition, referring to the major elements, different raster analyses of 12 samples of mortars have been carried out. The chemical

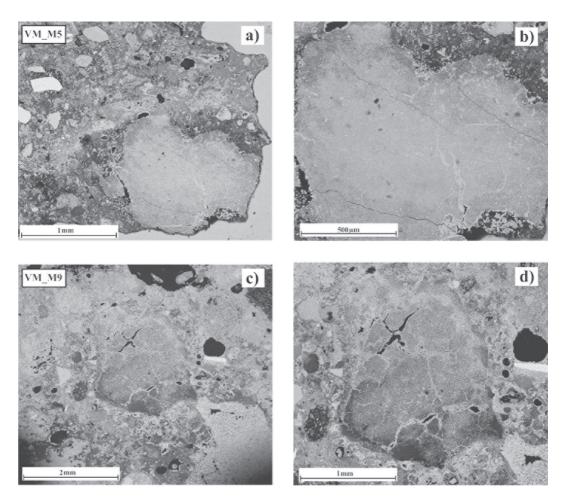


Figure 6. BSE–SEM images reporting the morphological features of lumps identified in the mortar samples.

composition indicates that the studied mortars are mainly composed of CaO, with high values of CaO+MgO comprised between about 80 and 96%. SEM-EDS results as well as HI values are reported in Table 3. The Hydraulicity Index shows values ranging between 0.03 and 0.25. Samples VM\_4, VM\_M2, VM\_M3 and VM\_M9, fall in the field of aerial lime (H.I. < 0.10). On the contrary samples VM\_2, VM\_M1, VM-M4, VM\_M5 show a high H.I., making it to fall in average hydraulic limes (0.16 < H.I. < 0.31). Finally two samples, VM\_3 and VL\_M1 did

not show any lumps in the binder, while sample VM 1 is borderline with the aerial lime field.

The binary diagram in Figure 7 suggests the presence of two type of limestone used for the preparation of the samples: pure and a marly limestone.

Regarding to the pozzolana, used as aggregate, it is represented mainly by the pumices fragments. These components could provide information on their type of provenance, so SEM-EDS microanalysis was carried out.

It was necessary to consider the probable

Table 3. Average values of major oxides (wt%) determined through SEM-EDS analysis of lumps.

Sample		$SiO_2$ $Al_2O_3$	MgO	CaO	$Na_2O$	$K_2O$	$Cl_2O$	$SO_3$	$Fe_2O_3$	Total	CaO+MgO S	CaO+MgO SiO+Al $_2$ O $_3$ +Fe $_2$ O $_3$ (SiO $_2$ +Al $_2$ O $_3$ )	$CaO/(SiO_2 + AI_2O_3)$	MgO+Fe <sub>2</sub> O <sub>3</sub>	H.I.
LUMPS															
$VM_1$	7.84	3.34	5.18	83.62	0.00	00.00	0.00	0.00	0.00	100	88.81	11.18	7.48	5.18	0.13
$VM_2$	15.34	3.92	7.58	70.68	0.87	09.0	0.46	90.0	0.49	100	78.26	19.75	3.67	8.07	0.25
$^{VM}_{-3}$	1	1	1			1		1		1		ı		1	
$VM_4$	6.34	2.28	1.78	89.10	0.29	0.09	0.11	0.00	0.00	100	88.06	8.63	10.33	1.78	60.0
VM_M1	10.76	3.29	5.14	78.88	0.57	0.62	0.30	0.15	0.30	100	84.02	14.35	5.61	5.43	0.17
VM_M2	2.79	1.28	12.42	83.44	0.00	0.00	0.00	90.0	0.00	100	98.86	4.07	20.51	12.42	0.04
VM_M3	7.27	2.07	7.77	82.25	0.15	0.00	0.22	0.27	0.00	100	90.03	9.34	8.81	7.77	0.10
VM_M4 14.23	14.23	3.25	17.42	62.47	1.25	0:30	1.07	0.00	0.00	100	79.89	17.48	3.57	17.42	0.22
VM_M5 11.03	11.03	2.53	8.68	75.33	1.13	0.16	0.29	98.0	0.00	100	84.00	13.56	5.55	8.68	0.16
VM_M6 10.49 2.31	10.49	2.31	8.78	75.90	1.01	0.20	0.70	0.62	0.00	100	84.68	12.80	5.93	8.78	0.15
VM_M9	2.34	0.93	3.86	91.56	0.00	0.00	0.00	1.33	0.00	100	95.43	3.26	28.05	3.86	0.03
VL_M1	•	•	•	•	•	•							,		
$H.J. = (A1_2O_3 + SiO_2 + Fe_2O_3)/(CaO + MgO).$	) <sub>3</sub> +SiO <sub>2</sub>	+Fe <sub>2</sub> O <sub>3</sub> )/	(CaO+1	MgO).											

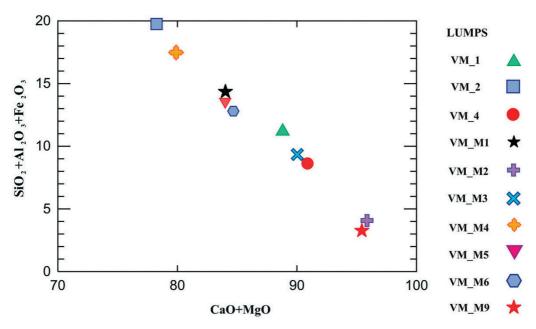


Figure 7. Binary diagram Al<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub>+Fe<sub>2</sub>O<sub>3</sub> vs CaO+MgO concerning SEM-EDS analysis of lumps. The concentrations used are those obtained by SEM-EDS analysis and reported in Tables 3.

alteration suffered by mortars because of their long stay into underwater environment; for this reason Chemical Index of Alteration (CIA) and Chemical Index Weathering (CIW) were considered. CIA (Nesbitt and Young 1984; Young, 1999) and CIW (Harnois, 1988) are calculated according to the formula:

$$CIA=[\%A1_2O_3/(\%A1_2O_3+\%CaO+\%Na_2O+\%K_2O)]*100$$
  
 $CIW=[\%A1_2O_3/(\%A1_2O_3+\%CaO+\%Na_2O)]*100$ 

Results are summarized in Table 4. It shows the average compositional values obtained by the analysis of three pumices in each mortar sample. CIA and CIW vary respectively from 57 to 73, suggesting a considerable weathering of the inclusions probably related to the interaction with submarine environment; for this reason a

clear determination of the provenance of the aggregate based on geochemical data about major elements is not possible. However, it is conceivable a local provenance of the raw materials considering the position of Baia in the Phlegraean Fields area.

#### Conclusion

This preliminary study provides interesting information about the mortars and their production technology employed in the archaeological site of Baia.

Results obtained from petrographic analysis, showed the presence of different technology of production of mortars in term of type of aggregate, ratio binder/aggregate. In some samples they are marble fragments, testifying to the Roman marble re-use in the mixture of mortars. In particular, there is a good correlation

Table 4. SEM-EDS microanalysis of pumices in mortars.

wt%	Na <sub>2</sub> O	MgO	$Al_2O_3$	SiO <sub>2</sub>	Cl <sub>2</sub> O	K <sub>2</sub> O	CaO	$Fe_2O_3$	Total	CIA	CIW
VL_M1	5.09	1.09	18.20	63.37	1.06	6.85	1.69	2.65	100	57.18	72.86
VM_1	4.74	1.08	18.44	63.11	0.85	7.05	1.71	3.02	100	57.73	74.09
VM_2	4.67	1.14	18.59	63.56	0.70	7.12	1.79	2.43	100	57.79	74.21
VM_3	5.01	1.04	18.03	62.96	1.03	7.03	1.75	3.15	100	56.66	72.73
VM_4	5.34	1.41	18.36	62.84	0.79	6.88	1.77	2.61	100	56.75	72.08
VM_M1	4.21	1.04	17.93	63.46	1.04	7.21	1.78	3.33	100	57.60	74.96
VM_M2	4.18	1.06	17.87	63.28	0.95	7.43	1.94	3.29	100	56.87	74.49
VM_M3	5.34	1.02	18.32	63.28	1.00	6.22	1.78	3.04	100	57.86	72.01
VM_M4	5.32	0.99	18.30	62.93	1.09	6.57	1.66	3.14	100	57.46	72.39
VM_M5	5.36	1.05	17.95	63.45	1.04	6.54	1.71	2.90	100	56.88	71.74
VM_M6	5.02	0.97	18.11	63.16	1.04	6.70	1.81	3.19	100	57.24	72.61
VM_M9	5.06	1.01	17.86	63.30	1.05	7.00	1.69	3.03	100	56.50	72.57

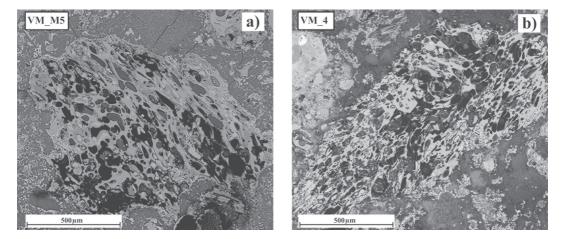


Figure 8. BSE–SEM images showing the common microtexture that characterizes the pozzolan fragments constituted mainly by vesiculated pumices occurring within the aggregate fraction. The microphotos refer to samples  $VM_4$  and  $VM_5$ 

between the location of sampling sites within the different residential rooms (Figure 2) and the minero-petrographic, morphologic and chemical features of the analysed fragments.

Regarding the study of the lumps, the SEM-EDS analysis, has allowed to define that the lime used for the mortars production is both aerial and hydraulic binder.

The obtained data, give the first important information about the characterization of mortars used in the underwater city of Baia. In particular, this study is crucial since the most recent guidelines of scientific and international cultural heritage protection bodies agree in willing the promotion of underwater archaeological and historical heritage.

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#### References

- Aloise P., Ricca M., La Russa M.F., Ruffolo S.A., Belfiore C.M., Padeletti G. and Crisci G.M. (2013) Diagnostic analysis of stone materials from under water excavations: the case study of the Roman archaeological site of Baia (Naples, Italy). *Applied Physics A: Materials Science and Processing*, 114, 655-662.
- Amoroso G. (2002) Trattato di scienza della conservazione dei monumenti. Etica della conservazione, degrado dei monumenti, interventi conservativi, consolidanti e protettivi. Alinea editrice, Firenze.
- Ausiello G. and Maione C. (2014) Learning to "SUSTAIN" Trough the culture of recycle f.- Madeo and M. A. Schnabel (eds.), Across: Architectural Research through to Practice: 48<sup>th</sup>

- International Conference of the Architectural Science Association 2014, pp. 87-98.
- Bakolas A., Biscontin G., Moropoulou A. and Zendri E. (1995) - Characterization of the lumps in the mortars of historic masonry. *Thermochimica Acta*, 269-270, 809-816.
- Belfiore C., La Russa M.F., Mazzoleni P., Pezzino A. and Viccaro M. (2010) Technological study of "ghiara" mortars from the historical city centre of Catania (Eastern Sicily, Italy) and petrochemical characterization of raw materials. *Environmental Earth Science*, 61, 995-1003.
- Belfiore C.B., Fichera G.V., La Russa M.F., Pezzino A., Ruffolo S.A., Galli G. and Barca D. (2015) A Multidisciplinary Approach for the Archaeometric Study of Pozzolanic Aggregate in Roman Mortars: The Case of Villa dei Quintili (Rome, Italy) *Archeometry*, 57 (2), 269-296.
- Bodnar R.J., Cannatelli C., De Vivo B., Lima A., Belkin H.E. and Milia A. (2007) Quantitative model for magma degassing and ground deformation (bradyseism) at Campi Flegrei, Italy: Implications for future eruptions. *Geology*, 35, 791-794, DOI: 10.1130/G23653A.1.
- Boynton R.S. (1980) Chemistry and technology of lime and limestone (2° edizione). New York: John Wiley & Sons.
- Collepardi M. (2003) La lezione dei romani: durabilità e sostenibilità delle opere architettoniche e strutturali. Proceedings of III Convegno AIMAT "Restauro e Conservazione dei Beni Culturali: Materiali e Tecniche", Cassino, Italy.
- Crisci G.M., La Russa M.F., Macchione M., Malagodi M., Palermo A. M. and Ruffolo S.A. (2010) - Study of archaeological underwater finds: deterioration and conservation. *Applied Physics A*, 100, 855.
- Davidde B. (2002) Underwater archaeological parks: a new perspective and a challenge for conservation-the Italian panorama. *The International Journal of Nautical Archaeology*, 31, 83-88, DOI: IO.1006/ijna.2002.1001.
- Di Fraia G. (1993) Nuove evidenze topografiche e monumentali di Baia sommersa. *Archaeologia Subacquea. Studi, ricerche, documenti*, 1, 21-48.
- Fichera G.V., Belfiore C.M., La Russa M.F. and Pezzino A. (2012) - Technological and geochemical study of historical mortars from the Roman "Villa dei Quintili" (Rome, Italy).

- Rendiconti Online Società Geologica Italiana, 21(1), 659-660.
- Fichera G.V., Belfiore C.M., La Russa M.F., Ruffolo S.A., Barca D., Frontoni R., Galli G. and Pezzino A. (2015) Limestone Provenance in Roman Lime-Volcanic Ash Mortars from the Villa dei Quintili, Rome. *Geoarchaeology: An International Journal*, 30, 79-99, DOI 10.1002/gea.21504.
- Giavarini C., Samuelli M., Ferretti A. and Santarelli M.L. (2006) - Mechanical characteristics of Roman opus caementicium. In S. K. Kourkolis (Ed.), Fracture and failure of natural building stone, 107-120, Dordrecht, Springer.
- Jackson M.D and Marra F. (2006) Roman stone masonry: Volcanic foundations of the ancient city. American Journal of Archaeology, 110, 403-436.
- Jackson M.D., Kosso C., Marra F. and Hay R. (2006) Geological basis of Vitruvius' empirical observations of materials characteristics of rock utilized in Roman masonry. In: M. Dunkeld, J. Campbell, H. Louw, M. Tutton, B. Addis, & R. Thorne (Eds.), Proceedings of the Second International Congress of Construction History Queen's College, University of Cambridge, 2, 1685-1702. London, The Construction History Society.
- Jackson M.D., Logan J.M., Scheetz B.E., Deocampo D.M., Cawood C.G., Marra F., Vitti M. and Ungaro L. (2009) - Review: Assessment of material characteristics of ancient concretes, Grande Aula, Markets of Trajan, Rome. *Journal* of Archaeological Science, 36, 2481-2492.
- Jackson M.D., Deocampo D., Marra F., and Scheetz B. (2010) - Mid-Pleistocene pozzolanic volcanic ash in ancient Roman concretes. *Geoarchaeology:* An International Journal, 25 (1), 36-74.
- Miriello D., Barca D., Bloise A., Ciarallo A., Crisci G.M., De Rose T., Gattuso C., Gazineo F. and La Russa M.F. (2010a) - Characterisation of archaeological mortars from Pompeii (Campania, Italy) and identification of construction phases by compositional data analysis. *Journal of Archaeological Science*, 37, 2207-2223.
- Miriello D., Bloise A., Crisci G.M., Barrese E. and Apollaro C. (2010b) - Effects of milling: possible factor influencing the durability of historical mortars. *Archaeometry*, 52, 668-679.

- Miriello D., Bloise A., Crisci G.M., Apollaro C. and La Marca A. (2011) Characterisation of archaeological mortars and plasters from kyme (Turkey). *Journal of Archaeological Science*, 38, 794-80.
- Moropoulou A., Bakolas A. and Bisbikou A. (2000)
   Investigation of the technology of historic mortars. *Journal of Cultural Heritage*, 1, 45-58.
- Özkaya Ö.A. and Böke H. (2009) Properties of Roman bricks and mortars used in Serapis temple in the city of Pergamon. *Materials Characterization*, 60, 995-1000.
- Pavia S. and Caro S. (2008) An investigation of Roman mortar technology through the petrographic analysis of archaeological material. Construction and Building materials, 22, 1807-181
- Pecchioni E., Fratini F. and Cantisani E. (2008) -Le malte antiche e moderne: tra tradizione ed innovazione. Pàtron Editore, Bologna.
- Ricca M., La Russa M.F., Ruffolo S. A., Davidde B., Barca D. and Crisci G.M., (2014) - Mosaic marble tesserae from the underwater archaeological site of Baia (Naples, Italy): determination of the provenance. *European Journal of Mineralogy*, 26(2), 323-331.
- Ricci S., Davidde B., Bartolini M. and Priori G.F. (2009) - Bioerosion of lapideous artefacts found in the archaeological site of Baia (Naples). Archaeologia Maritima Mediterranea, An International Journal on Underwater Archaeology, 6, 167-186.
- Sanchez-Moral S., Luque L., Canaveras J.C., Soler V., Garcia-Guinea J. and Aparicio A. (2004) Lime pozzolana mortars in Roman catacombs: composition, structures and restoration. *Cement and Concrete Research*, 35, 1555-1565.
- Silva D.A., Wenk H.R. and Monteiro P.J.M. (2005)
   Comparative investigation of mortars from Roman Colosseum and cistern. *Thermochimica Acta*, 438, 35-40.
- Wentworth C.K. (1922) A scale of grade and class terms for clastic sediments. *The Journal of Geology*, 30 (5), 377-392.
- Whitbread I.K. (1995) Greek Transport Amphorae. A Petrological and Archaeological Study p. 146, Athens.