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Earthen and hydraulic mortars used at Lavrion during classical antiquity (5th–4th century BC) – A fundamental relationship between earthen building tradition and sophisticated hydraulic binders and concrete

ABSTRACT: *In Lavrion, silver-bearing ores of lead have been processed to produce silver since prehistoric times. During the fifth and the fourth century BC, an intense exploitation of these ores took place, correlated with a certain historical context of a decisive culmination of wealth and political power of the Athenian Polis (city state). As a result, built structures associated with ore-processing are still ubiquitous at a huge scale in the area. This paper focuses on the mortars, both hydraulic and earthen, used in these structures. At first, a commonly shared building pattern is acknowledged and explained. Earthen mortars were used as structural mortars of stone masonry, while hydraulic mortars were used only as renders. The study on earthen mortars revealed properties similar to those suggested in modern earth-building handbooks and standards. In addition, the production of earth mortars with discretely varying characteristics according to their use, is a noteworthy find. The hydraulic mortars were applied on structures in contact with water or where industrial activity took place. The system of plastering comprised of two distinct materials, both hydraulic: 1) The thin waterproofing layer and 2) the substrate mortar, for which our ongoing research, combined with results of past studies, reveals that it is a hydraulic concrete with extraordinary properties such as high compressive strength, high density and low porosity.*

KEYWORDS: EARTH MORTARS, HYDRAULIC BINDERS, ANCIENT CONCRETE, LAVRION, METALLURGY

Introduction

Lavrion region, located in southeast Attica, approximately 50 km from Athens, is well-known since the remote past until our days for its silver-bearing ores. Their exploitation began in prehistoric times (Kakavogianni, et al., 2018) and went on – not without interruptions – until its cessation in 1977 (Conophagos, 1980, p.51). The most intense mining activities occurred during the fifth and the fourth century BC, when, apparently, Lavrion was transformed into a kind of an "industrial zone" – to use an analogy – of the city-state of Athens. K. Konophagos' (Conophagos, 1980, p.145) estimate of a produce of circa 3,500,000 kg of silver hints to the extraordinary scale of production during this era. It is also worth noting that one of the first and biggest industries of Greece, established in the 19th century at Lavrio, was predominantly based on processing the tailings and the slags left in situ in huge heaps by the ancient Athenians. Besides the socioeconomic reasons, which led to the flourish of mining activity during classical antiquity, there is also an important technological factor, a breakthrough, which made it possible to extract even a few grams of silver content per ton of ore. Regarding the technological aspect of the ore processing, one can include the mortars used in the various structures, which are the main concern of this paper.

As mentioned above, the heydays of Lavrion were during the 5th and the 4th century BC. As a result of these intense mining activities, there is a plethora of visible archaeological remains in an area of more than 45,000 acres (Kapetanios, 2013, p.185). The built parts of these remains belong principally to hundreds of ore processing workshop modules, i.e., installations for the enrichment of the ore and its preparation for the furnaces. Generally, each module consists of an ore crushing-and-grinding compartment, an ore-washery, an associated cistern, dwellings and ancillary structures. Structures are made of rubble or semi-dressed masonry, the stone units of which are from locally quarried schist, marble and limestone. The size of the units varies, depending on the masonry

Fig. 1: Representative examples of the materials and the techniques used. Stone masonry and earth block masonry, both coated with thick hydraulic renders. The floors are made of various layers of hydraulic mortar. Stone masonry and earth block masonry constructed with earth mortars and plastered with hydraulic mortars constitute a building pattern (photo: N. Meimaroglou).

thickness. There are also adobe masonries, some of which have remarkably survived until our days (Fig. 1). Adobe masonry is built on a stone masonry base in order to be protected from rising damp, while direct contact between rainwater and adobe bricks is prevented by a thick plaster. Ashlar masonry may also be used, less frequently though, in certain components of a workshop complex such as strong and high retaining walls and cistern walls. Nevertheless, most of the structures were constructed with the use of mortars of which two main types can be clearly identified: earth mortars and hydraulic mortars.

Discrete use of hydraulic and earthen mortars and the reasons for this “strange” choice

At first, the discrete application of earthen and hydraulic mortars in these ancient structures must be identified and distinguished. On the one hand, earth-based mortars were used as structural mortars, either in filling the joints or as an infill of three-leaf stone masonry. On the other hand, hydraulic mortars were used only as renders in cisterns, on the floors of the washeries or even at some rooms. They were never used as load bearing elements, something readily apparent in the architecture of classical antiquity in general. One can say that this discrete use of these mortars indicates a characteristic building pattern, a building mode that proves to be typical in every structure related with ore processing (Fig. 1). The question that arises is, why ancient Athenians used earth mortars for structural purposes, since they had the knowledge and the technology to produce hydraulic mortars of high efficiency? This is a tricky question with no unambiguous answer. The possible reasons for this preference are discussed below.

The scarcity of fuel

This first answer comes from far away, from Egypt. A similar question was posed there as well: why did the ancient Egyptians use only gypsum mortars, until at least Ptolemaic times when lime mortars were introduced in their architecture, while there was an abundance of limestone and lime technology was known? This question puzzled archaeologists and engineers alike. The confusion became even greater by the presence of calcium carbonate in Egyptian mortars and renders which led researchers to believe that there was an intentional admixture of lime (Mallinson and Davies, 1987).

It was finally shown that calcium carbonate was just an impurity derived from the raw material in which it occurs naturally, not a deliberate addition, and so the binding material was gypsum (Lucas, 1948). The answer given for the preference of gypsum instead of lime, which is relevant to the case of Lavrion, is the scarcity of fuel. Rock gypsum needs only 130 – 170 °C to form hemihydrates and can be burnt on an open hearth. Limestone on the other hand needs 800 – 900 °C degrees of constant temperature for several hours or even days to decarbonate and produce hot lime. Consequently, much more fuel is needed for lime production, as well as kilns and special arrangements to maintain the temperature. It is known that in Lavrion huge quantities of fuel were necessary for the furnaces and the cupellation process.

Therefore, one can assume that scarcity of fuel is a reason that partly explains why the ancient Greeks did not use hydraulic mortars as load bearing element instead of earth mortars.

Ancient Greek building tradition

Monumental buildings of Athens were made with ashlar masonry, in which no mortar at all was used, while in other buildings of less significance, only earth mortars were used as structural mortars. Thus, the use of earthen mortars in Lavrion is also a matter of building history and tradition. In this respect, the second answer is the deep

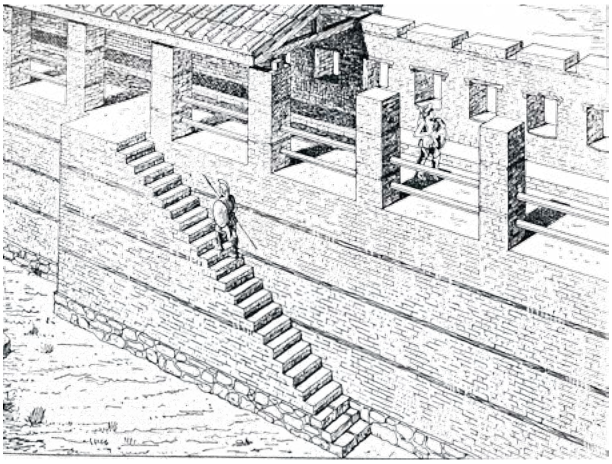

Fig. 2: Representation of the adobe defensive wall of the city-state of Athens by Orlandos (1955, p.79 fig.38).

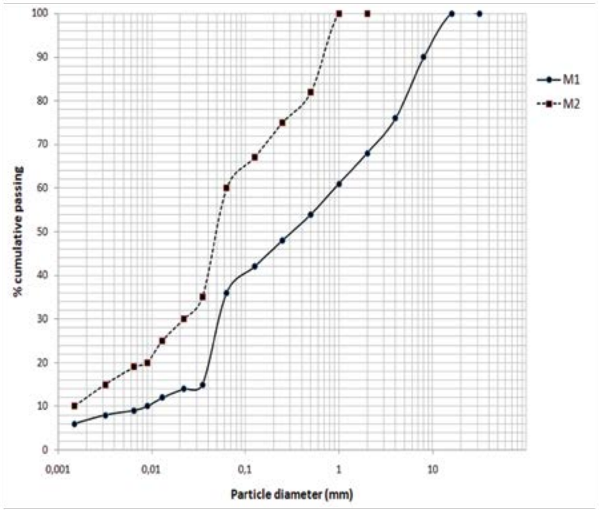

Fig. 3: Granulometric curves of the infill earth mortar (M1) and the joint earth mortar (M2) (chart: N. Meimaroglou).

knowledge of the advantages and limitations of earthen building materials by the ancient Greeks as part of their building culture. As mentioned by A.K. Orlandos in his book on the building materials of ancient Greeks (Orlandos, 1994, p.65–83), adobes and earth mortars were used extensively; he cites ancient writers such as Aristophanes, Aristotle, Xenophon and Thucydides who mention earth building techniques in their writings, or Plato who refers to the defensive walls of Athens as "earthen wall" depicting this way the use of adobes in their construction (Fig. 2).

Important buildings like the temple of Hera at Olympia, the first temple of Apollo at Aegina or the mausoleum of Halicarnassus were also constructed with earthen materials. Even in the 'golden age' of Pericles, when ashlar masonry reached probably its highest peak, the city at the foot of the Acropolis was mainly built by adobe bricks (Guillaud and Alva, 2003).

In addition, adobe bricks had a fixed size, depending on their private or public use, revealing some kind of standardization. For instance, the square adobe brick *pentadoron*, with a side of 1.25 feet, was used for public buildings while the adobe brick *tetradoron* with a side of 1 foot was used for private buildings (Orlandos, 1994, p.74).

Furthermore, great care was taken on soil selection for the production of the unbaked bricks. There were specialised workshops (called plinthourgia) and craftsmen specialised in adobe brick production. In order to understand the extent of use of adobe bricks by ancient Greeks, it is worth noting that not only adobe bricks had a commercial value, ranging from three to six drachmas per 100 bricks, but also the surfaces for drying the adobes, made of cane, were considered a commercial good (Orlandos, 1994, pp.72, 82).

Conclusively, earth building was an essential part of ancient Greek building tradition and an elaborated process of earthen building materials production had been developed. Therefore, the use of earth mortars at Lavrion structures, instead of hydraulic mortars, comes as a natural outcome.

Properties of earthen mortar

The property most often employed as a criterion for the characterization of a soil and for assessing its suitability as a building material, is texture (Delgado and Guerrero, 2005, p.241). Texture is the content in particles of different sizes of a soil and in order to assess it, two methods are usually applied: 1) the wet sieving method, to define the granularity of the sand and the gravel and 2) the hydrometer method to define the content of the different soil fractions, i.e., the content of clay, silt and sand. Among these fractions, clay sized fraction is of major importance, since in earth mortars and earthen building materials in general, clay acts as a binder as does the lime in lime mortars or cement in cement mortars and concrete. Therefore, cohesion, adhesion and finally strength are all attributed to clay. But clay is also responsible for the main drawback of earth building materials, which is volume change. In general terms, it can be said that the greater the clay content is in a mortar, the higher its strength but also the higher its volume change and cracking (Meimaroglou and Mouzakis, 2019). In modern earth building standards and handbooks, the clay content or texture is always mentioned and the suggested values range from 5–25% depending on the technique and the type of clay (Danso, 2018).

Using the hydrometer method (according to ASTM 422), it was found that ancient earth mortars from Lavrion comply with modern standards in terms of texture. Their clay content ranges from 8–18%, as suggested in modern literature. The claim that these values are not coincidental, but the result of a thorough mortar production is further

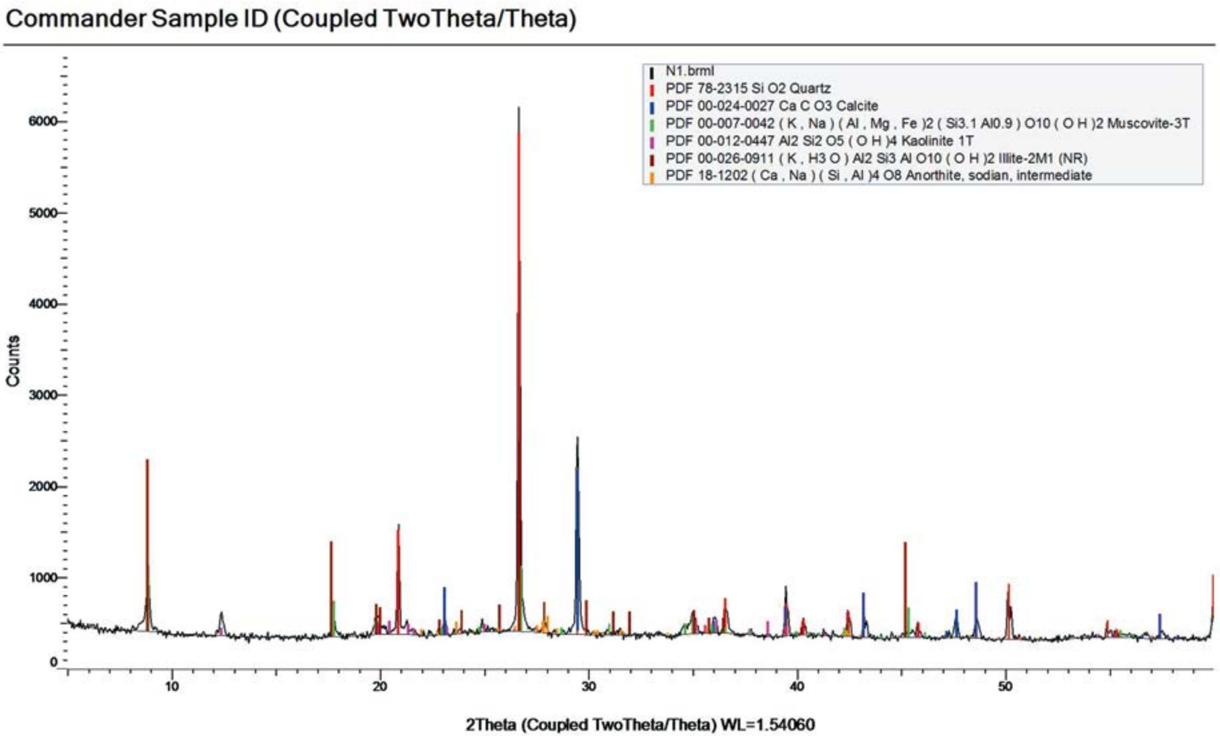

Fig. 4: Typical XRD diagram of an earth mortar from Lavrion (diffractogram: N. Meimaroglou).

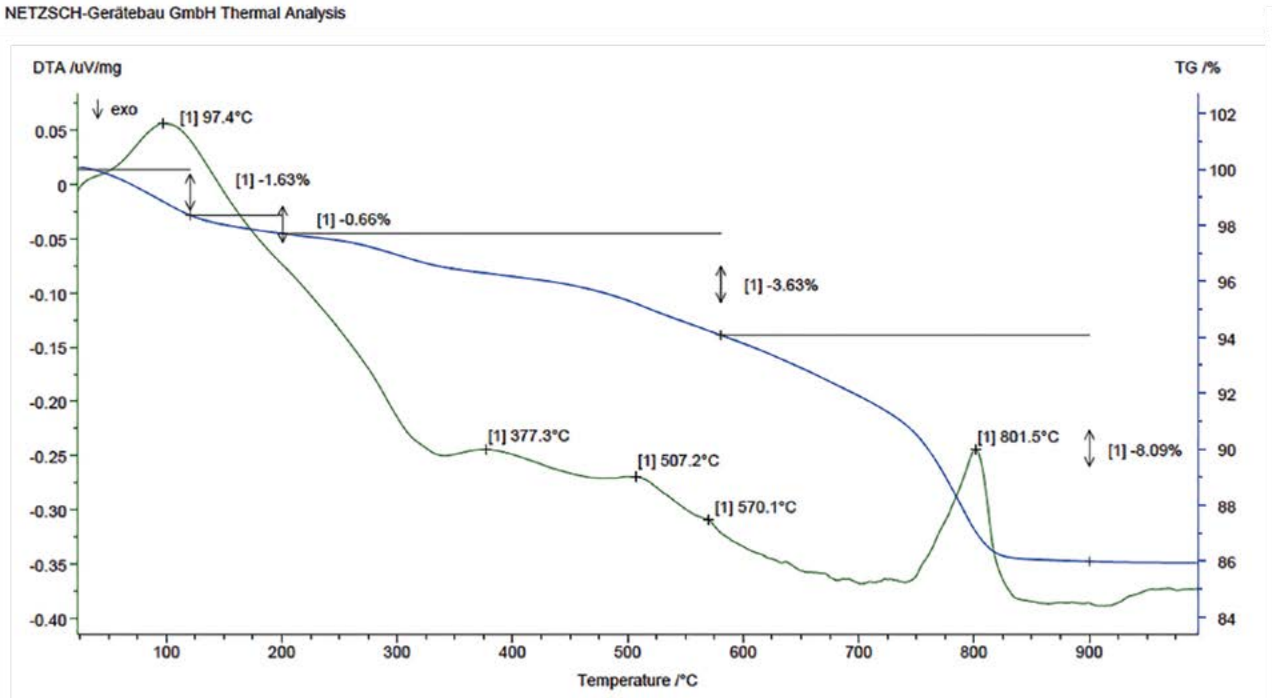

Fig. 5: TG-DTA diagram of an earth mortar from Lavrion (graph: A. Bakolas and N. Meimaroglou).

supported by the results of the wet sieving. The two granulometric curves, presented in Fig. 3, are the outcome of analysis with both hydrometer, to find the clay and silt content and the sieving procedure, to draw the grading curve of the aggregates. They derived from earth mortars of the same masonry. One mortar sample was taken from the infill (M1) and the other from the joints (M2).

The joint mortar (M2), as it can be observed in Fig. 3, has a maximum aggregate diameter of 1 mm and a clay content of 18%. The fact that this mortar is fine-grained permits it to fill the thin joints, while the high clay content ensures a high compressive strength, which is necessary for the load-bearing outer leaves of the masonry. On the other hand, the infill mortar (M1) is completely different. It has a clay content of only 9% and aggregates up to 15 mm. Apart from sand, there is also gravel, in exactly the same proportion: 32% is the sand and 32% is the gravel. These characteristics allow the infill mortar to fulfil its role in the masonry system, which is to provide a bond between the outer leaves. In order to do so, coarse aggregates and a low clay content are necessary, to reduce volume change and shrinkage cracking. As a result, the masonry has strong mortars with fine aggregates in the joints to provide strength to the wall and weaker mortars with coarser aggregate in the infill, to reduce shrinkage and provide bond between the masonry leaves. The exact same principle was observed in recent research on mechanical properties of stone masonry with earth mortars (Meimaroglou and Mouzakis, 2018) and it can't be accidental.

Furthermore, X-ray diffraction (XRD) analysis, to identify the crystalline compounds and thermogravimetric/differential thermal analysis (TG/DTA) to identify physicochemical transitions were also performed. For some typical diagrams see Figs. 4 and 5. The major phase revealed by XRD analysis (Fig. 4) is quartz while the secondary one consists of calcite, muscovite/illite and kaolinite. The TG/DTA diagram (Fig. 5) is typical of an earth mortar. Mass loss under 120 °C represents physically bound water. Mass loss between 120 – 200 °C represents interlayer water and between 200 – 600 °C the chemically bound water. At temperatures above ca. 800 °C, $CaCO_3$ decomposes. Endothermal peaks at 307.2 °C and 507.2 °C can be attributed to clay minerals. The endothermal peak at 570.1 °C is attributed to the transformation from α-quartz to β-quartz. It is also worth noting the high content of calcium carbonate (18.4% $CaCO_3$) and the absence of swelling clays that could hinder the performance of the earth mortars.

Properties of hydraulic mortars

Mining and metallurgic practices demanded effective and rational management of water resources. In a dry area, with no springs, rain and the subsequently formed ravines were the sole water-sources. This historical, geophysical and climatic context gave rise to an extensive, large scale hydraulic system managing billions of tons of water when operating in full scale during the second half of the 4th century BC. Recent research has elucidated aspects of this system and has pointed out the connection between water management and the productivity of workshops (van Liefferringe, et al., 2014). The technology employed, besides the elaborate built parts (dams and built ravine-bands, on- and under- ground cisterns, aqueducts, distribution and hydrostatic pressure regulating tanks, ore-washeries, etc.), included the use of hydraulic mortars of extraordinary composition, strength and waterproof properties, which are still not fully understood.

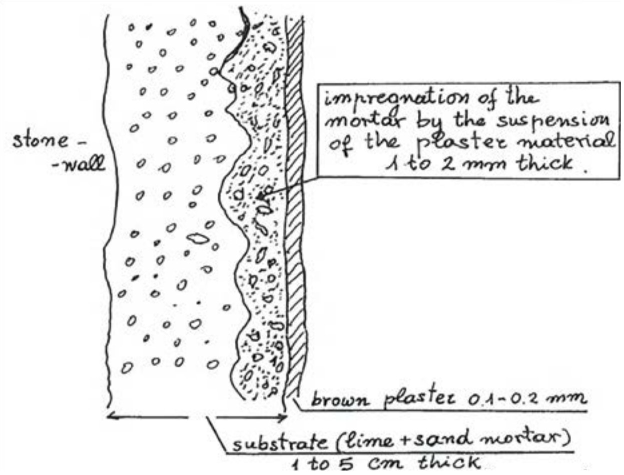

Fig. 6: A typical section of a masonry from Lavrio showing the system of plastering (drawing and comments after Papadimitriou and Kordatos, 1995, p.278 fig.3).

These hydraulic mortars were applied on structures in contact with water or where industrial activity took place (cisterns, floors and walls of the washeries, some ancillary structures etc.). Two hydraulic mortars with different function and composition were used for plastering (Fig. 6): 1) the outermost brown waterproofing thin layer of plaster which has been thoroughly studied (Conophagos and Badecas, 1974; Papadimitriou and Kordatos 1995) and 2) and the concrete substrate, for which only a few studies have been conducted. Our ongoing research, combined with the existing studies, suggest that a binder of hydraulic nature was used for the substrate and elucidate some of its exceptional properties.

The brown plaster

Initially, it was thought that the outermost coat, the thin brown plaster, consists of ground litharge mixed with lime (Conophagos and Badeca, 1974; Badeka, 1974). But it was noticed that the material did not give reflections in XRD analysis, apart from that belonging to calcite, despite that SEM-EDS analysis revealed a high content of lead, manganese, zinc, alumina and silica. So, it was assumed that this brown waterproofing render consists of lime combined with a mixture of ores and litharge which were previously melted together and quenched to obtain a non-crystalline, amorphous material. This material in a fluid suspension was applied on the substrate in layers with a brush (Papadimitriou and Kordatos, 1995).

What is untold until now, but important from a technological aspect, is that this remarkable technology reveals a deep, sophisticated knowledge of hydraulicity. Firstly, the utilization of slags in construction is something relatively modern. Metallurgical slags are used nowadays as supplementary cementitious materials in Portland cement concrete mixtures, in a way pretty much similar to the ancient one. This procedure is described in a few words as melting – quenching –grinding.

The reason behind this procedure is not that simple. One of the main factors affecting the pozzolanic activity of a natural or artificial pozzolan is the $SiO_2 + Al_2O_3 + Fe_2O_3$ content. ASTM C618 standard defines their minimum content at 70%.

But silica, alumina and iron oxides can be found everywhere in nature and in various forms. For example, soil's clays have high content of silica and alumina. Also quartz, the second most abundant mineral on earth's surface, is crystalline silica. But soils, as well as quartz are inert. They do not have pozzolanic activity, which means that they do not react with calcium hydroxide to form hydraulic compounds as calcium silicates or calcium aluminates. But while common soil doesn't react with lime, soil from Santorini Island, Phlegraean fields or Trass from Germany do. The same holds true for soils after sintering to form pottery, ceramics or bricks. If these products are finely ground, they also react with lime.

This different behaviour of SiO_2, Al_2O_3 and Fe_2O_3 is the result of two other factors, apart from the content, which affect the pozzolanic activity: the amorphous or the poorly crystalline fabric (with a few exceptions as the zeolites) and the fineness. Volcanic pozzolans have most times a significant content of fine, amorphous or poorly crystalline components, which explains the pozzolanic activity of the earth from Santorini, Trass and Phlegraean fields. Clay minerals possess a crystalline structure and are therefore unreactive, but after calcining at 700–950 °C, this structure is destroyed and a quasi-amorphous structure is obtained. If thermal treatment exceeds this temperature, clays regain a crystalline structure and are again unreactive. Therefore old pottery and bricks are suitable, after grinding, for use as pozzolans while modern bricks calcined at higher temperatures are not.

The same principles are applied for the use of slags as pozzolanic additives. They should be mainly amorphous and with a high specific surface. However, if they are allowed to cool in the air, recrystallization occurs. In modern industry, they must be cooled rapidly most times by pouring them in water to become a granular, amorphous and thus pozzolanic material (Wang, 2016, pp.99–100, 315). This knowledge that we possess nowadays and apply in industrial processing of slags was presumably unknown to ancient civilizations. They used pozzolans, either natural or artificial, by accident and by trial and error. The common narrative is that they found by chance that if the specific earth from Santorini or Pozzuoli is mixed with lime, they get a far better product and so they evolved this technique. Consequently, the apparent knowledge by ancient Athenians at Lavrion that some materials as litharge and slags are inactive but if you sinter them, then quench them and ground them, they became active and this is the only way for the material to possess pozzolanic properties, is a knowledge many steps beyond our understanding of ancient building technology.

The substrate: Typical lime mortar or hydraulic concrete?

On the outer layer, the brown waterproofing plaster, systematic research has been undertaken. On the contrary, the substrate mortar has been to a great extent disregarded, because the general idea is that it is a typical aerial lime mortar, an intermediate coat between the masonry and the brown plaster with the exceptional properties mentioned above. Characterization of this material gets even more complicated as each of the few studies undertaken so far had a different purpose and were conducted by different researchers. However, these previous studies combined with our ongoing own one show that the aforementioned general idea, i.e. that the substrate is a common aerial lime mortar playing just the role of an intermediate layer, is erroneous. In the following sections, it is shown that the binder of the substrate is of hydraulic nature combined with a large number of gravel-sized aggregates, with a diameter often greater than 10 mm, leading to a material that simulates the properties of a high-performance concrete.

Previous studies and our ongoing research

E. Badeka, in her pioneering PhD thesis back in 1974 examined, among others, renders from cisterns from Lavrion (Badeka 1974, pp.38–94). She assumed that the substrate is concrete made of hydraulic lime and not aerial lime. This is based on XRD analysis, on polarized light microscopy analysis and on the high contents of silica and alumina in the binder matrix determined through XRF analysis.

C.A. Langton and D.M. Roy conducted research on ancient building materials with the aim to optimize modern borehole plugging and shaft sealing materials used to isolate nuclear waste (Langton and Roy, 1984, p.543). Their main concern was the aspects associated with the durability of the ancient concrete. Besides mortars from Italy and Cyprus, they examined some mortar samples of a dam and cisterns from Lavrion. Based on the results of the chemical, mineralogical and petrographic analyses, they assumed that the binder is hydraulic lime, derived from locally quarried impure limestone.

Mishara in 1989 studied renders from Demoliaki, Megala Pefka and Soureza. His aim once again was not to investigate the substrate, but to prove that the brown outer layer was a deliberate fabrication and not the result of a natural process (Mishara, 1989). In his study, a few samples of the substrate were subjected to SEM-EDS analysis in order to be compared with the outer coat. These samples presented a significant content of silica, alumina, lead, manganese and zinc apart from calcium. The author assumed that impure limestone, most likely gangue or plynites, were calcined and so, the lime that was produced had hydraulic properties.

E. Photos-Jones and J. E. Jones studied a wide range of materials from an excavated workshop on the northern side of the Agrileza valley (Photos-Jones and Jones, 1994). They examined tailings, metallurgical waste, soils as well as some plasters, among which some substrate samples. Again, a significant content of silica and alumina in the binder matrix was found.

The aim of a study by A. Galanou, G. Dogani, and K. Lessai was to suggest a recipe and prepare restoration mortars (Galanou, et al., 2008). To do so they studied a few samples of existing mortars, of both the brown plaster and the inner concrete. Their FTIR analysis, thermal analysis, chemical analysis, and microscopy show, for once more, the hydraulic character of these mortars.

Finally, our ongoing study of specimens obtained from floors and renders from washeries, as well as cisterns, confirms the scattered results mentioned above and proves the hydraulic character of the substrate mortar beyond doubt. Mineralogical analysis showed the presence of hydraulic compounds in all samples as it can be seen in a typical XRD diagram at Fig. 7. In addition, after separating the binder from the aggregates and treating it with acid to remove the calcite, a very distinctive hump appeared between 20 – 30° 2ϴ-diffraction angles in XRD analysis (Fig. 8). This hump can be attributed to calcium aluminate silicate hydrates gel (CASH), which is amorphous, not giving any reflection in XRD analysis.

Furthermore, thermogravimetric analysis (TG) revealed that the ratio of carbon dioxide/chemically bound water is in the range between 3.9 and 8. This range is characteristic of lime with hydraulic properties (Moropoulou, et al., 2005). Thermal analysis is a well-established method in mortar characterization (Middendorf, et al., 2005). The weight losses between 200 and 600 °C are attributed to chemically bound or hydraulic water and at temperatures above 600 °C to the decomposition of the carbonates. The ratio between these two values expresses inversely the hydraulicity of a mortar and has been proved useful in the classification of mortars (Bakolas, et al., 1998). The claim that it is a hydraulic mortar is further corroborated by XRF analysis which showed a significant content of silica, alumina as well as of metals and minerals linked

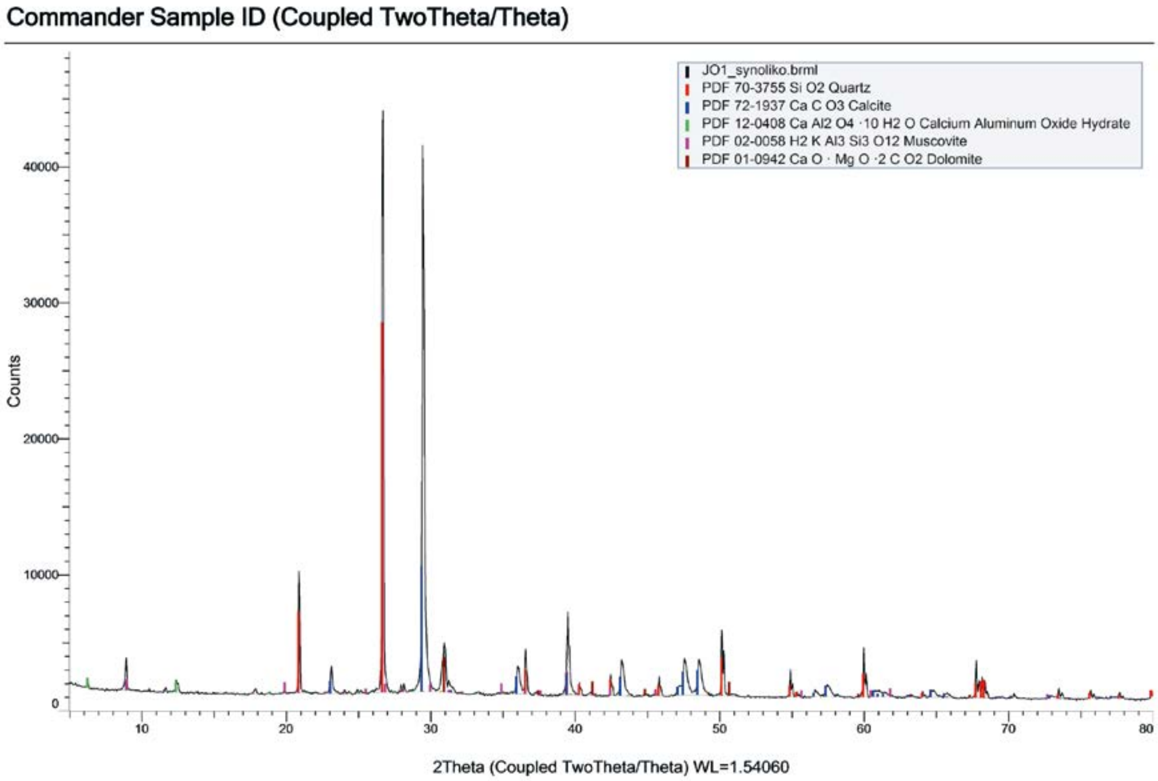

Fig.7: A typical XRD diagram of a Lavrion mortar (diffractogram: N. Meimaroglou).

with the ore processing, both in the bulk specimen and in the binder matrix.

Finally, polarised light microscopy of thin sections was applied. Images captured in parallel and crossed Nicols gave a deeper insight of the nature of the binder. They revealed calcium silicate phases (Fig. 9a) and the presence of amorphous and/or isotropic material (Fig. 9b. c) which, in some instances, has reacted with the binder matrix, as it can be assumed by the formation of rims around amorphous particles (Fig. 9d. e). In addition, metallic minerals (magnetite?) were observed as it can be seen in Fig. 9f.

Intriguing properties of this ancient concrete

Preliminary results of the study on the substrate show not only that it is hydraulic, but that it possesses some properties which could characterize it as unique. These are:

- High compressive strength. Compressive strength is the most fundamental property of building materials. Typical lime mortars used in historic structures have a compressive strength of between 0.5 – 3 N/mm^2 (Válek and Veiga, 2005). Nonetheless, in historic mortars it is most times impossible to measure directly strength because the mortars are in the joints and it is very difficult to form appropriate specimens. So, other methods, the results of which are indirect and unclear as those of the fragments methods, have been developed. The relatively modern breakthrough in the mechanical performance of the binding materials was the introduction of cement, but yet, Portland cement mortars had a compressive strength of 10 – 15 N/mm^2 until the 20th century and exceeded 20 N/mm^2 in the early to mid-20th century when the use of rotary kilns, instead of shaft kilns, became more widespread (Skempton, 1962). For Lavrion mortars, there was in some instances the rare opportunity to create cubic specimens and measure the actual strength (Fig. 10). In both our ongoing research and Badeca's study (Badeca, 1974), there were samples with a compressive strength exceeding 20 N/mm^2, showing that the mechanical characteristics of these mortars exceed our beliefs and knowledge on historic mortars.
- High adhesive strength between binder and aggregates. The bond strength, or adhesion between binder and aggregates, is a property that is very difficult to assess and quantify despite its importance. Under compressive loading of mortars and concrete, the bond between binder and aggregates is lost and cracks deviate mostly through the binder matrix which, even in the case of cement, is much weaker than the rock of the aggregates. By observing the patterns of the specimens' failure under compressive loading, it was noticed something remarkable: cracks did not deviate only through the binder matrix, but as it can be seen in Figure 10b, passed, in some cases,

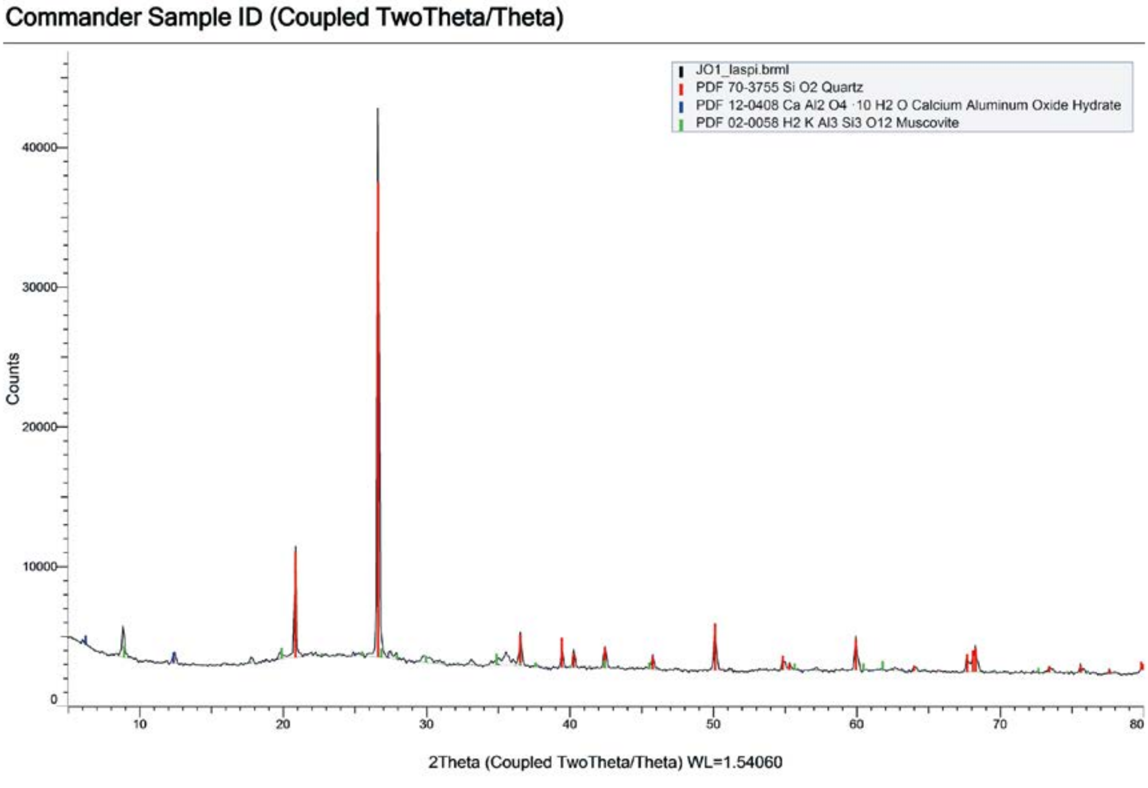

Fig. 8: XRD pattern of the acid treated sample. A distinctive hump (between 20–30° 2-theta) reveals the presence of amorphous material (diffractogram: N. Meimaroglou).

though the aggregates. This is something uncommon that shows the high adhesive capacity of the binder, something that can also be seen in Figure 10c, where an aggregate, on which the binder is tightly bonded, is presented.

- Low porosity and high density. Bulk density and porosity are two fundamental properties of building materials. For mortars in particular, porosity greatly affects their strength, their durability and the moisture transport properties (Thomson, et al., 2004). For lime or pozzolanic historic mortars the porosity is usually more than 30% and the density between 1.6–1.9 g/cm^3 (Moropoulou, et al., 2005). Modern normal-weight concrete has higher density, which EN 206-1 defines that it should be between 2–2.6 g/cm^3. In the case of Lavrion mortars, some of the samples had a porosity of less than 15% and a density higher than 2.1 g/cm^3. Similar results were also reached by Galanou, et al. (2008), who measured a porosity even lower than 10%. Once again, the results obtained are closer to modern concrete than to traditional mortars. A reason behind such extraordinary density and porosity values must be the thorough mixing and ramming with certain tools or devices for this purpose. We also have to envisage a material very different from the slurry or paste like materials that are used nowadays. It must have been

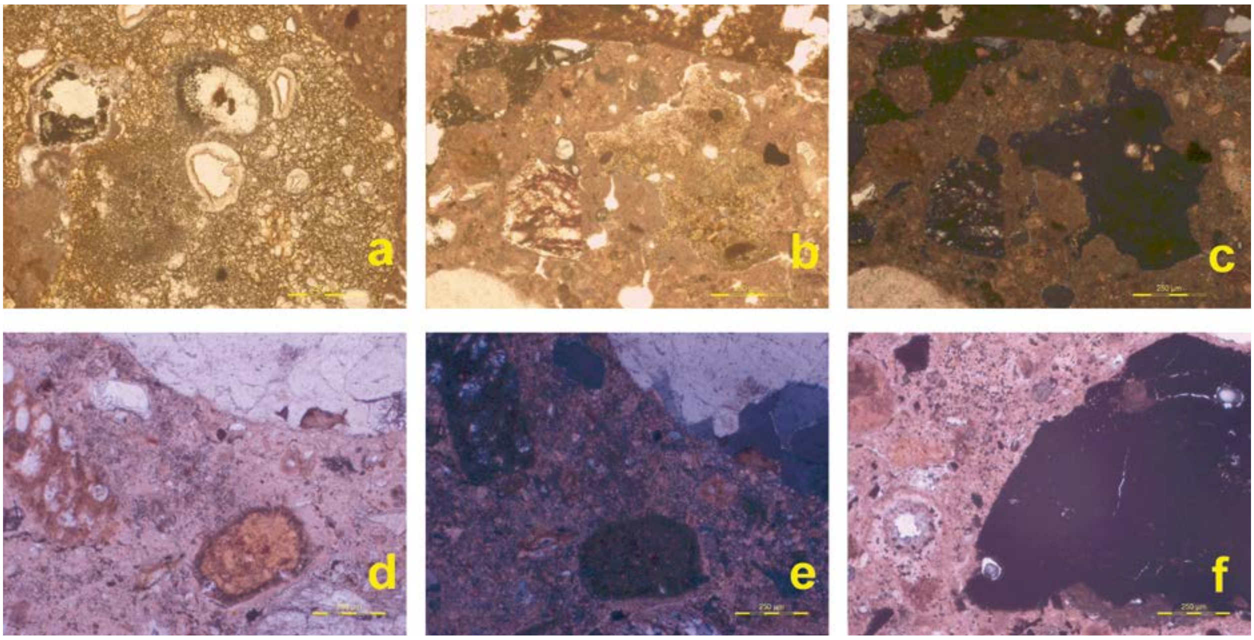

Fig. 9: a. Hydraulic phases of the binder. – b–c. amorphous material can be identified by a comparison between the images in parallel and crossed Nicols, respectively. – d–e. amorphous material (ceramic?) which seems to have react with the binder matrix. – f. Large metallic compounds (microphotographs of the polarized light microscopy: N. Meimaroglou and V. Skliros).

Fig. 10: (a) Assessment of compressive strength (b) Cracks deviating through aggregates during compressive strength testing, (c) High adhesive strength between binder and aggregates (photos: N. Meimaroglou).

a very stiff material, with very low water content at the expense of workability. This is the only way to ram and compact it because if excess water is present and there is no air entrained, it cannot be compacted. This is something that is suggested for Roman concrete and it must be also true for the Lavrion concrete.

Further research questions

As discussed above, the substrate mortar is not a typical lime mortar but a pre-Roman hydraulic concrete, with extreme durability as the longevity of these structures shows. The historical context, as discussed by many researchers (Artioli, et al., 2008; Maravelaki-Kalaitzaki, et al., 2003; Theodoridou, et al., 2013), as well as the technological context in which these hydraulic binders were created and used are of particular importance, but many questions still remain unanswered. Regarding the Lavrion concrete: 1) What kind of lime and pozzolanic materials could they have used for the production of this exceptional material? 2) Is there a standardized formula as suggested for Roman concrete (Brandon, et al., 2014, pp.3, 9, 15)? 3) Is there one type of concrete or more? This material must be the result of a long development through the centuries when these industrial structures were in use. Are different phases of this development recognizable?

Taking into account that the structures at Lavrion, in which concrete was used, are in their hundreds and that concrete served various functions as render on floors, rooms and cisterns, looking for potential answers to these questions is challenging. Apart from the research questions regarding Lavrion concrete, the major question that arises is, did ancient Greeks use concrete elsewhere? In this perspective, the concrete that covered the 5th century BC cistern at ancient Kamiros, Rhodes island (Fig. 11), which also presented high strength and density (Koui and Ftikos, 1998), as well as the work of R. Malinowski (1982), are a good start. It becomes apparent, that to address all these questions, a systematic and consistent interdisciplinary research is required. In this respect, the elaborate study on Roman maritime concrete through the Romacons project can serve as a paradigm (Oleson, et al., 2004; Brandon, et al., 2014).

Conclusions

Within this paper, an overall approach of the mortars used either as structural mortars or renders is presented. Some conclusive remarks are:

1. There is a characteristic building pattern in the structures related with ore processing. Earth mortars were used as structural load bearing mortars and hydraulic mortars as renders. The preferential use of earth mortars, instead of hydraulic mortars, as load-bearing elements, can be attributed to fuel scarcity and to the long-lasting tradition of using earthen building materials by ancient Greeks.
2. Earth mortars were carefully prepared with clay percentage and granularity similar to that which is proposed in modern earth building literature. The hydrometer method showed that the clay content was in the range of 8–18%. This range is appropriate to ensure adequate compressive strength with low volume change that could lead to severe cracking in cases, if a higher clay content was used. Furthermore, granulometric curves derived with wet sieving revealed that different earth mortars were used for different purposes. On the one hand, mortars with higher clay content and thus higher strength and binding capacity, with sand-sized aggregates up to 1 mm, were used to fill the stone masonry joints. On the other hand, mortars with low clay content and thus low volume change, with gravel-sized aggregates up to 15 mm, were used as infill mortar to provide bond between the external masonry leaves.

Fig. 11: a. Sample of Lavrion concrete (photo: N. Meimaroglou); – b. Sample of Kamiros concrete (from: Efstathiadis, 2004, p.1 fig.1).

3. The outermost brown waterproofing thin coat has already been thoroughly examined in previous research and has been found to consist of lime mixed with a mixture of ores or/and litharge and slags, which were previously melted together and quenched to obtain a non-crystalline, amorphous material. What is untold so far is that should this procedure – melting quenching and then grinding – not be applied, the material wouldn't possess these remarkable hydraulic properties. Therefore, a knowledge and perception of pozzolanic activity and hydraulicity by the craftsmen of that time should be assumed.
4. Finally, the preliminary results of our ongoing research on the substrate mortar, combined with the few available studies, suggest that it is not a typical lime mortar but a concrete whose binder possesses hydraulic properties. This was confirmed by polarized light microscopy where amorphous-isotropic phases were identified and by TG-DTG and XRD analyses where hydraulic compounds were found. Furthermore, physical and mechanical tests revealed some characteristics uncommon in historic mortars. These are: high compressive strength exceeding 20 N/mm^2 in some samples, high adhesive strength between binder and aggregates, high density which in some instances was higher 2.1 g/cm^3 and low porosity which was measured even lower than 15%. All these characteristics are indicative of an extraordinary material that needs further research to elucidate aspects related to its technology, its evolution and of the history of hydraulic binders in general.

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Bibliography

Artioli, G., Secco, M. and Addis, A., 2019. The Vitruvian legacy: mortars and binders before and after the Roman world. *EMU Notes in Mineralogy*, 20, pp.151–202.

Badeka, H., 1974. *Στεγανοποιητικά Κονιάματα Αρχαίων Ελληνικών Δεξαμενών Ύδατος*. Unpublished PhD Thesis, NTUA (with English abstract).

Bakolas, A., Biscontin, G., Moropoulou, A. and Zendri, E, 1998. Characterization of structural Byzantine mortars by thermogravimetric analysis. *Thermochimica Acta*, 321, pp.151–160.

Brandon, C.J., Hohlfelder, R.L., Jackson, M.D., and Oleson, J.P,. 2014. *Building for Eternity. The history and technology of Roman concrete engineering in the sea*. Oxford, Philadelphia: Oxbow.

Conophagos, C. and Badeca, H., 1974. The water cisterns of ore washeries in Laurion and their special hydraulic mortar. *Proceedings of the Academy of Athens*, 48, pp.251–261.

Conophagos, C., 1980. *Le Laurium antique et la technique Grecque de la production de l'argent*. Athens: Ekdotike Hellados.

Danso, H., 2018. Suitability of soil for earth construction as building material. *Advancements in Civil Engineering & Technology*, 2(3), pp.1–13.

Delgado, M.C.J. and Guerrero, I.C., 2007. The selection of soils for unstabilized earth building: A normative review. *Construction and Building Materials*, 21(2), pp.237–251.

Efstathiadis, E, 2004. Παγκοσμίως Πρωτοποριακή η Αρχαία Ελληνική Τεχνολογία Υλικών Κατασκευών και οι Εφαρμογές της στα Τεχνικά Έργα, 1. Αρχαίο Ελληνικό Τσιμέντο. *Τεχνικά Χρονικά: Διμηνιαία Εκδοση. TEE*, 3, pp.1–14.

Galanou, A., Dogani, G., and Iessai, K., 2008. Conservation study of four metallurgical workshops from Agia Triada. Research report within a working project assigned by Ephorate of Antiquities of East Attica, Athens: Lithou Sintirisis.

Guillaud, H. and Alva, A., 2003. Historical earthen architecture and construction in the Mediterranean Region. What future for such an exceptional cultural legacy? In: S. Huerta, ed., 2003. *First International Congress on Construction History, Madrid, 20–24.01.2003*. Madrid: Instituto Juan de Herrera, Escuela Técnica Superior de Arquitectura. pp.1107–1117

Kakavogianni, O., Douni, K. and Nezeri F., 2008. Silver metallurgical finds dating from the end of the final Neolithic period until the middle Bronze Age in the area of the Mesogeia. In: I. Tzachili, ed., 2008. *Aegean Metallurgy in the Bronze Age. Proceedings of an International Symposium held at the University of Crete, Rethymnon, Greece, on November 19–21, 2004*. Athens: Ta Pragmata, pp.45–57.

Kapetanios, A., 2013. Ο χώρος και οι άνθρωποι στην αρχαία τοπογραφία της Λαυρεωτικής. In: Μ. Δόγκα-Τόλη and Σταυρούλα Οικονόμου, eds., 2013. *Αρχαιολογικές συμβολές. Τόμος Α' Αττική*. ΚΣΤ' και Β' ΕΠΚΑ. Μουσείο Κυκλαδικής Τέχνης, pp.183–198.

Koui M. and Ftikos Ch., 1998. The ancient Kamirian water storage tank: A proof of concrete technology and durability for three millenniums. *Materials and Structures*, 31(9), pp.623–627.

Langton, C. A. and Roy, D.M., 1984. *Longevity of borehole and shaft sealing materials: characterization of ancient cement based building materials*. MRS Proceedings, 26. Cambridge: Cambridge University Press, pp.543–549.

Lucas, A., 1948. *Ancient Egyptian Materials and Industries*. London: Edward Arnold Ltd.

Malinowski, R., 1982. Durable ancient mortars and concretes. *Nordic Concrete Research*, 1, pp.19.1–19.22.

Mallinson, L.G. and Davies, I.L., 1987. *A historical examination of concrete*. Luxembourg: Office for Official Publications of the European Communities.

Maravelaki-Kalaitzaki, P., Bakolas, A., and Moropoulou, A., 2003. Physico-chemical study of Cretan ancient mortars. *Cement and Concrete Research*, 33(5), pp.651–661.

Meimaroglou, N. and Mouzakis, H., 2018. Mechanical properties of three-leaf masonry walls constructed with natural stones and mud mortar. *Engineering Structures*, 172, pp.869–876.

Meimaroglou, N. and Mouzakis, Ch., 2019. Cation Exchange Capacity (CEC), texture, consistency and organic matter in soil assessment for earth construction: The case of earth mortars. *Construction and Building Materials*, 221, pp.27–39.

Middendorf, B., Hughes, J., Callebaut, K., Baronio, G., and Papayianni, I., 2005. Investigative methods for the characterisation of historic mortars. Part 1: Mineralogical characterisation. *Materials and Structures*, 38, pp.761–769.

Mishara, J., 1989. The plasters of the ore washing structures at Lavrion. In: Y. Maniatis, ed., 1989. Archaeometry: Proceedings of the 25th International Symposium, Athens 1986. Amsterdam: Elsevier, pp.191–205.

Moropoulou, A., Bakolas, A. and Anagnostopoulou, S., 2005. Composite materials in ancient structures. *Cement & Concrete Composites*, 27, pp.295–300.

Oleson, J.P., Brandon, C.J, Cramer, S.M., Cucitore, R., Gotti, E., and Hohlfelder, R. L., 2004. The ROMACONS Project: A Contribution to the Historical and Engineering Analysis of Hydraulic Concrete in Roman Maritime Structure. *The International Journal of Nautical Archaeology*, 33(2), pp.199–229.

Orlandos, A.K., 1994. *Τα υλικά δομής των αρχαίων Ελλήνων και οι τρόποι εφαρμογής αυτών κατά τους συγγραφείς, τας επιγραφάς και τα μνημεία. Second edition. A*thens: The Archaeological Society at Athens.

Papadimitriou, G. and Kordatos, J, 1995. The brown waterproofing plaster of the ancient cisterns in Laurion and its weathering and degradation. In: Y. Maniatis, Herz, N., and Bassiakos, Y., eds., 1995. *The study of marble and other stones used in antiquity*. London: Archetype Publications Ltd., pp.277–284.

Papayianni, I. and Stefanidou, M. 2006. Strength-porosity relationships in lime-pozzolan mortars. *Construction and Building Materials*, 20(9), pp.700–705.

Photos-Jones, E. and Jones, J.E., 1994. The Building and industrial remains at Agrileza, Laurion (fourth century BC) and their contribution to the workings at the site. *The Annual of the British School at Athens*, 89, pp.307–358

Skempton, A.W., 1962. Portland Cements, 1843–1887. *Transactions of the Newcomen Society*, 35(1), pp.117–152.

Theodoridou, M., Ioannou, I., and Philokyprou, M., 2013. New evidence of early use of artificial pozzolanic material in mortars. *Journal of Archaeological Science*, 40(8), pp.3263–3269.

Thomson, M., Lindqvist, J.E., Elsen, J., and Groot, C. 2004 Porosity of mortars. In: C. Groot, G. Ashall, and J. Hughes, eds., 2004. *Characterisation of Old Mortars with Respect to their Repair: A state of the art*. Paris: RILEM Publications, pp.77–106.

Válek, J. and Veiga, R., 2005. Characterisation of mechanical properties of historic mortars – testing of irregular samples. In: C.A. Brebbia and A. Torpiano, eds., 2005. *Structural Studies, Repairs and Maintenance of Heritage Architecture*. *Ninth International Conference on Structural Studies, Repairs and Maintenance of Heritage Architecture.* WIT Transactions on the Built Environment, 83. Southampton: WIT, pp.365–374.

Van Liefferinge, K., Van den Berg, M., Stal, C., Docter, R., De Wulf, A., Verhoest, N.E.C., 2014. Reconsidering the role of Thorikos within the Laurion silver mining area (Attica, Greece) through hydrological analyses. *Journal of Archaeological Science*, 41, pp.272–284.

Wang, G.C., 2016. *The Utilization of Slag in Civil Infrastructure Construction*. Amsterdam: Woodhead Publishing.

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