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CHARACTERIZATION OF LATE PREHISTORIC PLASTERS AND MORTARS FROM ERIMI – *LAONIN TOU PORAKOU* (LIMASSOL, CYPRUS)

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ABSTRACT:

Several plasters and mortars from the Middle Bronze Age site of Erimi-*Laonin tou Porakou* (Cyprus) were analyzed in order to perform a technological characterization. Morphological (SEM), elemental (EDX), mineralogical (XRPD), petrographic (polarized OM, SEM-EDX), thermal (TGA) and spectroscopic (FTIR) techniques were applied. Plasters and mortars were identified as pyrotechnological lime products, obtained using local raw materials and containing a moderate amount of spathic calcite fragments. Use of organic fibres was ascertained and a seminal use of a crumbled ceramic as additive was evidenced.

Keywords: Cyprus, Bronze Age, Lime Plasters and Mortars, Multitechnique characterization, Technology of production.

INTRODUCTION

In very recent years the archaeometric investigation of ancient plasters and mortars in Cyprus has

become more and more fertile (Philokyprou, 2012a, 2012b; Theodoridou et al., 2013). These studies have gone beyond the previous work, highlighting the inaccuracies in defining and characterizing plasters and mortars based on their evaluation using only a macroscopic visual exam, as denounced by Wright (1992) who complained the confusion between gypsum- and lime-based materials. Moreover, as far as lime-based materials are concerned, this confusion extended also to the identification of real burnt lime and/or simply crushed limestone, both known in Bronze Age Cyprus and still used today in modern constructions. The pyrotechnology of limestone to obtain lime plasters/mortars is based on the lime cycle, consisting of three stages: calcination, hydration or slaking and carbonation. Calcination is the thermal stage that transforms calcium carbonate into calcium oxide (quicklime) and carbon dioxide at temperatures in the range of 750-850°C, according to the reaction:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

The hydration step consists in the highly exothermic reaction between calcium oxide and water to obtain calcium hydroxide (slaked lime):

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

Through drying and ageing processes, calcium hydroxide undergoes carbonation by absorbing atmospheric carbon dioxide and thus reforms calcium carbonate, which is chemically indistinguishable from the original limestone and represents the plaster/mortar binder:

$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

The carbonation process consists of many steps and mainly depends on the CO_2 diffusion rate into the material pores and on the CO_2 dissolution rate, which is primarily controlled by the water content.

As to the use and diffusion of this pyrotechnological material during recent Prehistory, already in 1975 Gourdin and Kingery argued that “true [burnt] lime plasters were utilized in the aceramic Neolithic” in a wide area covering Syria and Israel (Gourdin and Kingery, 1975). Kingery et al. (1988) argue that the invention of the limestone burning process to obtain lime

plasters/mortars can be traced back to the Epipaleolithic in the Levant since the Kebaran period, and the use of lime-based materials in architecture has been present since the Natufian period. Recent studies on Cypriot plasters/mortars have highlighted the use of both limestone and gypsum plasters during the Neolithic (Kalavassos *Tenta* and Khirokitia) and the Chalcolithic (Kissonerga *Mosphilia*), with some decline during the Early and Middle Bronze Ages (henceforth, respectively, EC and MC), when mud mortars were mainly employed for floors and walls (Philokyprou, 2012a). However, structures made of or floors covered by lime plaster were found in all the major EC-MC sites such as Sotira *Kaminoudhia* (Swiny et al., 2003), Marki *Alonia* (Frankel and Webb, 1996, 2006) and Alambra *Mouttes* (Philokyprou, 2012a). Despite this archaeological evidence, archaeometric data from EC and MC contexts in Cyprus are rather scarce when compared to Late Bronze Age (henceforth LC) contexts (Philokyprou, 2012a, 2012b).

As far as the technology of production is concerned, the possible hydraulic character of lime mortars requires a special focus. Hydraulicity consists in the capability of hardening in the presence of water or moisture; hydraulic mortars display waterproof properties, strengthen earlier and show greater resistance than aerial materials. Volcanic pozzolanes, which are the typical natural hydraulic additive, are not available in Cyprus, where the addition of artificial pozzolanes (i.e. baked clay or ceramics) is known since the Late Bronze Age (Philokyprou, 2012a; Theodoridou et al., 2013). All the above mentioned researches guided the present study towards a multi-technique archaeometric investigation to provide an overall morphological, compositional and technological characterization of the Middle Bronze Age plasters/mortars from the site of Erimi-*Laonin tou Porakou*, with the aim of contributing to the study of Cypriot Bronze Age architectural use of plasters and binders (Bombardieri et al., forthcoming-b).

The archaeological site of Erimi-*Laonin tou Porakou* is located in the Limassol district (Cyprus), on a wide *plateau* on the left bank of the middle valley of the Kouris River. The valley is located within an extended sedimentary geological formation (the Pakhna formation), which characterizes a large area on the southwest side of the Troodos complex. The formation is marked

by a gentle hilly landscape that mainly consists of marlstone and gypsum, with siltstone and argillite interlayers (especially in the river valleys); moreover many of the *plateaux* display a thick layer of *harvara*, sometimes accompanied by *terra-rossa* deposits. *Harvara* is a typical Cypriot term that is usually translated as "limestone" but more often represents surface layers of secondary calcite. The archaeological site revealed two occupational periods: the first is dated to the Bronze Age and has two phases of occupation [Phase A: MC III – LC I A (1750-1450 B.C. ca.), Phase B: EC III – MC II (2100-1750 B.C. ca.)], while the second, known only from surface materials, dates to the Late Roman period (300-750 A.D.). The top of the hill is extensively occupied by a workshop complex (Area A) with several basins and flowing channels used for *in loco* manufacturing and working activities, while Area B is presumably inhabited by living/residential units. A large necropolis (Area E) occupies the natural south-sloping lower terraces. The local architectural style includes the construction of rooms by directly carving the bedrock, and the use of plasters/mortars for coating basins, daubing walls and for the construction of different functional elements (bins, pits, emplacements, hearts, kilns, etc.) (Bombardieri, 2013).

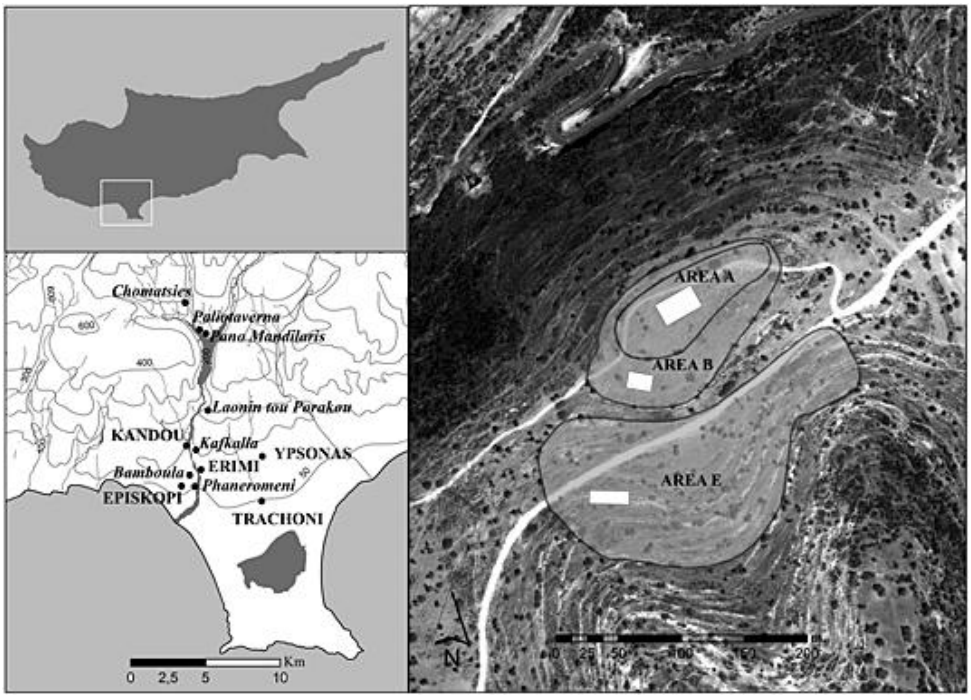


Figure 1. A map of the island of Cyprus, showing the location of the site of Erimi – Laonin tou Porakou, and a GIS overlay of the excavated trenches/areas on the Ikonos II satellite image.

During Phase B, limestone plasters/mortars were used extensively throughout the site, both in production contexts (Area A) and in the supposed living/residential units (Area B). Functional areas, mainly outdoor working areas as well as roofed rooms were constructed, in part, by carving into the limestone outcropping. This served as a possible attempt to protect against infiltration, both from humidity and also small rodents (Amadio and Chelazzi, 2013). In the subsequent Phase A the use and function of the workshop complex is likely the same as the former Phase B, however the architectural pattern seems to partially change. In this phase, large limestone slabs replaced the massive use of binders for the construction of bins, kilns and thresholds, and the use of plasters/mortars remained limited to supporting new features, coating basins and bins and levelling floors (Amadio and Chelazzi, 2013; Bombardieri et al., forthcoming-a).

SAMPLING AND ANALYTICAL TECHNIQUES

During the 2011 and 2012 excavation campaigns at Erimi-*Laonin tou Porakou*, 22 representative samples of plaster/mortar-based materials from different functional contexts and architectural features (Table 1) were collected and subjected to a multitechnique characterization.

Table 1. Description of the analyzed samples of plasters/mortars. Area: production contexts (Area A) or living/residential units (Area B); Phase: occupational phase [A: MC III – LC I A (1750-1450 B.C. ca.), B: EC III – MC II (2100-1750 B.C. ca.)]; M/P: mortar or plaster. The assignment is done according to the functional location; Fibers/Rhapides/Spicules/Pottery: X indicates occurrence.

Sample	Area	Phase	Object	M/P	Fibers	Raphides	Spicules	Pottery
24	A	A/B	Vessel emplacement	M	X	X		X
25a	A	A	Floor	P				
25b	A	B	Vessel emplacement	M	X	X		X
43	A	A	Floor	P			X	
44	A	A	Floor	P	X			
45	A	A	Coat of a basin	P	X			
46	A	B	Floor	P			X	
47	A	B	Floor	P				
48	A	B	Vessel emplacement	M				X
49	A	B	Hearth	M	X	X		
50	A	B	Coat of a basin	P	X	X	X	
51	A	B	Layer directly covering the bedrock	M (?)				
52	A	B	Layer directly covering the bedrock	M (?)		X	X	

53	A	A	Floor	P				
54	A	B	Bench (?)	M	X			
55	A	B	Coat of a basin	P				X
56	A	B	Coat of a basin	P	X	X		
57	A	B	Coat of a basin	P	X	X	X	
58	A	B	Coat of a basin	P	X		X	
59	A	B	Coat of a basin	P	X	X	X	
60	B	A	Architectural support	M	X	X		
61	A	A	Coat of a bin	P	X		X	

Morphological examinations (Scanning Electron Microscopy, SEM) and elemental composition (Energy Dispersive X-ray, EDX) analyses were carried out with a SEM-VP EVO50 (Carl Zeiss AG, Deutschland) microscope coupled with INCA x-sight model 7636 (Oxford Instruments, Concorde, MA, USA) microprobe at the following operating conditions: working distance = 8-12 mm, probe current = 200 pA, accelerating potential = 20 kV, counting time = 120 s. Petrographic analyses were carried out by a Cambridge S360 Scanning Electron Microscope connected to an Oxford Instruments Inca Energy 200 EDS equipped with an Oxford SATW Pentafet Si(Li) detector. The analyses were conducted in the following conditions: working distance = 25 mm, probe current = 200 pA, accelerating potential = 20 kV, counting time = 60 s. Natural oxides and silicates (Astimex Scientific Limited; Ontario, Canada) were acquired as standards. A cobalt standard was used for instrumental calibration and the relative abundance of the elements was calculated by the instrument software, using the ZAF correction.

The morphological examination was carried out in the secondary electrons (SE) mode on fresh fracture samples. The polished sections for the chemical analyses were obtained by encompassing the appropriate amount of samples in an epoxidic resin. The obtained sections were subjected to an abrasive treatment on silicon carbide papers with a 500 and 1000 grit size and polished with a 1 μm granulometry diamond paste on special clothes. The fresh fractures and the polished sections were then mounted on aluminium stubs using carbon tape and were covered with a coating of Au–Pd and graphite, respectively. The Au-Pd layer of approximately 20 nm thick was deposited using a coating unit SCD 050 Sputter Coater (Bal-Tec, Scotia, NY, USA) and the graphitization was performed by carbon rod evaporator under high vacuum (10^{-4} torr) conditions using a coating unit IMETEC K 950 equipped with a turbo-molecular pump (Balzer inc, Minnesota,

USA). The thickness of the C layer was about 300 nm.

EDX analyses were carried out in the backscattered electrons (BS) mode on polished sections at 200X magnification, by scanning rectangular areas or by spot analyses on smaller aggregates.

X-Ray Powder Diffraction (XRPD) patterns were collected using an Analytical X'Pert Pro (PANalytical B.V., Almelo, The Netherlands) equipped with an X'Celerator detector powder diffractometer using Cu K_α radiation generated at 40 kV and 40 mA. The 2θ range was from 5 to 90°. For the measurement, the appropriate amount of sample ground in an agate mortar was placed in a quartz sample holder and compressed with a glass slide. The X'Pert HighScore software was used for the evaluation of the diffraction patterns and the identification of the mineralogical phases. Petrographic examinations were carried out using an Olympus BX-41 optical microscope, equipped with a digital Jenoptic camera. 30 μm-thick sections were prepared and observed under polarized transmitted light, and images were acquired with a ProGres capture pro 2.6.

A Leica MZ16 stereomicroscope was employed for the Optical Microscopy (OM) observation of the samples.

Fourier Transform Infra-Red (FTIR) spectra were acquired by means of a Jasco 6700 spectrophotometer using the sample preparation procedure and the spectrophotometric method conditions described by Chu et al (2008).

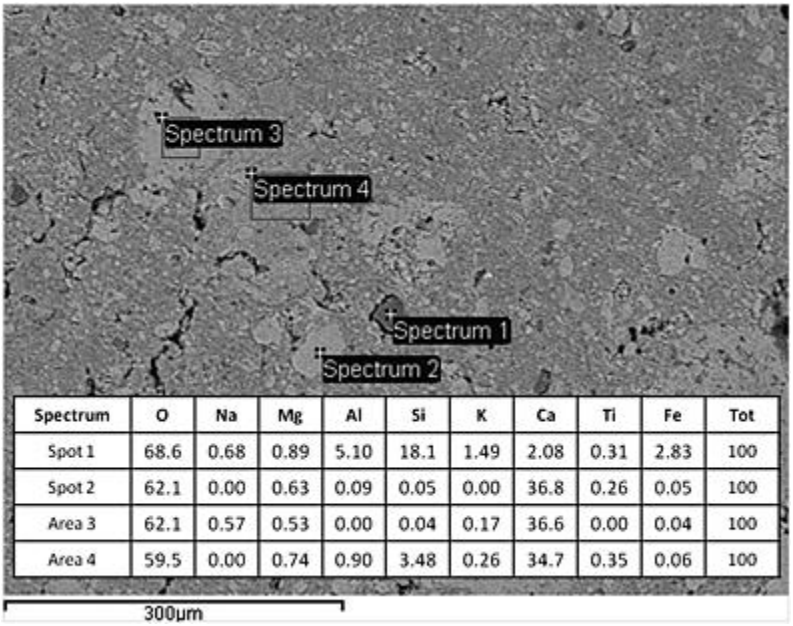
Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were simultaneously conducted by a SDTQ600 Thermal Analyzer (TA Instruments, New Castle, DE, USA) using a standard of aluminium oxide, following the procedure reported by Moropoulou et al. (1995).

RESULTS AND DISCUSSION

Chemical and mineralogical composition

The macroscopic evaluation of the samples produced several differences in terms of colour (which

ranged from white to light pink to grey with variation), presence/absence and type of aggregates, hardness and friability. Nevertheless, EDX scan analyses carried out in the BS mode on the matrix of all 22 samples showed good uniformity in elemental composition, with Ca as the major detected element, Si as the second element in terms of relative abundance, and lower quantities of Na, Mg, Al, K, Ti and Fe (Figure 2, area 4). S was completely absent in the EDX spectrum, highlighting the fact that the analyzed samples consist of lime plasters/mortars and not gypsum.



Spectrum	O	Na	Mg	Al	Si	K	Ca	Ti	Fe	Tot
Spot 1	68.6	0.68	0.89	5.10	18.1	1.49	2.08	0.31	2.83	100
Spot 2	62.1	0.00	0.63	0.09	0.05	0.00	36.8	0.26	0.05	100
Area 3	62.1	0.57	0.53	0.00	0.04	0.17	36.6	0.00	0.04	100
Area 4	59.5	0.00	0.74	0.90	3.48	0.26	34.7	0.35	0.06	100

Figure 2. A SEM–BS image and EDX analyses (polished section) on sample P48. Spot 1, ceramic inclusion; Spot 2 and Area 3, calcite aggregates; Area 4, binder (marly carbonate).

X-Ray Powder Diffraction (XRPD) evaluation obviously confirmed this observation, as the two detected mineralogical phases were calcite ($CaCO_3$) and quartz (SiO_2).

No other signals were observed in the XRPD patterns, presumably due to their very low amounts (below the detection limit of the instrument) or the lack of crystallinity of other eventually present minerals.

These results lead to the conclusion that limestone was the raw material used in the mortar/plaster manufacture at the site of Erimi-*Laonin tou Porakou* during MC. Moreover, as we have already demonstrated in a previous paper on ceramic assemblage from the Kouris Valley (Davit et al., in press), the local craftsmen possessed good pyrotechnological skills, such as those

required to produce burnt lime plasters/mortars. Thus, it is not surprising that with this skillset, in addition to the better mechanical properties of lime with respect to gypsum mortars/plasters (Gourdin and Kingery, 1975, Kingery et al., 1988), lime was the selected material. Moreover, it is not unexpected that lime was the only material of choice for mortar/plaster production and that gypsum based materials were not found at the site, since it has been demonstrated that, at other Cypriot archaeological sites, only one type of plaster/mortar was preferred, either gypsum or lime (Philokyprou, 2012a).

The petrographic SEM-EDX examination of the samples revealed the slightly marly limestone nature of the binder (see Figure 2, area 4, showing about 4% of Si) and allowed for the identification and evaluation of aggregates/inclusions. The amount of aggregates was generally quite limited, leading to an estimation of a maximum binder/aggregates ratio around 1:1 (on the basis of visual examination of SEM-BS images). The most abundant aggregate was spathic (in regard to having good cleavage) calcite, followed by quartz, albite-rich plagioclase, biotite, spinel (chromite), iron and titanium oxides (ilmenite, magnetite) and other minerals of ophiolitic origin (rutile and pyroxen, as a chromium-bearing diopside and chlorite).

Three samples (P24, P25b and P48) displayed the presence of about 10% v/v relative abundance of ceramic fragments (Table 1). This relatively high content of crushed bricks or pottery leads to the hypothesis that this is a deliberate addition and not an accidental contamination.

A sample of a local calcareous soil was also analyzed to verify the hypothesis that local limestone was used as a raw material for the production of lime for plasters/mortars on the site. The SEM-EDX petrographic examination of this sample showed the qualitative and semi-quantitative correspondence of the aggregates in the limestone and in the plaster/mortar binders leading to the conclusion that the local limestone was the only material of choice for lime production at Erimi-*Laonin tou Porakou* and that the inclusions identified in the matrix (with the eventual exception of the limestone aggregates and the exception of ceramic) were already present in the raw material and not added during the manufacturing process.

Given the probable abundance of waste materials such as limestone flakes and blocks produced by carving bedrock for building at the site, it is reasonable to posit that functional features were manufactured through the use of lime plasters/mortars. Floors, emplacements and hearths were all made with lime-based materials, and pits, bins and basins display the frequent use of internal lime plaster coatings (Amadio and Chelazzi, 2013; Bombardieri, 2013).

The employment of local raw materials seems to fit well into the type of community that was living at Erimi-*Laonin tou Porakou*. The archaeological evidence indicates a small community with a focus on manufacturing, specifically oriented toward the manufacture of textiles, and supported by the wide extent and central location of the workshop area (Bombardieri, 2013).

Technology of production

Aggregates and inclusions

The presence of calcareous fragments dispersed in the plaster/mortar binder might be due to an intentional addition of limestone aggregates or can be ascribed (Bruni et al., 1997; Miriello et al., 2011; Stefanidou et al., 2012) to the slaking and maturing of the lime during and after the production process. In particular it has been reported (Miriello et al., 2011) that an insufficient seasoning of the quicklime, together with a low water content during the mixing phase, can lead to the formation of fairly large nodules of slaked lime that become lime lumps (Bakolas et al., 1995) due to the carbonation process.

As for the present study, calcareous fragments recognized in the matrix showed dimensions ranging from a few μm to a few tens of mm, and their composition is richer in Ca and poorer in Si and other minor elements when compared to the binder (Figure 2). The composition of the fragments and of the binder can be considered similar, as reported in the literature on the subject (Stefanidou et al., 2012). This observation might indicate a common origin of the binder and of the lime fragments. The SEM morphological examination of many of the largest calcite fragments revealed the presence

of unaltered fossils and bioclasts (Figure 3a), indicating that the material composing these biggest fragments had not been subjected to a heating or firing process that would have decomposed the shells. The microscopic evaluation of the binder, however, showed the presence of thermally decomposed fossils and bioclasts (Figure 3b). Different hypotheses can be formulated to explain these results. The first is that the temperature during calcination was too low or that the calcination time was too short. It is reported (Gourdin and Kingery, 1975) that when calcination has not been completed, the original rock remains incompletely decomposed, leaving an unreacted limestone core surrounded by fine recarbonated lime. A second hypothesis points to the possibility that the larger fragments could have been added as aggregates while the smaller lime fragments could be lumps. However, this hypothesis seems unlikely due to the total absence of a reaction rim also around the smaller lime fragments. In fact the hydrated lime of the incipient lumps can react with Si and Al in the binder, forming a reaction rim that is clearly visible in microscopic observation and that is particularly rich in Ca, Si and Al (Stefanidou et al., 2012). The third hypothesis is that all the lime fragments were added as aggregates, presumably obtained by grinding local calcareous sedimentary stones (Theodoridou et al., 2013), to the calcined limestone.

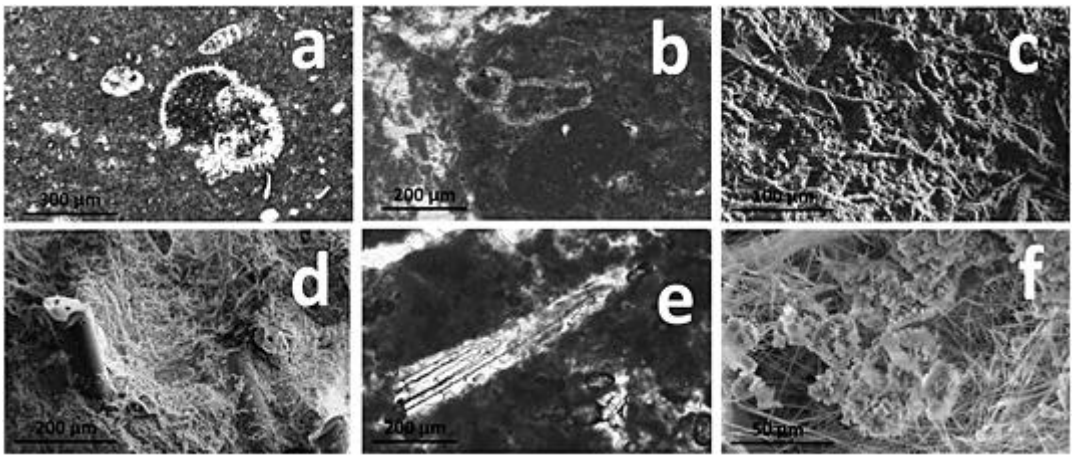


Figure 3. Unaltered (a) and altered (b) fossils and bioclasts (polarized OM), fibres embedded in the binder (c, SEM), sponge spicules (d, SEM and e, polarized OM), and raphides/calcite crystals (f, SEM).

Another type of inclusion found in almost all the layers coating bins and basins, two of the emplacements, one floor, one sample (P60) used for the connection of two architectural/structural

elements and a few other samples is vegetable fibres (Table 1). The amount of fibres, the diameter of which are 1 to 5 μm, is usually more than 50% v/v (on the basis of visual examination of SEM-SE images), and they are intimately in contact with the binder (Figure 3c). The use of these vegetable fibres seems to be directly connected to the destination of use of the material and is often related to the need to reduce cracking and increase the stability and the resistance of the final outcome (Stefanidou et al., 2012).

Finally, two peculiar findings should be mentioned. Around a third of the samples showed the sporadic presence of monaxon sponge spicules (diameter up to 70 μm, length up to 5 mm; Table 1, Figures 3d and 3e), skeletal siliceous structures. Spicules are colourless, hardly visible to the naked eye and they were already observed in the calcareous deposits constituting the Pakhna formation (Francesco Dela Pierre, personal communication). Besides, their presence is very scarce and not related to specific features (Table 1), therefore we concluded that their occurrence is unintentional.

Moreover, SEM-EDX evaluation revealed the presence of isolated aggregates of needle-shaped $Ca_xC_yO_z$ crystals (Figure 3f, diameter around 1 μm, length up 70-80 μm) that could be identified as calcium oxalate raphides,or carbonate crystals (Crowther, 2009) in nine out of the 22 samples (Table 1). The possible sources of these crystalline microfossils could be both from sponges and plants. Almost all the samples containing raphides/carbonate crystals showed the associated presence of vegetable fibres, while the correspondence with the sponge spicules was not so marked. The main hypothesis is that the presence of the raphides/carbonate crystals is directly connected to the addition of the fibres during manufacturing.

The recorded association between organic fibres and raphides/carbonate crystals finds corroboration in the productive and palaeo-environmental setting of the site. Palaeo-botanical studies have been carried out on the filling soils sampled from several different basins and storage vessels (*pithoi*) in the workshop complex and have shown the widespread presence of *Boraginacae* (Elena Vassio, personal communication), invasive plants very common in the area and used for dyeing and for their medicinal properties (Sinclair, 1992). The plants of the *Boraginacae* family, in fact, produce

and accumulate phytoliths and cystoliths (including raphides) in their tissues (Watson and Dallwitz, 1992). Given the recorded presence of mineralized *Boraginacae* seeds in the excavated contexts at Erimi-*Laonin tou Porakou*, the hypothesis of the finding of raphides in many of the analyzed samples is particularly consistent.

Pyrotechnology

As reported by Wright (1992), both the use of burnt lime and/or crushed limestone is known in ancient Cyprus and is still used in modern buildings. As for the site of Erimi-*Laonin tou Porakou*, the direct use of unburnt limestone could be hypothesized in the case of floors.

As Weiner (2010) highlighted, calcite is a widespread mineral in archaeological sites and its origin can mainly be geological or anthropogenic. Anthropogenic calcite is the product of pyrotechnology, but from a chemical point of view, geological and anthropogenic calcite are indistinguishable.

Weiner (2010), Chu et al. (2008) and Regev et al. (2010) showed that FTIR can be used as a technique to evaluate the degree of crystallinity of calcite in plasters/mortars and to distinguish between raw limestone objects and pyrotechnological products. Calcite has three characteristic IR absorption peaks in the range between 400 and 4000 cm^{-1}: ν_3 at 1420 cm^{-1} (asymmetric stretch) ν_2 at 874 cm^{-1} (out-of-plane bending) and ν_4 at 713 cm^{-1} (in-plane bending). It has been shown that the ratio of the ν_2/ν_4 peak heights reflects the extent of atomic disorder in the calcite crystal. In particular, Chu et al. (2008) fired two different limestone samples at different temperatures between 700 and 900°C and obtained ν_2/ν_4 ratios ranging from a minimum value of 3.3 to a maximum of 7.7 (using spectra for ν_2/ν_4 calculations that had ν_3 peaks with full width at half maximum FWHM values between 110 and 130 cm^{-1} to evaluate the grinding effect).

FTIR experiments in the present studies showed that the ν_2/ν_4 ratio ranged between 3.7 and 4.4, while the value obtained for the sample of local calcareous soil was 3, the typical value for geological calcite. The results showed that all the samples are pyrotechnological products and that natural limestone was not used at the site, not even for floors. Nonetheless, the relatively low values

of the ν_2/ν_4 ratio lead to several considerations. First, the temperatures reached during the calcination step were probably not so high and/or were not maintained for a very long time. On the other hand, these quite low values can be explained by taking into account the presence of the unburnt limestone fragments, which lower the resulting ν_2/ν_4 ratio.

Moreover the SEM examination of the samples revealed a structure composed of microscopic rounded particles with a homogeneous and fine granulometry (particle dimensions around 1-5 μm; Figure 4) and these morphological observations complied with the hypothesis that the samples were not simply crushed limestone but anthropogenic objects (Kingery et al., 1988; Philokyprou, 2012a). Finally, the presence of thermally decomposed fossils and foraminifera shells in the binder of the plaster/mortars (Figure 3b), already observed and commented on, confirms a firing step occurred during the manufacturing process.

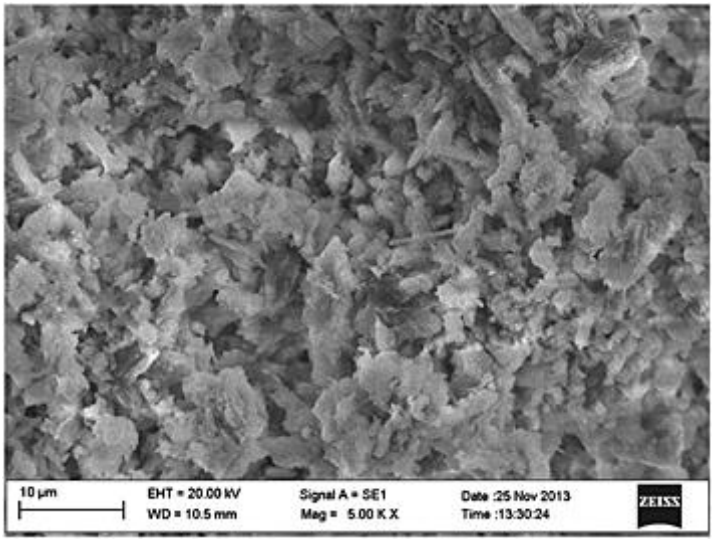
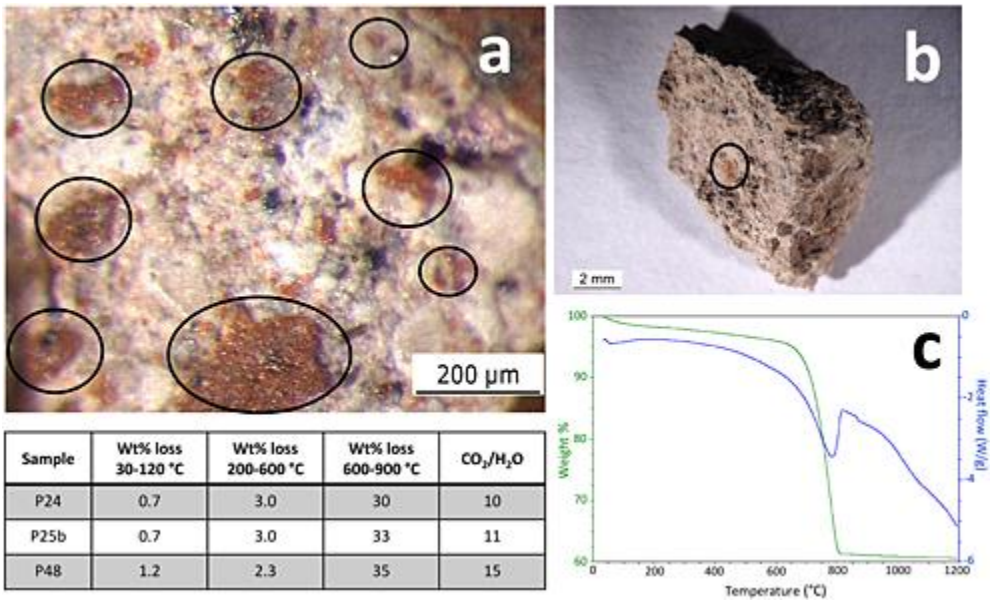


Figure 4. An SEM–SE image (5000×) of sample P50 (fresh fracture).

Hydraulicity

The observation under a stereoscopic microscope of three samples, namely P24, P25b and P48, showed the presence of orange inclusions whose dimensions ranged from a few tens of μm to 1-2 mm (Figure 5a). Spot EDX analysis performed on these inclusions showed higher amounts of Si, Al, K and Fe and a lower quantity of Ca (Figure 2, Spot 1) when compared to the binder (Figure 2,

Area 4) and suggests the use of crushed ceramics during the preparation of mortars used for the supports of big vessels for foodstuff storage. The presence of this artificial pozzolanic additive is usually commented as an indication of the intentional aim to produce a hydraulic material (Moropoulou et al., 2005; Moropoulou et al., 1995; Theodoridou et al., 2013).



Sample	Wt% loss 30-120 °C	Wt% loss 200-600 °C	Wt% loss 600-900 °C	CO_3/H_2O
P24	0.7	3.0	30	10
P25b	0.7	3.0	33	11
P48	1.2	2.3	35	15

Figure 5. Stereomicroscopic images (a, b), TGA–DSC analyses (c) of sample P48 and a table illustrating the TGA wt% losses of samples P24, P25b and P48.

Thermal analysis (TGA-DSC) is a very useful tool in the characterization of historic plasters/mortars since it allows the identification of various components in the material as a whole (binder plus aggregates and/or additives) and to monitor the reactions that occur in the sample when heated in an appropriate and controlled temperature interval. To evaluate the thermal characteristics of the two samples, the methodology suggested by Moropoulou (2005; Moropoulou et al., 1995) was applied. The table in Figure 5 illustrates the results obtained from TGA-DSC analysis (Figure 5c). When our data was compared with those reported by Moropoulou (2005), it was observed that the percentage of physically bound water (wt% loss between 30 and 120°C) is below 1% (the limit value between lime and hydraulic lime mortars) for samples P24 and P25b, while it is slightly higher for sample P48. The amount of structurally bound water (wt% loss between 200 and 600°C) falls in the typical range for lime mortars (equal or below 3%), while the weight loss over 600°C,

which represents the carbon dioxide content, is anomalous (for a lime plaster) only in the case of sample P24 (below 32%), leading to CO_2/H_2O ratio values higher than the upper limit for hydraulic lime mortars. Considering the overall results the two samples can be classified as lime mortars and not as hydraulic lime mortars, on the basis of Moropoulou's (2005) categorization.

On the other hand the calculation of the hydraulicity index (HI; Böke et al., 2008; Kurugöl and Güleç, 2012), which allows for a subtler distinction of the hydraulicity level, produced values in the range 0.1-0.2, indicating that the two samples can be classified as weakly hydraulic.

On the basis of these observations, it seems more plausible that the addition of crushed ceramics in mortars P24, P25b and P48 had the purpose of improving overall mechanical properties, with special respect to increase the mortars stiffness (Baronio et al., 1997; Tesárek et al., 2014), rather that to confer waterproof properties.

CONCLUSIONS

The present study highlights that the technology of manufacture of plasters and mortars at Erimi-*Laonin tou Porakou* from EC III to LC IA was based on the use of local limestone as raw material for the production of the binder. Moreover, samples from both Phases A and B from all architectural contexts (floors, coatings of basins and bins, emplacements, hearths, etc.) turned out to be pyrotechnological products. A very limited amount of aggregates was detected, leading to a maximum aggregates/binder ratio of 1:1. The most abundant inclusions were lime fragments of the same local origin as of the matrix, and their occurrence can be ascribed to an intentional addition after firing, to an incomplete calcination during the firing step or to the formation of lumps pending the drying and ageing processes. All other detected inclusions (with the exception of the ceramic fragments), are typical of the local limestone and are not an intentional addition.

The main point of note is the continuity in the pattern of lime plaster production through time. Although the transition between Phases A and B was marked by a distinctive change in the

architectural configuration, the mechanism of lime plaster production seems to have remained rather unchanged. In Phase B, lime plaster was the prevalent building material, while in Phase A the architectural scheme was enriched by the introduction of several features made of dressed stone (particularly for the building of bins and kilns). During this change, the production of lime plasters remained the same. In other words, the diachronic observation of the lime plaster-based features at Erimi-*Laonin tou Porakou*, shows a difference in the manufacturing process only according to their function and not in change over time.

From this point of view, the observation of the addition of aggregates such as artificial pozzolanes and/or organic fibres seems to suggest that the plaster formula was dictated by the function that it had in the final architectural element.

The addition of artificial pozzolanes can be recorded in cases where a greater resistance was requested, such as for the emplacements of big vessels, where the totality of the samples exhibits the addition of crumbled ceramic fractions (a feature that has not been recorded in any of the other samples). In this case, the addition of ceramic fragments does not seem to be related to a waterproofing function, but rather to confer low elasticity. The results of these firsts experiments with artificial pozzolanes was not the manufacture of a real hydraulic plaster, however this first attested use is rather remarkable and probably calls for a more diachronic approach when studying certain architectural components.

Secondly, the addition of organic fibres, mainly recorded in cases of emplacements and coatings of basins, is clearly due to a need for mechanical strength of the architectural elements themselves.

The simultaneous occurrence of raphides and organic fibres and their possible correlation with the exploitation of plants of the *Boraginacae* family might suggest a multi-functional use of raw materials (primarily for dyeing activities, and then for architectural purposes) and, at least, an homogeneous palaeoenvironmental background.

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