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DIPLOMA THESIS:

Technological Study of mortars from historic monuments in Greece.

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Introduction

The aim of this thesis is to provide a feasibility study on the application of different analytical techniques as well as on the potential of hand-handled pXRF on the technological studies of historic and traditional mortars, supplementary to the standard analytical and laboratory approaches.

In conservation of historic monuments, it is essential to thoroughly understand not only the condition but also the technology and structure of the materials used. Also the increasing need for use of repair mortars and the nature of such a composite material, make the study of mortars more frequent and essential. Everyone involved is this process should be familiar with some of the approaches and techniques, as well as the principles of them. This thesis is an effort towards this goal.

I would like to thank Dr. Vassilis Kilikoglou, Research Director in Demokritos, for the opportunity given to realize this thesis. Especially I would like to thank Dr. Ioannis Karatasios the support and guidance that made this effort possible.

Contents

Abstract

In theoretical part, chapter 1, uses and types of historic mortars in Greece, especially building mortars, are reviewed. In chapter 2, also theoretical, the aims, results and limitation of analytical techniques used for the study of mortars are discussed.

Presentation of experimental methodology and samples follows. Forty eight (48) samples were available for study. They were photographed, described macroscopically and initially grouped. XRF measurements were taken. Results proved difficult to evaluate without a more thorough study. A further selection of fourteen (14) samples was made, in order to be studied with other analytical and laboratory techniques.

After the separation of aggregates and binder and the study of fractured surfaces and samples under a stereoscope, porosity measurements were made, XRD analysis of the fine powder produced (<0,063mm), SEM analysis (including EDX measurements of binder) and mechanical tests when adequate sample size was available.

The discussion of the results has been divided in two parts:

- comparative presentation for each technique (chapter 4.1 to 4.6) and
- analytic presentation of results and observation on each sample (chapter 5.1 to 5.4).

In conclusions, grouping of experimental results is made and evaluation of use of pXRF is attempted.

1 Uses and types of historic mortars

The classification of mortars can be based on the type of their binder: clay or mud mortar, lime mortar etc. The historic use of binders also illustrates the use of various types of mortars through time.

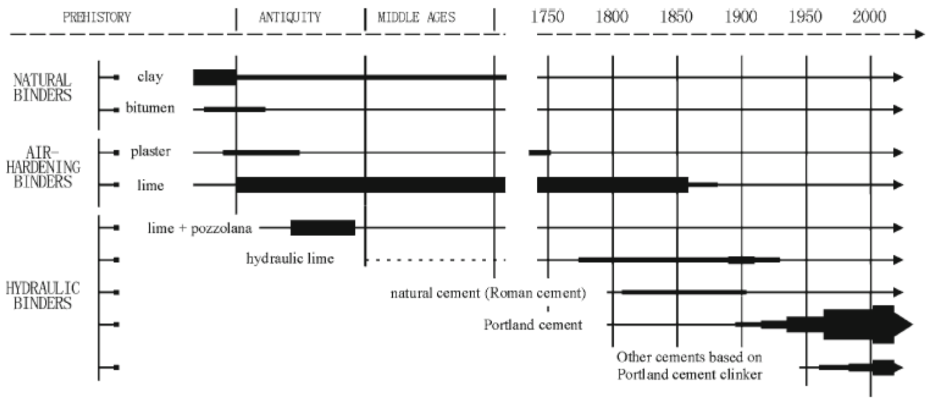


Fig. 1 Use of binders during history (Adapted from Furlan and Bissegger [1])

(Elsen J., 2012)

Additives and different combinations of raw materials results in mortars with different physical and mechanical properties. Moreover, the combination of non hydraulic components can provide some hydraulic properties on the final mortar. From that is evident that history of mortar technology is more complex than what we may originally think.

The next important factor that one must have in mind, is that mortars were never something self sustained or autonomous. They were always essential part of buildings or architectural structures and as such they had specific functions and roles to serve. They had to fulfill certain criteria deriving from their use; they were used as lining materials in cisterns, wells, aqueducts, shafts and duct drains, as supporting materials for pavements and mosaics, as plasters on external and internal walls, as supporting materials for frescoes and as joint mortars on masonry structures. Their history is parallel and linked to architectural and structural evolutions and can only be viewed through them. (Πάχτα, 2011)

Having all these in mind, when we follow the history of Greek historic mortars, we follow at the same time the history of binders and architectural structures in Greece.

The first mortars are clay mortars, used in prehistoric times. Clay was first used either in order to seal holes and voids in wooden structures (settlements made of wood and branches) or even earlier in caves: in pavements etc. Mud-mortars were manufactured nearby the construction work and clay was often mixed with organic (herbs, roots, straw, reeds) and inorganic (sand, gravel) materials. The use of lime at these first structures has been established in different studies (Κυροπούλου, 2016), (Karkanas, 2002) (Karkanas & Stratouli, 2008) (Karkanas, 2007) (Karkanas & Efstratiou, 2015). A fine example of Neolithic settlements in Greece are those of Sesklo and Dimini, date to the 6th millennium BC (Pachta, et al., 2014)

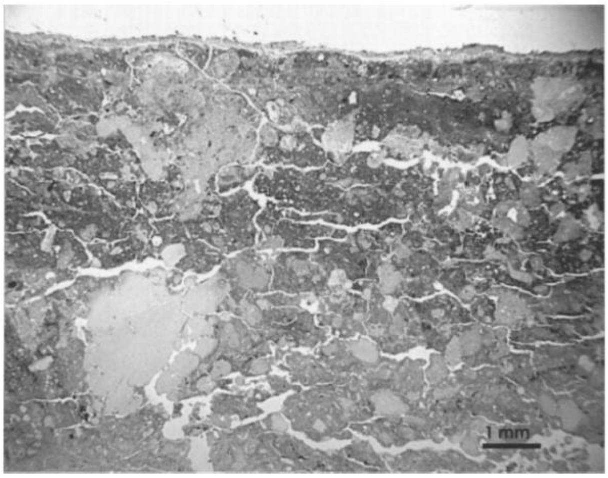


FIG. 3. Photomicrograph of a plastered floor with large quantites (30–40%) of lime inclusions and horizontal fissuring produced by compaction on the surface of the floor.

1 Drakaina cave, Karkanas

Nevertheless, although the use of lime has been identified in prehistoric times, it was first systematically used in Crete (Minoan palace in Knossos, 1.500bC) (Κυροπούλου, 2016) (Πάχτα, 2011). It has been stated that Romans must have borrowed the use of lime from Greeks (Blezard, 2003), During this period, mortars were scarcely used as bearing or building mortars at least for major structures. Building mortars were only used in some minor rare cases (Μπούρας cited in Πάχτα, 2011) but they were widely used as finishing mortars, sometimes bearing wall paintings. Systematic sturdy of pigments in those paintings, as well as those in Thera, reveal calcite as the main component of those mortars.

The same is also true in later periods. Stone was the main building material of important temples and monuments. Stones well cut, without the use of any material as binder (starting from Mycenean structures to Parthenon).

It seems though that, in special cases such as cisterns, mortars were used in combination with other materials. In these cases, surprisingly, hydraulic mortars and additives have been found, in different layers, proving that the technology of mortars has evolved. In the case of Thera, Santorini Orlandos states that the mortars used in water thanks had 43% lime, 10% local pozzolan and 47% sea sand (Ορλάνδος, 1958). But there are also numerous of cases (Harbor of Piraeus/Zea), where these special kind of mortars were also used. These mortars contained a high percentage of large aggregates (0-20mm) and pozzolan (usually Santorini earth). They had high hydraulic characteristics and high mechanical strength. They were also very condensed and water proof and were probably placed in layers on to rock substrate (Πάχτα, 2011).

Some of the cisterns studied, dating from archaic period to Classical Antiquity, are the one in Temple of Athena in Kamiros, Rodes (waterproof 600m^3 water reservoir dated on middle 6th C BC) (Koui & Cr., 1998), and the ore washing basins in Laurion (5th C BC) (Conophagos 1974 cited in Pachta, et al., 2014).

εικ. 55 Μακροσκοπική φωτογραφία κονιοδέματος από την Κάμιρο (Eustathiadis, 1978)

εικ. 56 Στερεοσκοπική φωτογραφία κονιοδέματος από την Κάμιρο (Koui, Ftikos, 1998)

(Pictures taken from Pachta, Thesis)

In other cases, such us defensive walls, other building techniques were used (the need for a fast but also massive and solid construction must have played a major role). The term "έμπλεκτον" used by Vitruvius for some describes just a building technique. For others it also refers to the kind of mortar used in this technique; mortars with large aggregates, characterized as the first kind of concrete.

For minor constructions on the other hand, such as in simple houses, lime mortars with the addition of clayish materials was used. The sturdy of well preserved archaeological sites proves it. The first example is Akrotiri of Thera (1,700-1,400 BC): structural mortars were made of local origin clay, mixed with gravel, charcoal and straw. These joints stopped 2-3 cm below surface and this gap was covered with lime mortar which was externally engraved. (Palivou, 1999 cited in Pachta, et al., 2014)

Similarly, in Olynthos (Classic period, 5th C BC): structural mortars were also lime based with an addition of clayish material. But in parts of the walls that were in contact with water, pozzolan was added in order to increase their impermeability. The aggregates were of natural (river) origin, of 0-8 cm gradation and in a B/A ratio 1/2. (Papayianni & Stefanidou, 2007).

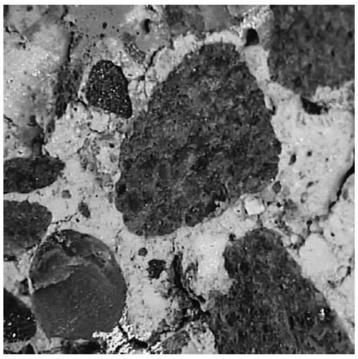


Fig. 2. Well-compacted floor mortar with shrinkage cracks (Stereoscope, ×8).

Fig. 3. Strong connected layers in rendering (Stereoscope, ×8).

2 From Papayianni & Stefanidou 2007

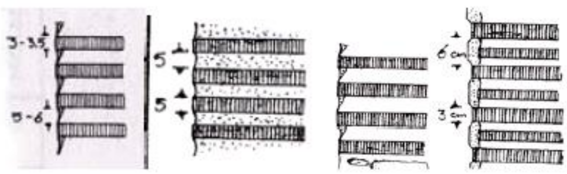
Another more often use of mortars, is their use as finishing layers in the cases when a lower quality stone was used such as porous limestone. In these cases these finishing layers were serving as protective coating to stone decay as well as a decorative one: Often the addition of marble powder in the mortar was aiming to give the impression of marble to a temple (Ορλάνδος, 1958)

Some observations on finishing mortars: The materials used were more carefully selected than those of bearing mortars. Their basic characteristic was that they were more fine graded, they were placed in layers having very good adhesion, and the finishing work on the last layer.

In Hellenistic period mortars were widely used in several wall structures, binding random placed stones (Pella's ancient Agora, Aigai palace, Dilos residences (2nd C BC) (Ορλάνδος, 1958) (Papayianni, et al., 2013), ancient theatre of Argos (3rd C BC) (Πάχτα, 2011), archaeological site of Loggos (4th C BC) (Stefanidou, et al., 2013)). This seems to be the basic building system used in this period.

Romans in the times that followed used mixture of lime and pozzolane as main component of their mortars (end of 3rd century b.C) and systematically add ceramic powder or crushed ceramics as aggregates in order to improve their hydraulic properties. Production of lime was a big part of their industry and their mortars are characterized of very pure lime and sand with very good granular degradation. (Adam, 2005)

The use of crushed brick and sand continued in later times. It characterizes mortar technology in Byzantium, where it was systematically used to improve hydraulic properties. Crushed brick is the main component that gave the characteristic pinkish color to those mortars and their durability in water. Those mixtures were a combination of lime, crushed brick and aggregates. In only some cases pozolan was added. The result was high strength, condensed mortars, lighter, capable of bearing loads and strongly bond different types of building materials: brick and stone. Mortars expanded in use (Moropoulou, et al., 2002) and gave new impetus to different architectural structures: Mortar joints were induced in walls made of layers of brick and stone, becoming thicker over time (2-5, even 6cm)



εικ. 71 Αναπαράσταση τομής αρμών επάλληλων φάσεων Ι.Ν. Αγ. Σοφίας Θεσσαλονίκης. Από αριστερά: Παλαιοχριστιανική φάση, $2^{η}$, $3^{η}$ (Theoharidou, 1988, Table I,II)

3 Pictures from Pachta, Thessis

Another result of these light weighted strong mortars, is the evolution of domes: From a static one-block structure of the Roman period, to plasticity of the Byzantine ones.

εικ. 28 Βυζαντινή θολοδομία. Από αριστερά ρωμαϊκό σταυροθόλιο, μοναστηριακός θόλος, βυζαντινό σταυροθόλιο (Μπούρας, 1999, σ.114)

In the years to follow this technique faded. During the Ottoman period (15th-19th C AD) structural mortars were mainly lime based (pure lime or lime with clay). Only in specific constructions (bath, cisterns) pozzolan and brick dust was added.

In Medieval (15th-19th C AD) Greek monuments (Dodecanese, Ionian islands, Crete), structural mortars mainly consisted of lime (in some cases pozzolan was added), natural or crushed aggregates and crushed brick (Maravelaki-Kalaitzaki, et al., 2003). They proved to have good resistance to marine environment, to which were exposed.

Trying to illustrate differences in the mortars structure through time, Pachta (Pachta, et al., 2014) proposed the following observations:

1. Binders / binding system.

Binding system is mainly lime based throughout all historic periods. Lime and pozzolan is used since Hellenistic period. In this period is often the use of lime and clayish material with pozzolan reaction. Pure lime mortars are first presented during Roman times. Both Greeks and Romans were aware of certain volcanic deposits that gave hydraulic properties. Greeks employed for this purpose the volcanic tuff from the island of Thera (Santorini earth) that still enjoys a high reputation on the Mediterranean. (Blezard, 2003)

Brick dust starts to be used in the matrix during Roman period, is generally used in Byzantium and continuous to the Ottoman period. In Medieval times mostly lime – pozzolan is used.

2. Aggregates' Granulometry

It seems that the most often gradations are 0-6mm and 0-8mm. A difference can be noted in Hellenistic mortars that a variety from 0-2.5 to 0-16 is noted.

3. Presence of inclusions

Inclusions that can be characterized as impurities (not additives) can be found in all eras. Calcite lumps are found in the majority of mortars and can be attributed to the lime grain accumulation during slaking. Clay lumps are scarcely found apart from mortars of the Hellenistic period. Charcoal particles have also been recorded to all periods but prevail in Ottoman mortars. Wooden fibers are also met probably as a mean to increase volume stability, while use the use of straw (for the same reason) is limited. Finally shells are mainly found in medieval times and can be attributed to aggregates from sea sites.

It seems that there is small variety of raw materials used in bearing mortars. The use of different binders was depending on the availability of raw materials and constructional tradition of its era. This availability of raw materials is a characteristic of architecture and mortar technology in Greece. The rule is convenience, and the less effort and time consuming technique. This was not a compromise to quality, but the aim was to achieve necessary results by using, as a rule, local nearby resources easily and fast. Even aggregates are gathered from nearby rivers, not produced (crashed limestone for example). On the other hand the need for moisture resistant mortars, made ancient masons to extend their expertise by trying mixed type binders, various aggregate types and gradations and different inclusions.

The discovery and use of Portland cement that followed, led to the loss of this technology. Today, we try to comprehend and retrieve this knowledge in order to better conserve our cultural heritage. The use of modern analytical techniques can help us, but, mortars as composite materials are characterized by reactions of their components, still active through time and make this goal (the retrieving of the original synthesis) difficult.

An evaluation of the investigation of these scientific techniques is essential in order to realize what they can offer and their limitations.

Photos of different mortar types (Πάχτα, 2011)

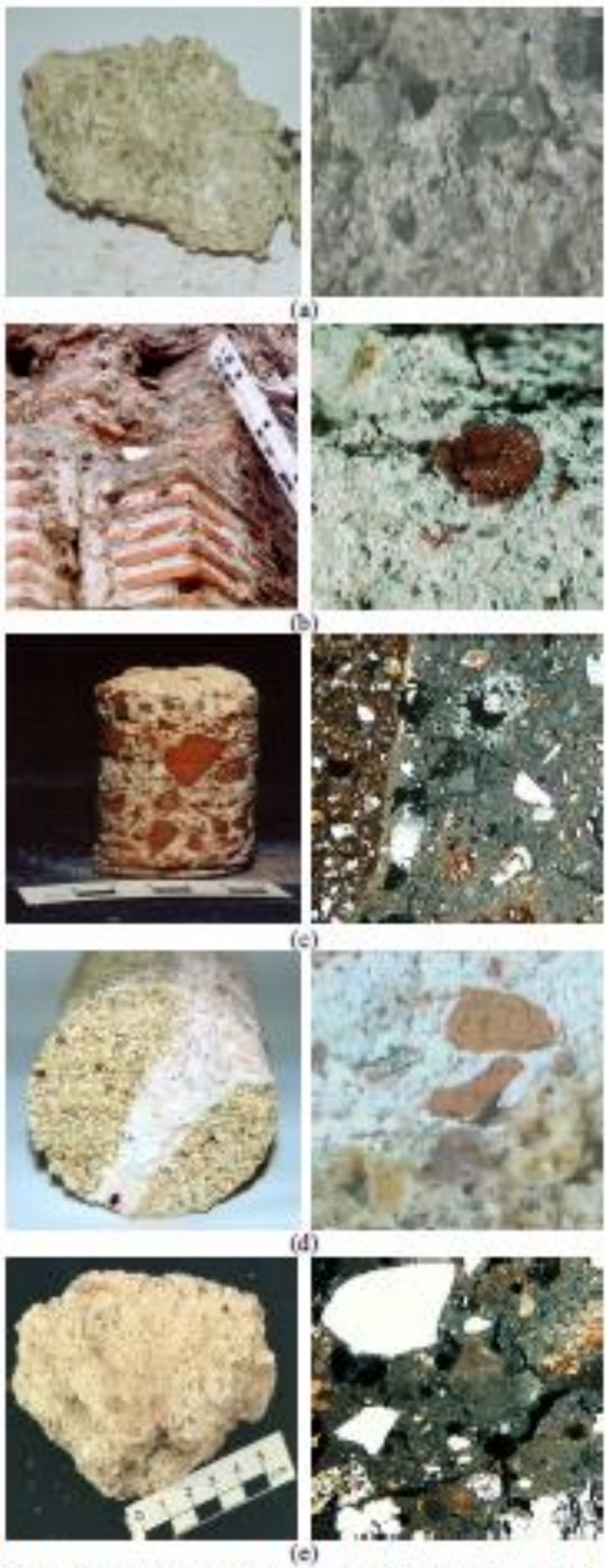


Fig. 1 Macroscopic and microscopic photos of structural mortars from various historic periods: (a) Hellenistic (Archaeological site of Loggos, 4th C BC); (b) Roman (Galerius Palace, 3rd C AD); (c) Byzantine (Saint Sophia, Thessaloniki, 8th C AD); (d) Ottoman (Bezesteni, 15th C AD); (e) Medieval (Medieval city of Rhodes, 15th C AD).

2 Analytical techniques used for characterization of historic mortars

The main reason for for evolution of mortar characterization techniques was the need of development of suitable repair mortars for historic buildings and the preservation of traditional building technology.

It is true that the knowledge of mechanical and physical properties of historic mortars is needed along with information of their chemical and mineralogical composition. A number of techniques are used for this purpose. The most important ones are listed below, with the basic properties which can be determined by the methods and their limitations.

Examination under a stereoscope.

It provides information on the thickness of coating layers, different applications / coats of mortar, cavities, fractures, cracks, macro porosity, presence of straw/hair/ceramics/fossils, presence of unmixed binder (lime lumps), aggregates or even pozzolan additives if large enough (first characterization and lithological characteristics). Moreover, microscopic or visual examination may guide a more thorough sampling procedure and the development of antiquate methodology. (Martinet & Quenee, 1999)

Preparation of samples

For other techniques to follow, preparation of samples is needed: eg separation of binder and aggregates.

So, in the next step, the sample is broken down and lightly ground in a mortar and pestle, the larger aggregate particles are removed by sieving (>

4.75mm) and the remaining material is ground until a fine powder is obtained (< 105μm) and dried. (Veiga, et al., n.d.) Following this procedure the binder-aggregate ratio is estimated, the gradation of aggregates and other techniques can be processed.

Acid dissolution and wet chemical analysis

Dissolution by acid is used for the determination of the binder-non carbonate aggregates ratio, by the acid digestion of the sample using HCl (Van Balen, et al., 1999) or HNO_3. (Martinet & Quenee, 1999). Carbonate aggregates are also dissolved by acid attack so cannot be analyzed by this method. This limitation can be overtaken by the use of optical microscopy (in transmitted polarized light) to identify them.

Determination of the chemical characteristics of the acid soluble fraction can follow by various methods including AAS, ICP, ion chromatography. Also measurement of silica residue, dissolved into acid solution (soluble silica) can be used for the estimation of hydraulicity of mortar. However, the presence of pozzolans can interfere. The temperature and strength of the acid used in dissolution influence the measured soluble silica, due to contributions from aggregates and additives. Measurements of pozzolanicity test by $Ca(OH)_2$ absorption by disaggregated mortar is used to estimate the content of pozzolanic materials but it depends on time of immersion and the reactivity of pozzolanic materials.

Optical microscopy

With the use of transmitted polarized light petrographic identification of aggregates and binder can be achieved as well as, textual/spatial interrelationships between compounds.

Porosity, cracking and secondary formations can be also observed. With the use of an image analysis system linked to the microscope we have the possibility to obtain the binder/aggregate ratio and porosity (air voids).
Limitations: poor resolution compared to SEM and the need of experienced personnel and high price of equipment.

X-ray Diffraction.

With this technique, identification of crystalline phases of binder (mineralogical determination), pozzolan tracer minerals, belite or alite (on hydraulic lime or portlant cement), crystallized alteration products is possible.
Also identification of mineralogical nature of binder is possible, particularly in the case of presence of crystallized alteration products
Limitations: bulk material analysis, no information on spatial interrelationships of mortar components, and no information of structure.

Thermal Analysis (DTA, TGA)

It is based on the identification of characteristic patterns of weight loss of minerals during controlled heating. Quantitative analysis is based on the TG curve, while DTA provides information for the qualitative identification of the components that undergo the weight losses.
The main limitation of this group of techniques is the identification of unknown constituents in the samples. It must be pointed out that differences with chemical analysis has been observed; there is difficulty in identifying existing components.

Scanning electron microscopy (SEM- EDX)

It is a powerful analytical facility, especially in the observation and characterization of heterogeneous organic and inorganic materials such as mortars. The sample is irradiated with a finely focused electron beam. This beam can be static or swept in a raster across the surface of the sample. Different signals, such us secondary electrons, backscatter electrons, characteristic x-rays can be used to examine and characterize morphologies and textual interrelationships of mortar components, including carbonates and hydrates of the binder (nature, form, structure), identification of alteration phases. Microstructure features or phenomena occurring on a micrometer of sub-micrometer scale can be observed. Qualitative and quantitative elementary composition, as well as identification of the alteration phases can be made.

Physical properties

Moisture content, porosity, water absorption coefficient can be determined according to standard laboratory tests and provide valuable data on the preservation and performance of historic mortars.

Mechanical properties

Compressive strength, modulus of elasticity/Young's modulus, flexural strength are measured for assessing the mechanical performance of building materials, when the size of the samples conforms with standard requirements for volume and dimensions.

The selection of the appropriate each time methods or their combination depends on the aim of characterization of mortars and the archaeological or conservation questions that have to be answered.

3 Experimental Methodology

There were several samples available for study, all coming from the area of Thessaly, Greece.

In particular there were 48 samples from the following sites:

- Agia Larisas, 7 samples
- Pythion, 14 samples
- Palaion Castle, 10 samples
- Agios Achillios, 8 samples
- Farsala, 7 samples.

The samples were photographed, described macroscopically and initially grouped.

XRF measurements of samples were contacted. The aim of XRF measurements was initially to examine the potential of running a preliminary study and characterization in field, in order to support the sampling process. Approximately 160 measurements were made, three for each sample, mainly on fractured surfaces. Since binder properties are essential for mortar characterization, the attempt was to measure the chemical characteristic of the binder.

Despite the effort made for analyzing only the binder, aggregates were also included in the measurements, due , to the size of the beam (d=8mm)   After that, it was decided a more conventional and thorough study of the samples and then evaluating the measurements.

Due to the time consuming tests, further selection from above samples was made, attempting not to take a representative sample not from each site, but a representative selection of the various mortar types usually found in historic mortars.

The selection made (14 samples) is presented in the following table.

Sample name	Description / Sampling info	
I.FOT.01: Agios Achillios no 1	Grave no1, 1st	
I.FOT.02: Agios Achillios no 2	Grave no 2	
I.FOT.03: Agios Achillios no 3	West wall, secondary built.	
I.FOT.04: Agios Achillios no 4	Apse of the north aisle	

I.FOT.05: Agios Achillios no 5	From the apse of basilica	
I.FOT.06: Agios Achillios no 6	South wall of basilica church	
I.FOT.07: Agios Achillios no 7	Subfoundation/subconstruction of the first phase of basilica.	
I.FOT.08: Agios Achillios no 8	North and south stylobate	
I.FOT.09: Palaion Castle of Volos no 3	Sector B, under the metallic bridge, east.	 

I.FOT.10: Farsala no 4	Farsala, South wall, west of the gate.	 
I.FOT.11: Pythio no 2	From sacred conch, inside the joint.	 
I.FOT.12: Pythio no 7	Southwest (later) addition	 

I.FOT.13: Agia Larissas no 2	11,7m west of South tower C. North.	
I.FOT.14: Agia Larissas no 9	East side, next to T25	

Several methodologies are bibliographically presented and standardized: flow charts have been proposed (like the ones in the next two pages).

In this study a simple approach was chosen:

1. Study of fractured surfaces and samples under a stereoscope.
2. Porosity measurements.
3. Separation of aggregates and binder
4. XRD analysis of the fine powder produced (<0,063cm)
5. SEM analysis (including EDX measurements of binder)
6. Mechanical tests when adequate sample size was available

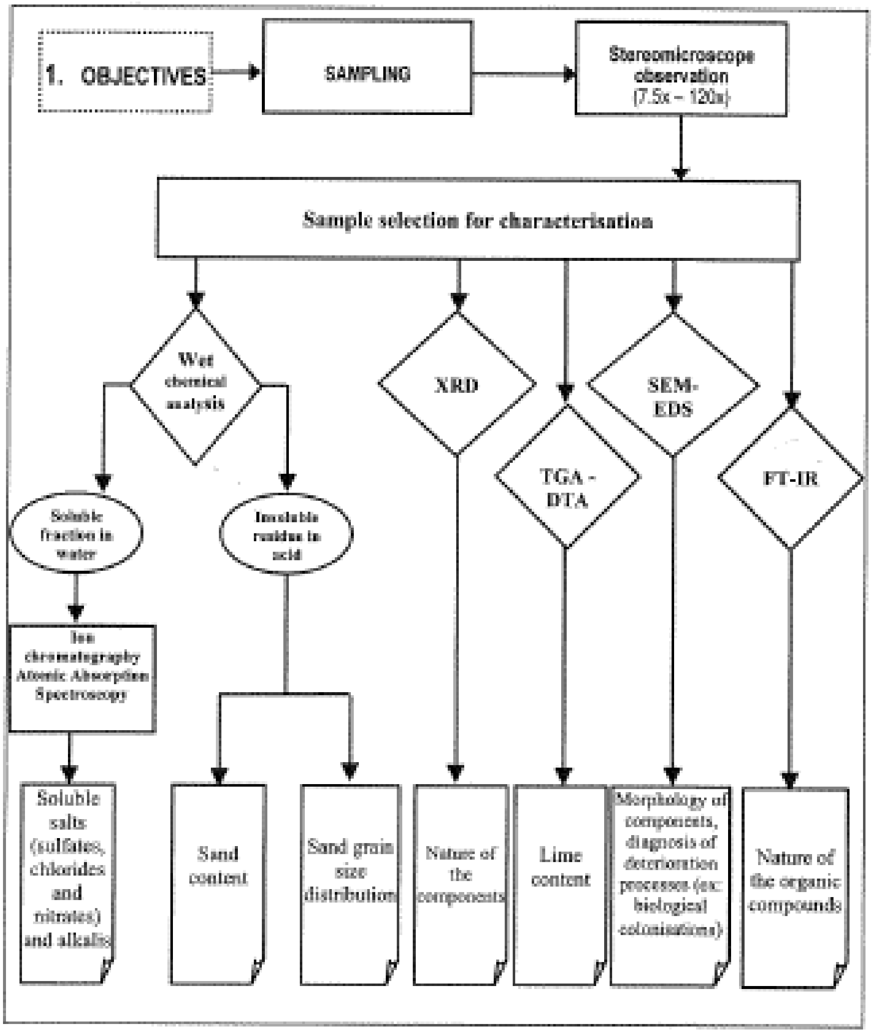
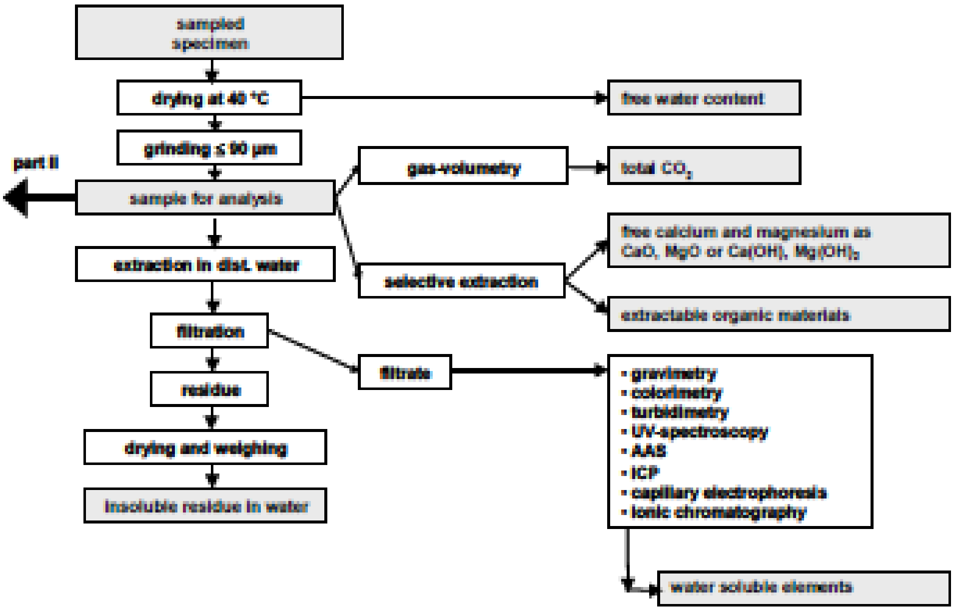


Figure 1: Scheme of the sequence of tests to identify the composition of ancient mortars

Flow chart proposed by Veiga, et al.

Appendix: Flowchart to illustrate a scheme for the mineralogical and petrographical characterisation of historic mortar

Part I:



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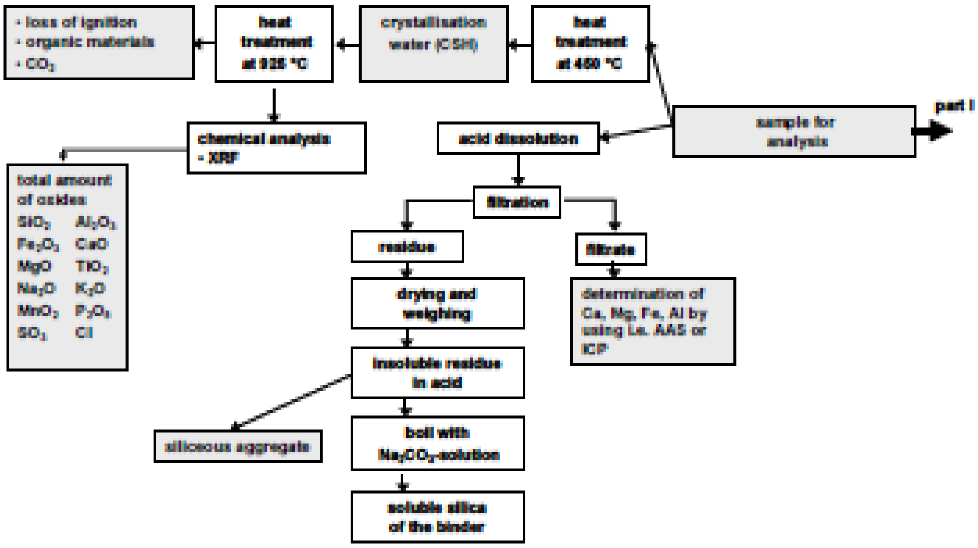


Flow chart propossed by Middendorf, et al., 2005

4 Results

The examination of mortars macroscopical characteristics was performed under stereoscope in fractured surfaces. Microstructure and other morphological characteristics on the other hand was studied be SEM.

Following the stereoscopical inspection, the samples were initially divided into the following categories:

1. Lime mortar with natural aggregates (I.FOT.01 - Agios Achillios 1)
2. Lime mortars with grated ceramics, including or not natural aggregates (I.FOT.02 - Agios Achillios 2, I.FOT.04 – Agios Achillios 4)
3. Lime mortar with flimsy structure, having large porous structure and big large aggregates (breccia) (I.FOT.03 – Agios Achillios 3, I.FOT.05 – Agios Achillios 5).
4. Light gray and greenish mortars with coherent structure, increased and uniform presence of small graded aggregates and increased mechanical strength (I.FOT.06 – Agios Achillios 6, I.FOT.07 – Agios Achillios7, I.FOT.08 – Agios Achillios 8) In this category two more samples are included (I.FOT.13-Agia Larisas 2, I.FOT.14 – Agia Larisas 9). A sub categorization is made not only due to their different origin but also due to the presence of a considerable amount of shale as aggregates.
5. Clay mortars with natural aggregates (I.FOT.11 – Pythio 2, I.FOT.12 – Pythio 7).
6. Lime mortar with grated ceramics and almost absence of other kind of aggregates (I.FOT.09 – Castro Palaion Volos 3 and I.FOT.10 – Farsala 4, I.FOT.12).

4.1 Porosity measurements

For the estimation of the porosity of each sample, three measurements were made:

- **Dry weight**

  Samples were dried in 60º C, until constant weight was obtained.

- **Water saturated weight**

  Samples were saturated for 48 hours and then measured

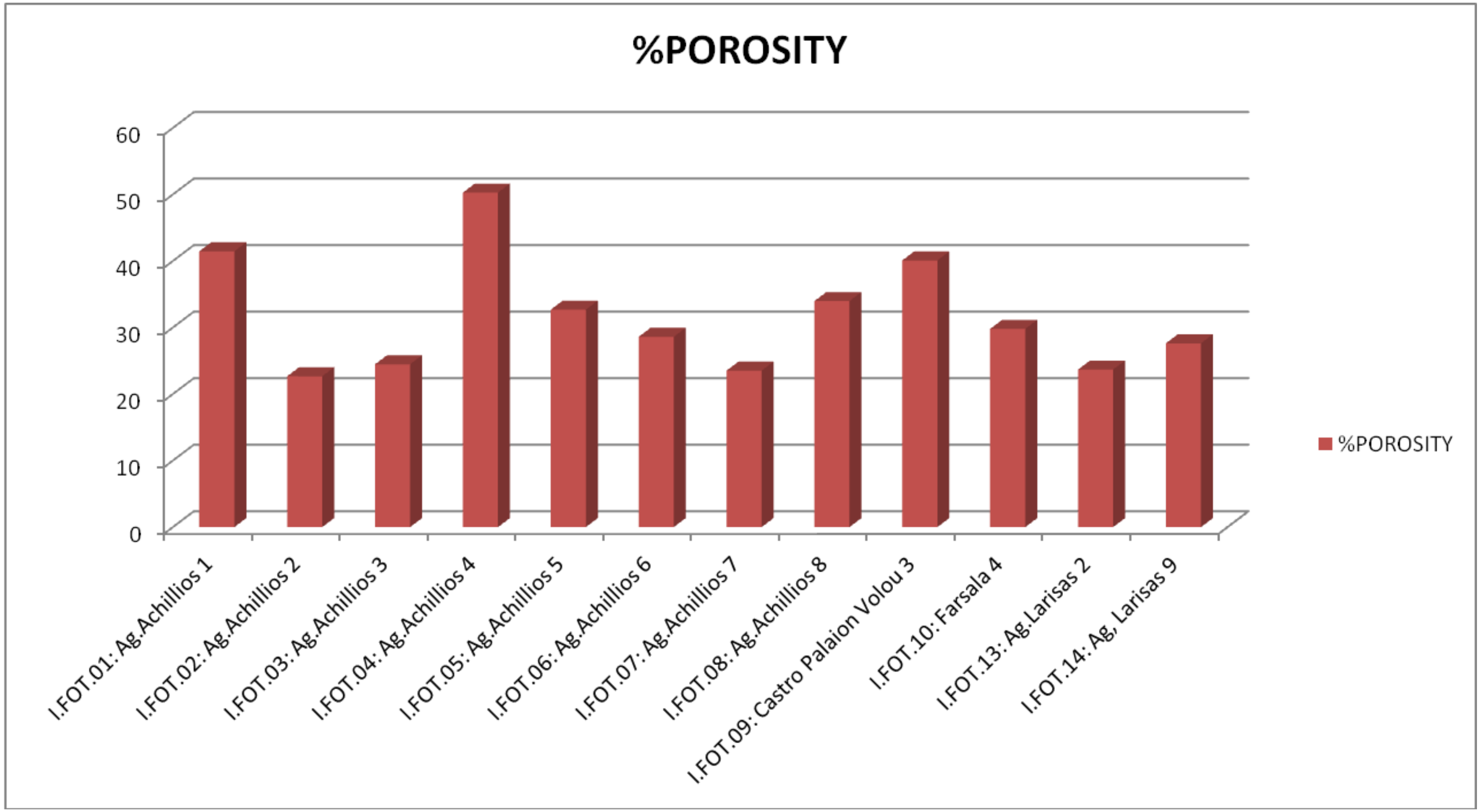
- **Hydrostatic weight**

  For this purpose a scale was safely placed over a small water basin. Samples were hanged underneath the scale in a net by a hook manufactured placed in the scale for the measurement of big samples. The water basin was filled with tap water and the previously saturated samples were immersed, while hanging from the scale.

  Each measurement is the average of three measurements.

Needless to say, clay mortars failed the test (they collapsed when immerged to the water).

Porosity results are presented in the following chart and table.



Porosity measurements

Porosity measurements

	M1	M2	M3	Vp (M3-M1)	Va (M3-M2)	Vr (M1-M2)	ρ_r	ρ_a	% POROSITY
	dry weight (g)	hydrostatic weight (g)	water saturated (g)	pore volume (cm^3)	apparent volume (cm^3)	real volume (cm^3)	real density	apparent density	
I.FOT.01: Ag.Achillios 1	121,42	72,8	155,84	34,42	83,04	48,62	2497,33	1462,19	41,45
I.FOT.02: Ag.Achillios 2	65,74	40,02	73,28	7,54	33,26	25,72	2555,99	1976,55	22,67
I.FOT.03: Ag.Achillios 3	185,18	106,4	210,7	25,52	104,30	78,78	2350,60	1775,46	24,47
I.FOT.04: Ag.Achillios 4	89,62	53,15	126,5	36,88	73,35	36,47	2457,36	1221,81	50,28
I.FOT.05: Ag.Achillios 5	62,24	36,8	74,59	12,35	37,79	25,44	2446,54	1647,00	32,68
I.FOT.06: Ag.Achillios 6	199,77	116,2	233,24	33,47	117,04	83,57	2390,45	1706,85	28,60
I.FOT.07: Ag.Achillios 7	70,83	40,65	80,11	9,28	39,46	30,18	2346,92	1794,98	23,52
I.FOT.08: Ag.Achillios 8	343,37	204,3	414,92	71,55	210,62	139,07	2469,04	1630,28	33,97
I.FOT.09: Castro Palaion, Volos 3	169,41	101,9	214,57	45,16	112,67	67,51	2509,41	1503,59	40,08

I.FOT.10: Farsala 4	207,24	123,2	242,9	35,66	119,70	84,04	2465,97	1731,33	29,79
I.FOT.11: Pythio 2	27,78	-	-	-	-	-	-	-	-
I.FOT.12: Pythio 7	67,29	-	-	-	-	-	-	-	-
I.FOT.13: Ag.Larisas 2	240,55	144	270,5	29,95	126,50	96,55	2491,46	1901,58	23,68
I.FOT.14: Agia Larisas 9	549,52	320,535	636,93	87,41	316,40	228,99	2399,81	1736,82	27,63

4.2 Mechanical properties.

In the following table, mortar compressive strength values are presented (f_c (MPa)).
It concerns samples for which it was possible to extract samples with a minimum edge size at least triple of the maximum grain size. Values mentioned concern only one measurement and should be considered indicative.

Sample	**Compressive Strength f_c (MPa)**
I.FOT.01 Agios Achillios 1	0,7
I.FOT.02 Agios Achillios 2	1,2
I.FOT.03 Agios Achillios 3	2.4
I.FOT.04 Agios Achillios 4	1,6
I.FOT. 05 Agios Achillios 5	2,6
I.FOT. 06 Agios Achillios 6	2,9
I.FOT. 07 Agios Achillios 7	3,2
I.FOT. 08 Agios Achillios 8	2,8
I.FOT. 09 Palaion Castle, Volos	3,7
I.FOT.10 Farsala 4	3,7
I.FOT.11 Pythio 2	0,7
I.FOT.12 Pythio 7	0,6
I.FOT.13 Agia Larisas 2	3,6
I.FOT. 14 Agia Larisas 9	3,4

Samples can be sorted in four categories:

	I.FOT. 1/11 /12	< 0,9
> 0,9	I.FOT. 2 / 4	< 1,7
>1,9	I.FOT. 3 / 5 / 6 / 8	< 3,0
> 3,0	I.FOT. 7 / 9/ 10/ 13 / 14	

4.3 Grain size distribution / Separation of binder and aggregates.

For this procedure ISO 3310-1:2000 set of sieves were used (diameters are given in tables) and the procedure was carried out manually.

At first samples were demoted in smaller parts with the use of chisel, hammer and a plier cutter. A wooden mortar and a porcelain pestle were used to further demote samples into powder.

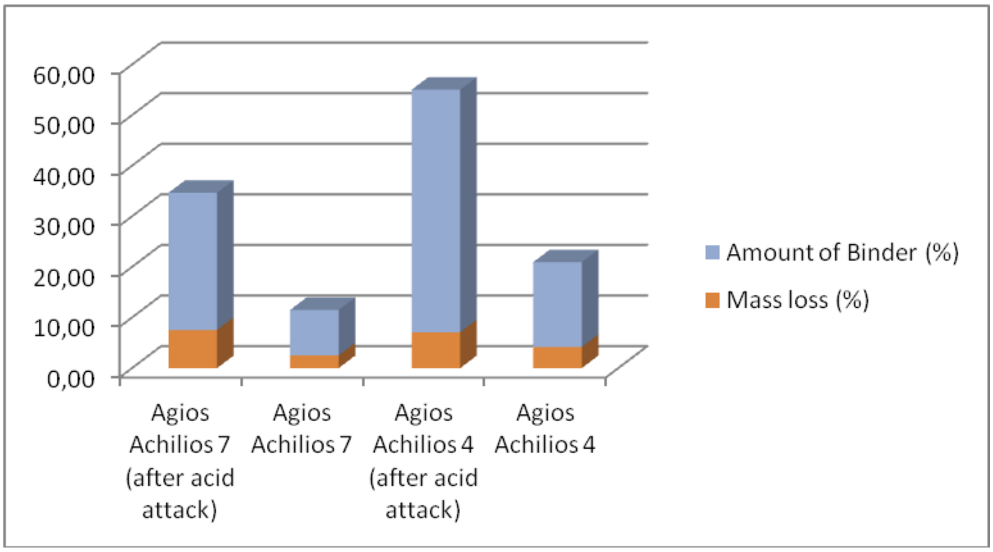
This material was sieved. Often this procedure was facilitated and shortened in time, by putting the fraction of the sample retained in one sieve again in the mortar, demoted and back to the same sieve. The color of the sample that changed was indicative of the process.

It must be stressed that this procedure was time and effort consuming and tedious. Results as evaluated afterwards, were not always satisfactory. Aggregate and powder ratio, did not agree with bibliographic references (usually 3:1). Since the binder seemed less than expected it was assumed that it was still adhered to the aggregate grains.

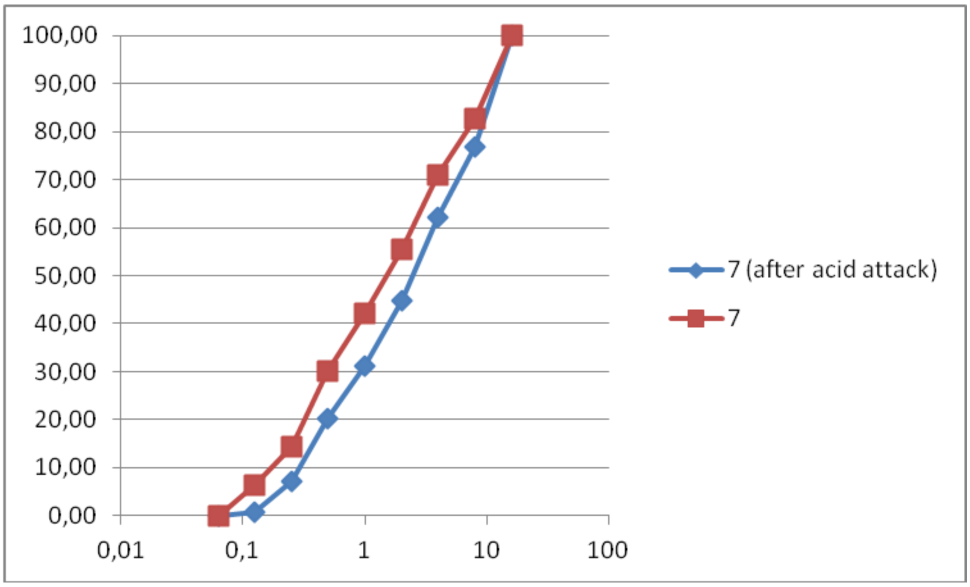
To prove this assumption aggregate clasts gathered from the samples were inspected in stereoscope. Residue of binder was evident in some samples, especially in the larger grains (see photos in page 34)

After this result was noted, two samples were selected, the one that gave the most extreme values of aggregate/binder ratio and one in desired limits. The samples were treated with acid (a mild solution of sulfuric acid) in order to remove and thus evaluate the quantity of calcium carbonate still binded on aggregate grains and thus influencing above ratio. Grain size distribution was again measured. It must be pointed out that this process, acid attack, is expected to have also a negative influence to the results. All carbonates are influenced; carbonate aggregates are also attacked thus smaller percentages than the real values are expected.

The influence of acid attack is best shown at the two following diagrams:



4 Influence of acid attack in binder and aggregate loss percentages

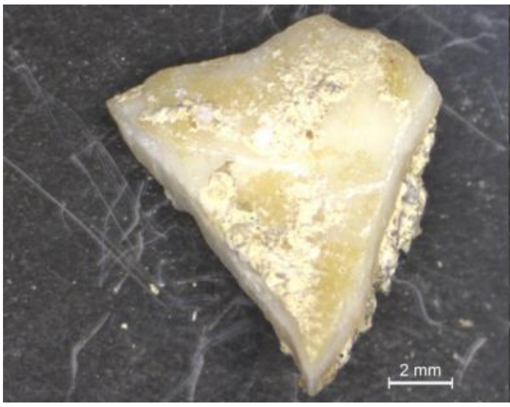


5 Influence of acid attack in grain size distribution of sample Agios Achillios 7

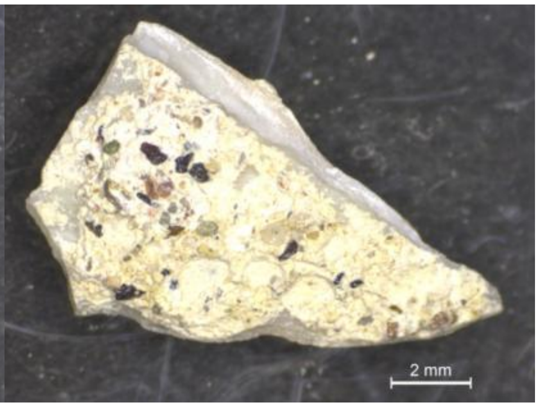
Photos of grains in stereoscope

6 Agios Achillios 7, Grain retained in 4mm sieve

Grain still holding mortar in a cavity.

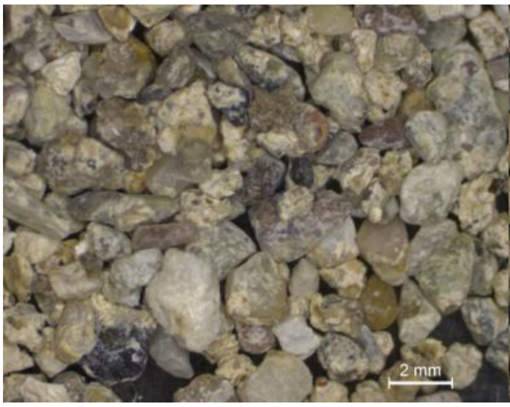


7 Agios Achillios 7, Grain

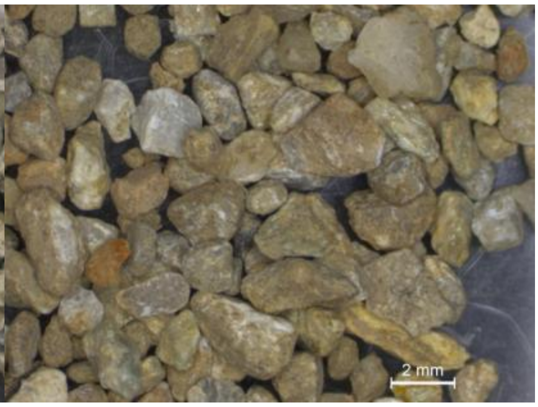


8 Agios Achillios 7, Grain

Two sides of the same grain: it holds a significant amount of mortar in one side.



9 Agios Achillios 7 Grains retained in 1mm sieve

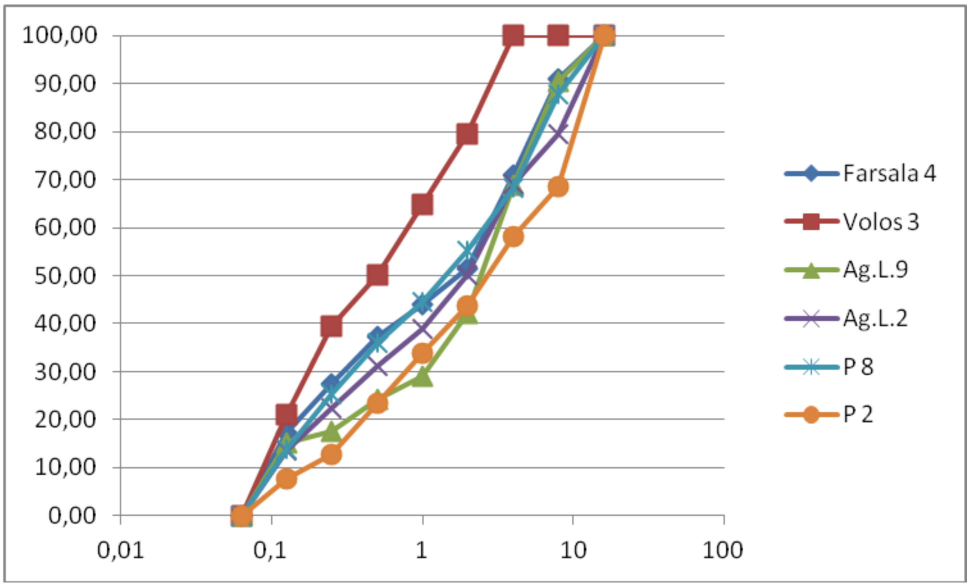


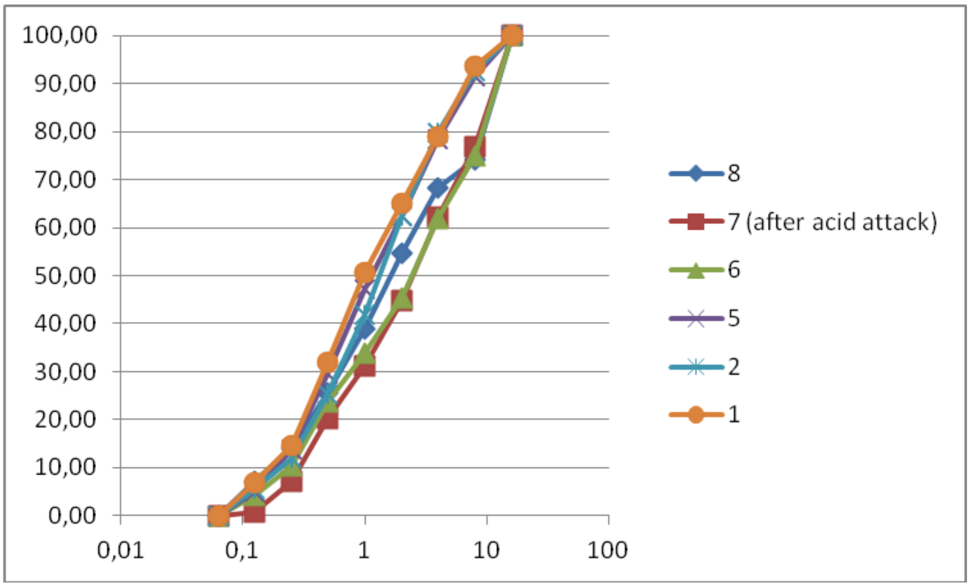
10 Pythio 7, Grains retained in 1mm
sieve

The difference in clarity of the grains between the two samples is evident.

Grain distribution results

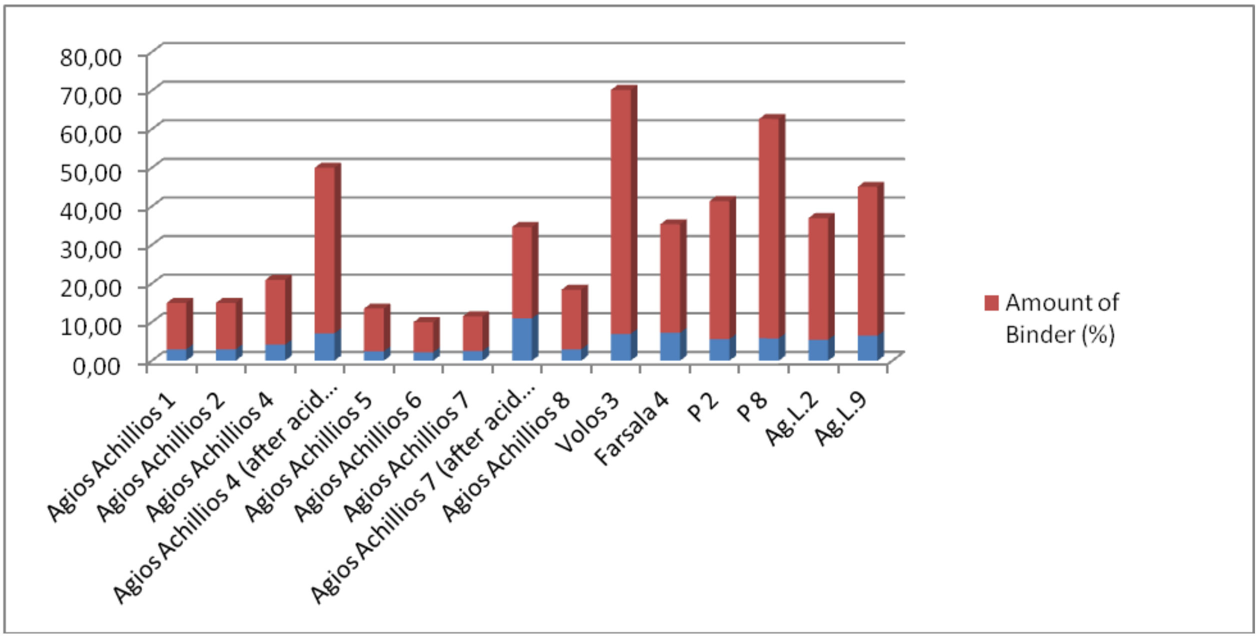
Results of all samples are presented into two groups in the following two diagrams:





Some other observations worth noted follow:

- Mass loss and binder aggregate ratio can be observed in the following diagram:



- Sample no 8 (Agios Achillios 8)

One and only (large) shell was revealed along with a small bone (probably by a small rodent).

- Sample no10 (Farsala 4)

It proved the harder and most difficult sample to handle. This probably explains the large amount of binder loss: it is probably relative to the time required for the aggregate separation. The only samples that have larger binder loss are those that were treated with acid.

- Sample no 9 (Volos, Palaion Castle no3)

While grading this sample feeble ceramics of light color were observed. The adherence of those ceramics with binder proved to be very strong. It was impossible not to break them and remove them. Most of them must have been demoted to dust, a fact that explains the large percentage of binder that is observed in this sample

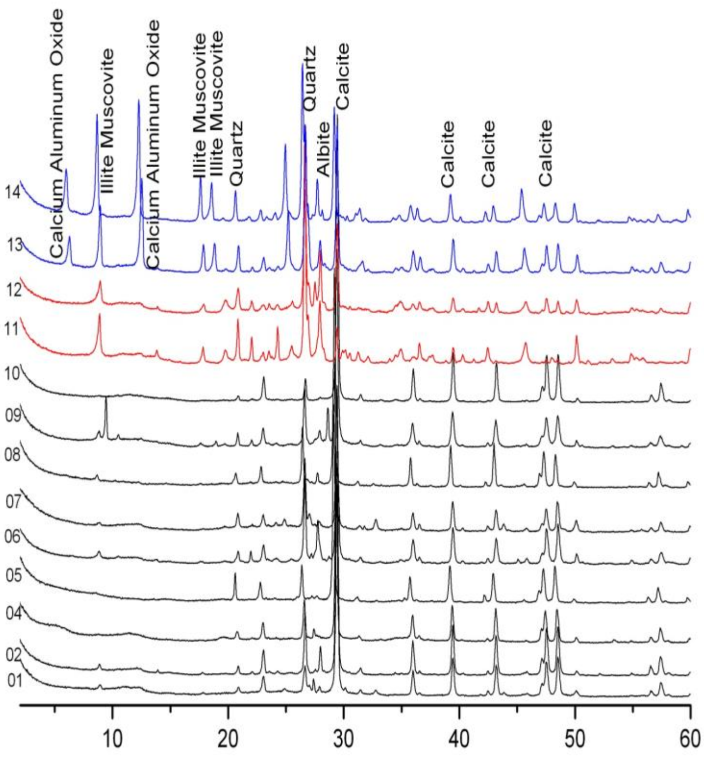
4.4 Minerological analysis

Results of XRD analysis are presented in the following diagrams.

The main phases traceable in the samples are calcite (lime carbonation product) and quartz.

Samples no 11 and 12 (diagrams in red color) show intense aluminosilicate admixtures (eg illite) as expected (they are the clay mortar samples).

Surprisingly, samples no 13 and 14 (diagrams marked with blue color) show phases that correspond to cement material (calcium Aluminum oxide), indicating that corresponding mortars were not as old as initially believed. (They correspond to restoration mortars rather than historic ones).



Results of XRD analysis

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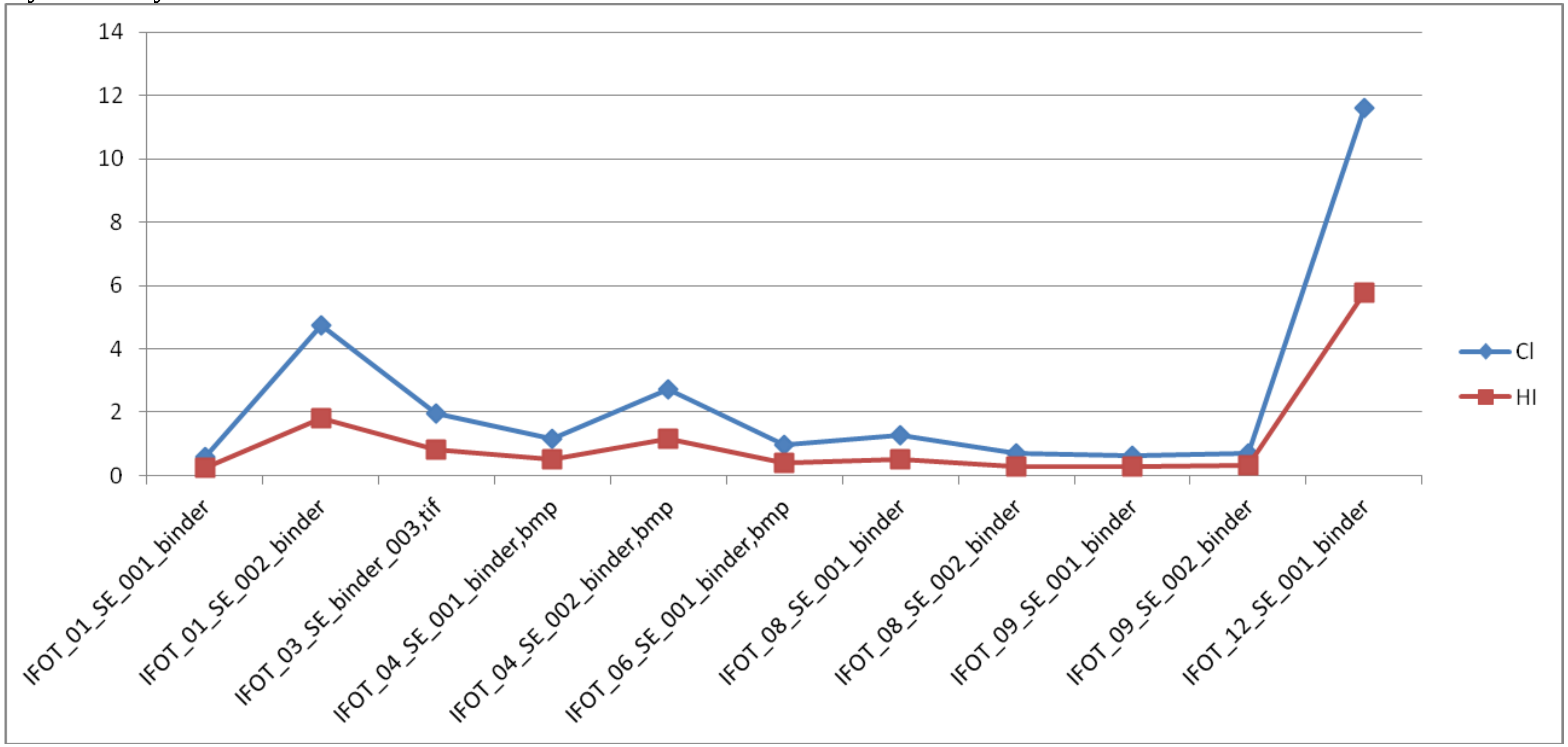
4.5 Chemical Analysis of binder by SEM / EDX

	I.FOT. 01	I.FOT. 02	I.FOT. 03	I.FOT. 04	I.FOT. 05	I.FOT. 06	I.FOT. 07	I.FOT. 08	I.FOT .09	I.FOT .10	I.FOT .11	I.FOT .12	I.FOT .13	I.FOT .14
	Ag.Ac h.1	**Ag.Ac h.2**	**Ag.Ac h.3**	**Ag.Ac h.4**	**Ag.Ac h.5**	**Ag.Ac h.6**	**Ag.Ac h.7**	**Ag.Ac h.8**	**CPV 3**	**Farsal a 4**	**Pythio 2**	**Pythio 7**	**Agia Larisa s 2**	**Agia Larisa s 7**
Na2O	0	2,2	1,1	1,2	1,2	1,2	0	0	2,6	0,8	0,6	0,3	0,5	0,4
MgO	1,9	2,2	3,2	3,3	3,4	1,8	1,7	0,9	3,9	0,8	1,1	2,6	5,4	4,7
Al2O3	3,6	3,1	6,3	5,6	4,1	2,2	5,3	5,9	8,2	8,3	1,6	18,6	14,6	15,1
SiO2	22,1	19,7	25,9	24,5	33,7	4,8	65,2	65,4	19,8	62,7	4,6	58,4	34,8	36,1
P2O5	0,5	1,8	1,6	0,9	1,7	2,2	0,2	0,2	2,4	0,2	1,8	0,0	1,1	0,9
SO3	0,6	0,9	1,6	1,5	1,8	1,6	1	0,7	1,9	0,5	0,8	0,0	0,7	0,4
Cl2O	2,2	0,5	0,6	1,9	1,1	0,9	0,5	0,4	0,8	1,2	0,4	0,1	0,3	0,2
K2O	0,5	0,7	1,9	1,7	0,6	0,7	0,9	1,2	1,5	0,6	0,6	4,3	3,3	3,3
CaO	65,9	66,3	54,5	57,1	50,1	83,1	22,3	22,4	56,2	21,2	84,5	9,1	25,9	28,6
MnO	0,5	1,1	0,9	0,4	0,4	0,2	0,4	0,5	0,6	0,7	0,7	0,2	0,8	0,5
Fe2O3	1,5	2,1	2,1	1,5	1,8	0,9	1,7	1,7	0,3	2,4	2,3	6,2	11,7	9,1
CuO	0,5	0,3	0,4	0,4	0,5	0,3	0,6	0,5	1,8	0,5	0,8	0,1	0,9	0,7
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Hydraulicity and Cl index in binders



The high percentage of Si and Al, give this plasmatic appearance to the last sample (clay mortar)

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4.6 XRF Measurements

Following the initial XRF measurements of samples, a new series of measurements were made. This time two fractions of the samples were measured: The fraction that could be considered as binder (maximum size <0,063mm), and the fraction of 0,5mm (grains of aggregates between 0,025 and 0,5mm). Again, three measurements were made, corresponding to each XRF measurement, for more accuracy.

This time the sample was not solid and easy to measure, it was powder and grains. So a decision upon the container had to be made. After examining (measuring with pXRF) available transparent bags, common kitchen wrap was chosen. It had the minimum amount of Si and Ca of all the available media, and thus interfered the less with our measurements.

The first observations that were made are the following:

1. Wrap measurements had an extremely high percentage of Cl (almost 99%)
2. Bal measurements were between 50 to 60%.

   This measurement made by pXRF, is an indicator of the percentage of failure in the quantative measurement (the percentage of the sample that failed to be quantified). This high percentage is probably due to X-ray scattering due to the state of the sample (powder and grains) and the masking effect of the wrap.

Despite above problems, an attempt was made to process the results. The average values of each element measured in wrap was subtracted from the corresponding measurement of the sample, in order to achieve the chemical analysis of each sample (a measurement corresponding to binder and another one corresponding to aggregates). The results after an initial elaboration are presented in tables 1 and 2

A further selection was made for binder measurements, choosing the elements that were analyzed by EDX and a comparison was made. It must be noted that, at the end, 25% of sample's quantitative measurement was compared.

Although the values achieved by the two types of methods are different in absolute values, they present the same trend

Table 1

Chemical Analysis of binder by XRF
(Raw data in wt %)

	01 Ag.Ach.1	02 Ag.Ach.2	04 Ag.Ach.4	05 Ag.Ach.5	06 Ag.Ach.6	07 Ag.Ach.7	08 Ag.Ach.8	09 CPV 3	10 Farsala 4	11 Pythio2	12 Pythio7	13 Ag.L.2	14 Ag.L. 9
Mg	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	4,41	0,00
Al	0,00	3,70	1,99	2,73	1,17	0,00	2,17	0,00	0,00	10,57	9,53	Y n	3,13
Si	17,87	15,28	19,69	15,00	7,52	24,32	22,40	12,62	9,24	45,44	35,57	19,95	22,44
P	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,62	0,00	0,00
S	0,00	0,27	0,81	0,09	0,34	0,00	0,23	0,20	0,10	0,00	0,00	0,00	0,11
K	0,83	2,65	2,12	1,88	1,32	3,10	1,60	2,30	1,19	11,09	7,94	2,99	4,16
Ca	78,65	71,36	69,61	77,34	87,24	67,47	69,50	78,46	83,47	9,92	29,01	57,24	53,84
Mn	0,09	0,14	0,06	0,08	0,07	0,36	0,11	0,08	0,15	0,43	0,34	0,10	0,20
Fe	2,55	6,60	5,71	2,87	2,34	4,75	3,99	6,33	5,85	22,56	17,00	11,38	16,12
Total	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

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Table 2
Chemical Analysis of aggregates by XRF
(Raw data in wt %)

	01 Ag.Ach.1 aggr.	02 Ag.Ach.2	04 Ag,Ach,4	05 Ag.Ach.5	06 Ag.Ach.6	07 Ag.Ach.7	08 Ag.Ach.08	09 CPV 3	10 Farsala4	11 Pytthio2	12 Pythio7.	13 Ag.L.2	14 Ag.L. 9
Ba	-	-	0,00	0,00	0,00	0,00	0,01	0,00	0,00	0,02	0,00	0,02	0,02
Sb	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Sn	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,01
Sr	0,03	0,04	0,03	0,04	0,04	0,04	0,05	0,08	0,06	0,03	0,04	0,04	0,03
Rb	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,01	0,00	0,02	0,01	0,01	0,02
Pb	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,01	0,00	0,00	0,00	0,00	0,00
Ni	0,00	0,05	0,11	0,08	0,05	0,16	0,04	0,05	0,00	0,00	0,00	0,03	0,01
Fe	4,99	7,94	17,13	10,04	8,85	19,42	8,94	11,41	21,48	11,42	5,72	17,80	25,06
Mn	0,09	0,11	0,26	0,13	0,16	0,42	0,12	0,18	0,30	0,04	0,03	0,16	0,23
Cr	0,10	0,20	0,21	0,15	0,12	0,28	0,13	0,20	0,08	0,06	0,00	0,16	0,17
V	0,00	0,01	0,07	0,01	0,02	0,06	0,01	0,04	0,10	0,06	0,01	0,07	0,10
Ti	0,21	0,21	0,98	0,28	0,26	0,45	0,24	0,54	1,36	0,82	0,68	0,90	1,37
Ca	75,22	62,37	45,98	54,88	67,13	22,53	56,74	65,77	51,94	11,65	64,46	43,53	24,95
K	0,74	1,68	2,00	2,03	1,74	2,15	1,48	2,43	1,71	7,12	3,46	3,20	5,46
Al	0,00	3,43	2,59	3,06	0,00	3,92	2,58	2,83	2,94	9,36	4,41	4,38	2,75
Si	18,63	19,60	30,48	29,19	21,64	50,57	29,46	16,45	19,63	59,21	21,17	29,71	39,83
S	0,00	0,11	0,16	0,11	0,00	0,00	0,19	0,00	0,39	0,20	0,00	0,00	0,00
Mg	0,00	4,25	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Total	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

5. Observations / Results per sample

5.1 Visual examination under a stereoscope.

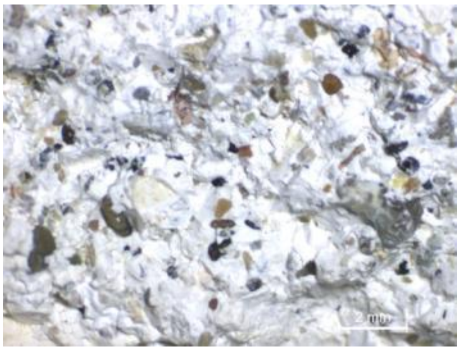
Sample name	Description
I.FOT.01: Agios Achillios no 1	Bright white binder. Mostly grey aggregates. Max grain size approximately 1.8cm.
I.FOT.02: Agios Achillios no 2	Pink to grayish binder, Aggregates with smoothed binders, maximum grain size 3cm (ceramic). White grains mostly but also dark ones can be observed.
I.FOT.03: Agios Achillios no 3	Grayish to white binder, more angular aggregates than no 2. Mostly white limestone, maximum aggregate size, 1.5 cm.
I.FOT.04: Agios Achillios no 4	Pink binder. Max grain size 3cm (white marble), ceramics as aggregates.
I.FOT.05: Agios Achillios no 5	Absence of ceramics. Maximum aggregate size 3cm mostly white and dark aggregates.
I.FOT.06: Agios Achillios no 6	White binder, gray limestone as aggregates and fewer dark grains.
I.FOT.07: Agios Achillios no 7	Grayish binder with lime lumps. Rounded aggregates. Presence of dark gray limestone.
I.FOT.08: Agios Achillios no 8	Grayish to white binder. Small dark rounded aggregates, white limestone and shale.
I.FOT.09: Palaion Castle of Volos no 3	Pink binder, large ceramics as aggregates along with white limestone. Secondary crystallization in fissures.
I.FOT.10: Farsala no 4	Sub white binder, light colored ceramics.
I.FOT.11: Pythio no 2	Clay mortar, light colored

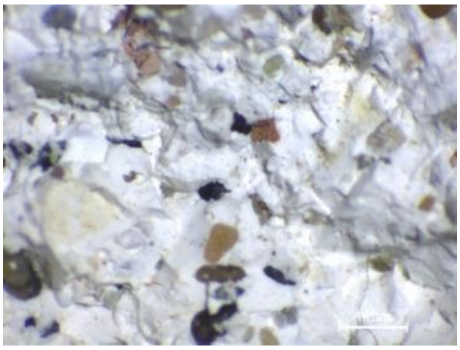
I.FOT.12: Pythio no 7	Dark, grayish binder with large aggregates.
I.FOT.13: Agia Larisas no 2	Grayish binder, light gray limestone as aggregates,
I.FOT.14: Agia Larisas no 9	The same as Agia Larisas no 2, but a bit more yellowish binder.

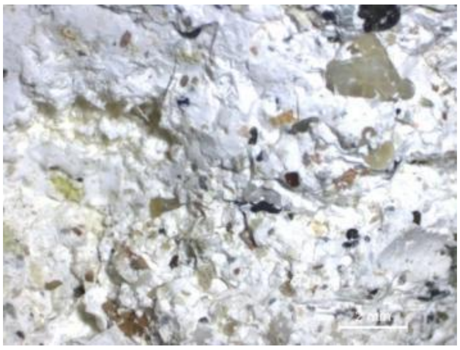
5.2 Examination on fractured surfaces

AG.AH._01

Bright white binder and extensive presence of ceramics as part of the aggregate matrix (AG.AH._01_02/3/4).







Smooth bright fractured surface (reflects like mirror). Dense aggregate matrix, grains in various sizes and angular shapes (AG.AH._01_04). One can also observe fractured aggregate grains, indicating good matrix-grain adhesion, a fissure network and the fracture surface following large aggregates network relief.

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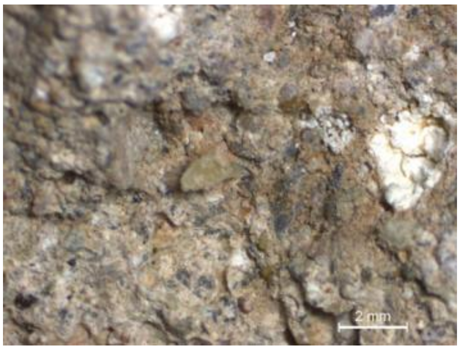
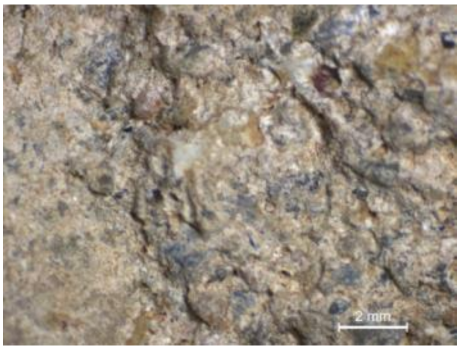
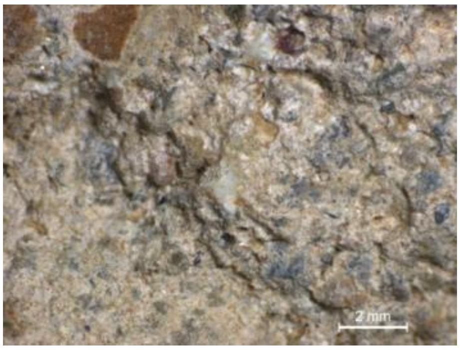
AG.AH._02

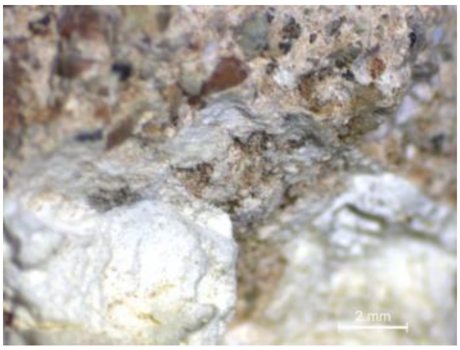
Quite different form AG.AH._2: Grayish binder and no evidence of ceramics. Otherwise aggregate matrix seems the same. Also, there is no evidence of broken aggregate grains, indicating poorer adhesion of binder and aggregates. (AG.AH._02_02/3/4).







Fissure network more evident (AG.AH._02_03/4) and presence of bright white large regions (excess of lime?) (AG.AH._02_05/6)



AG.AH._04

Once again presence of ceramics. Compared to AG.AH._01, the binder is grayish and not so bright, while there are even more ceramics present (AG.AH._04_01/2/3).

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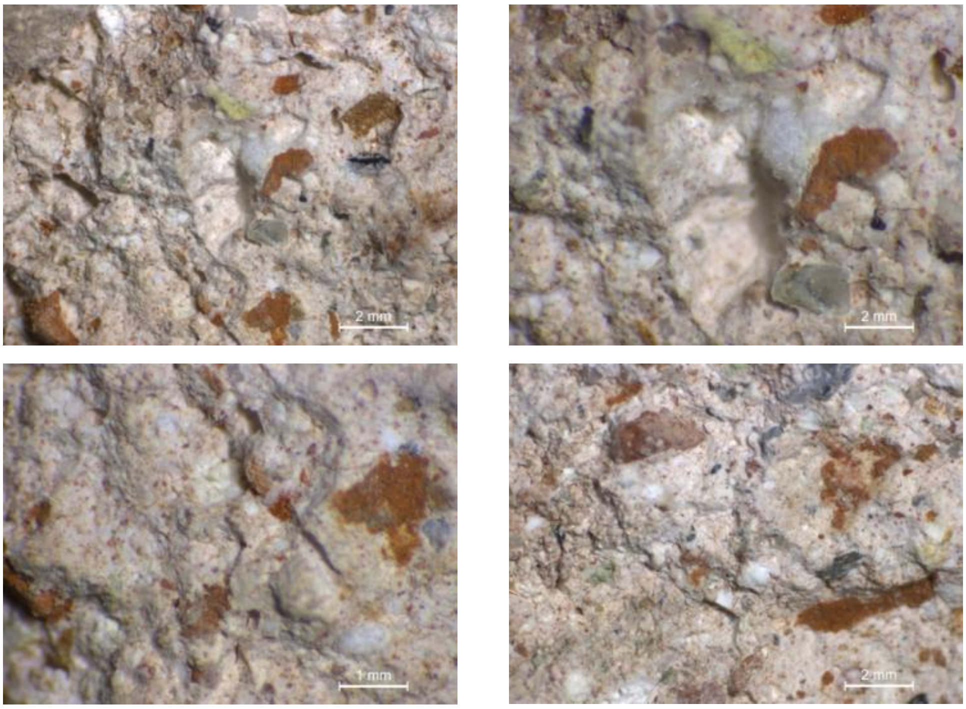
Regarding the rest aggregate grains, besides ceramics, light colored grains are dominant and most of them are not broken (AG.AH._04_02). On the contrary, most of the ceramics are broken and their boundaries are not clear (AG.AH._04_04).



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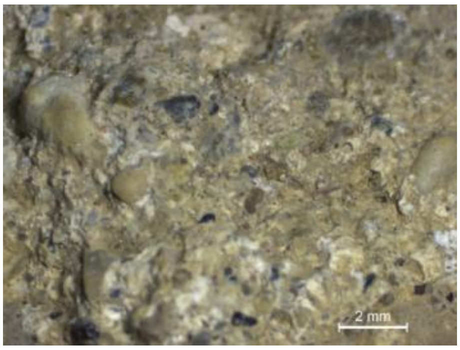
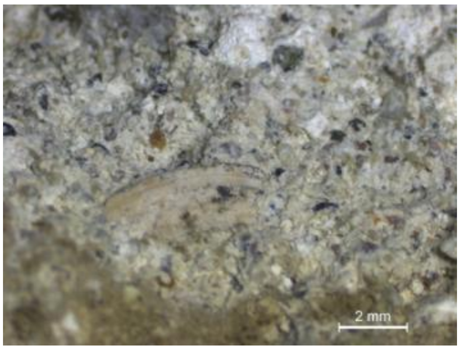
AG.AH._05

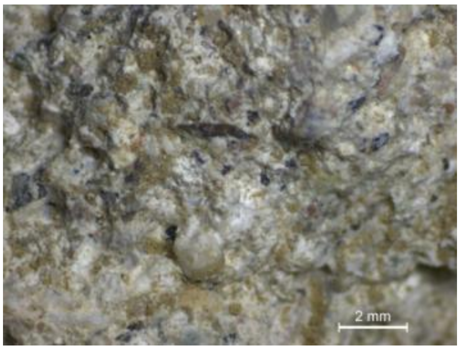
Absence of ceramics, grayish binder, rounded unbroken large aggregates. (AG.AH._05_01/2/3)

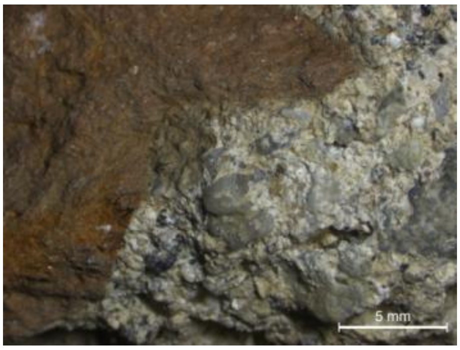
Possible more feeble binder: rounded grains are half covered with binder, half revealed. (AG.AH._05_02/3). Absence of fissures and cracks, binder is just gets away from sample’s fractured surface.

Altered grain. Seems like a ferrous stained region but it has clear bounders like an angular grain (AG.AH._05_04)









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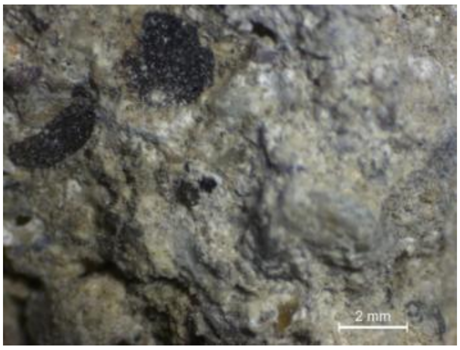
AG.AH._06

Absence of ceramics, white binder, rounded grains, presence of fissures and cracks. Compared to AG.AH._05 seems to have a coarser binder, more adhered to the grains. Compaired to AG.AH.-02, possible more feeble.

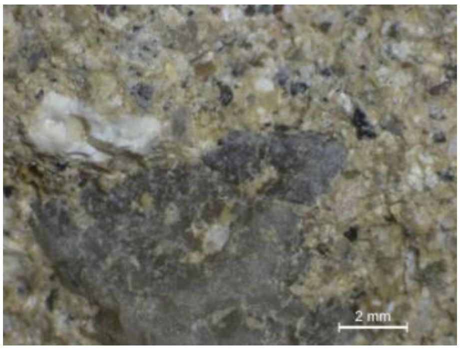
1

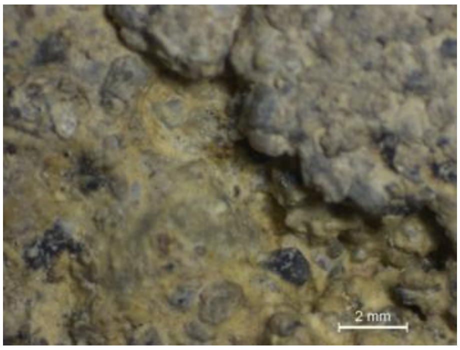


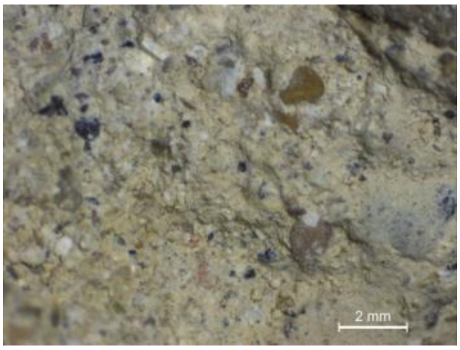
3

AG.AH._07

Beige, yellowish binder, absence of ceramics. Seems to be more binder present per volume to the sample than the previous samples of the same region. (AG.AH._07_01/2/3)







AG.AH._08

White binder similar toAG.AH._01 but with maybe more dark aggregate percentage. It

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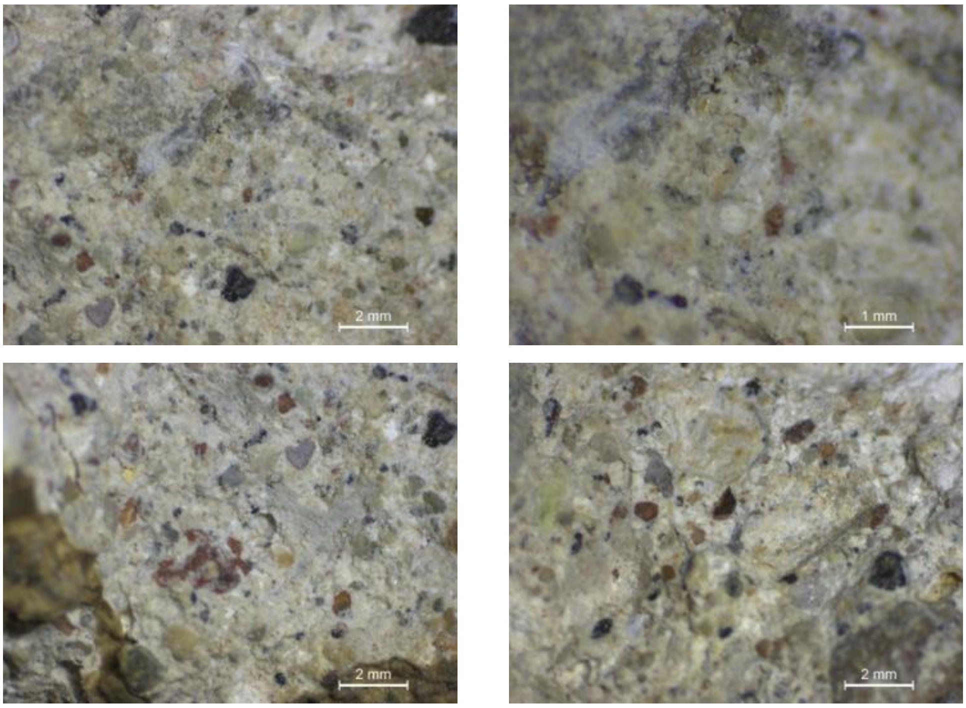
also seems that the fractured surface is less smooth (less bright, less reflectant) (AG.AH._08_01/2/3/4)



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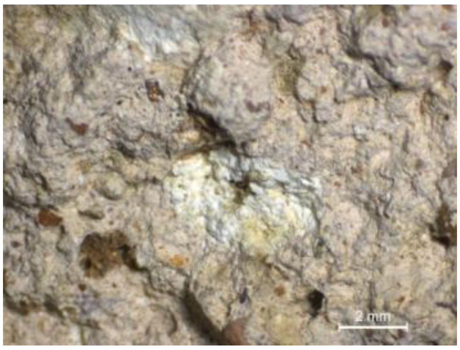
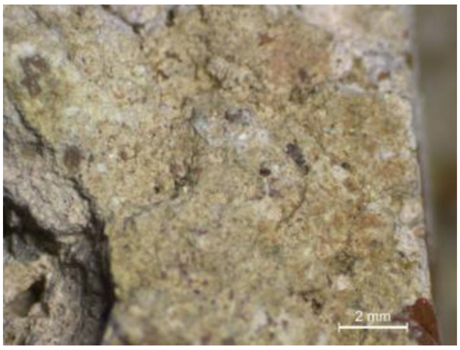
CPV-03

Presence of ceramics as part of the aggregate matrix (CPV_03_02) and possible ceramic powder in binder (see binder color in CPV_03_05). Bounders in ceramic aggregate grains are not clear (indications of chemical or alteration reactions in the interface).Small grains, maximum size of aggregates, around 0,3mm (CPV-03_03)

Network of fissures and cracks becoming visible (CPV_03_2/3).





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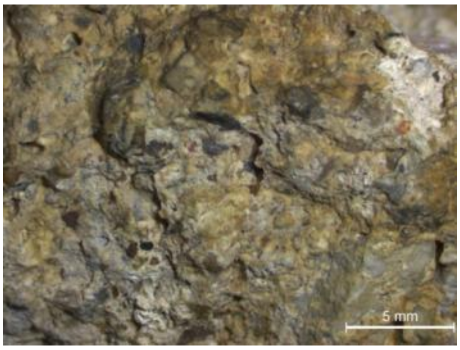
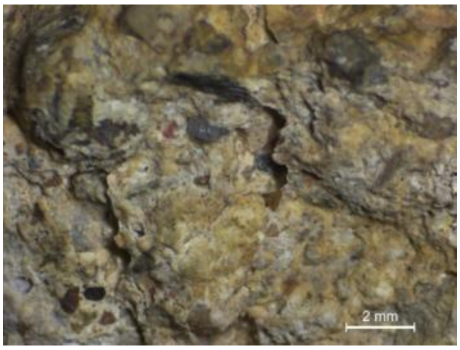
F4

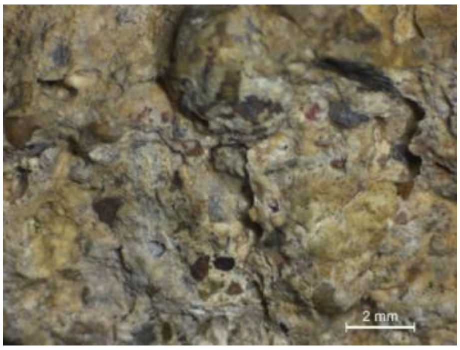
Grey – yellowish binder and rounded aggregates.

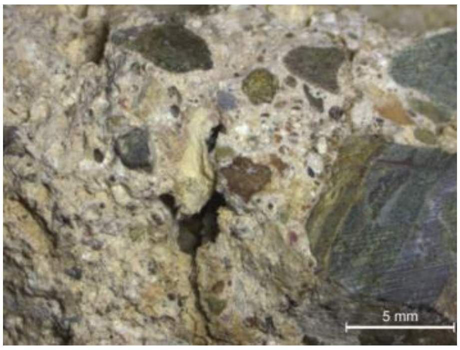
Fracture surface that follows the surface of aggregate matrix, without revealing aggregate grains (good adhesion of binder and aggregates). Fracture in flakes (parallel surfaces) (F4_01/2/3).

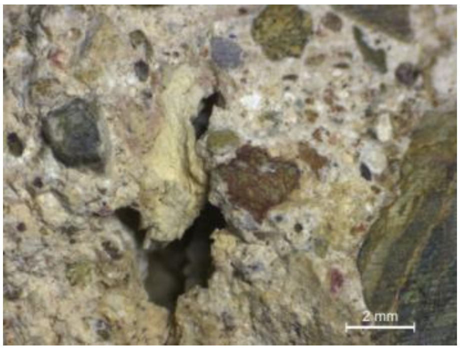
Cracks and void (F4_07 / 08)











Seems to have a compact matrix of aggregates, with a variety of grain size. Rounded larger grains, angular smaller dark ones.

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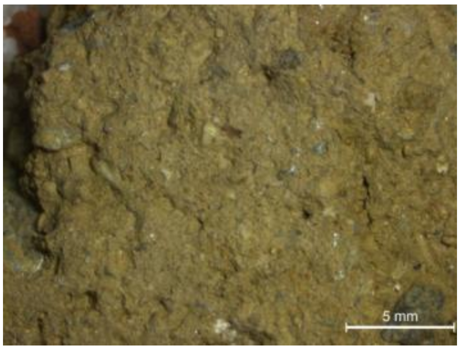
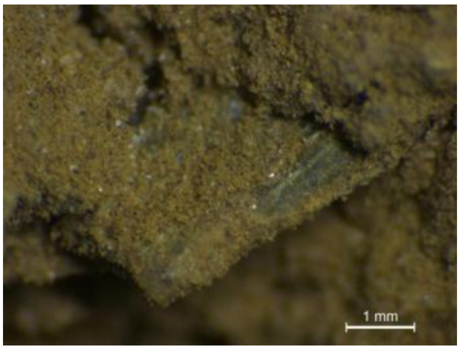
P2

Brawn, ground like color of binder (all pictures), having no good adhesion with aggregates and granular texture (P_02_09).

Small size of aggregate grain size (the larger light colored ones 0,5-0,7cm in size)

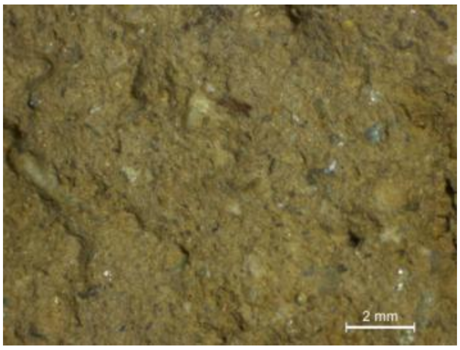


1

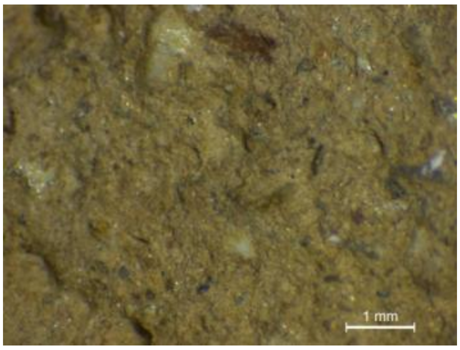


9

Possibly presence of micas (sparkling aggregates in P_02_04/3/2)



2



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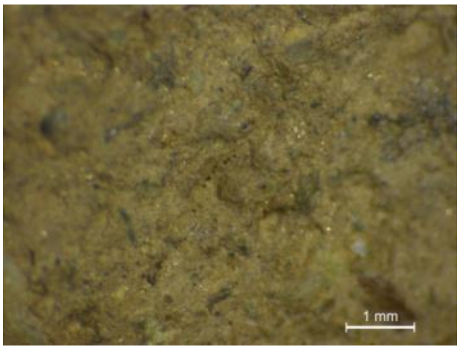

4

Flat fracture surfaces (due to small aggregate size and poor adhesion P_02_01/2)

Secondary crystalline white structures in fissures (P_02_6/7/8) indicating free flow of liquids.

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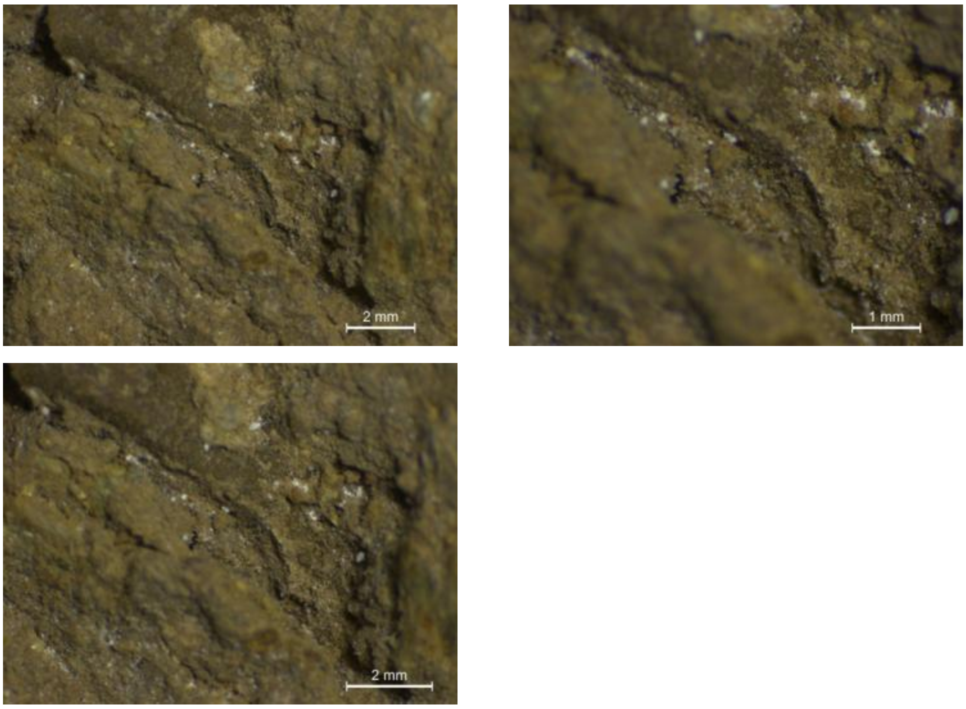
2 mm
1 mm
2 mm

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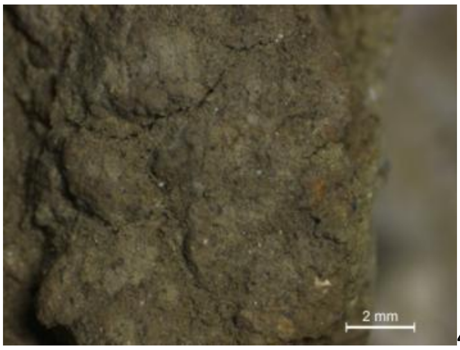
P7

Similar properties to P2. Same color and granular texture of binder (P_07_04/5/7).



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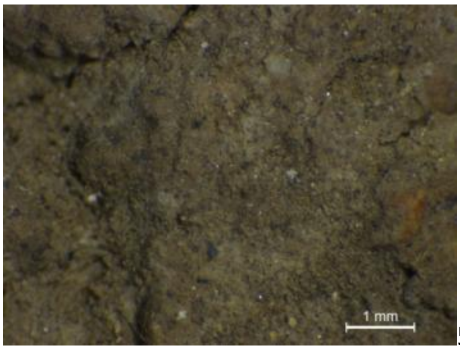

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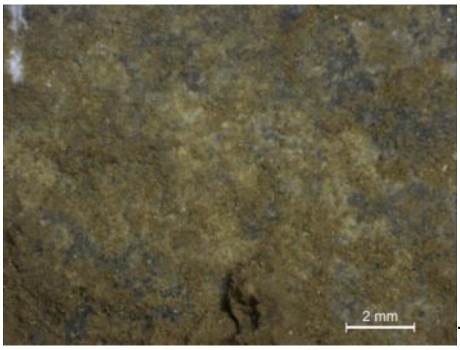

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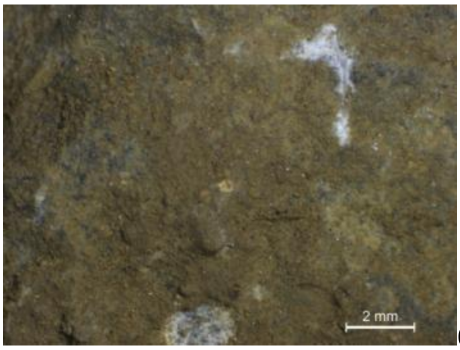

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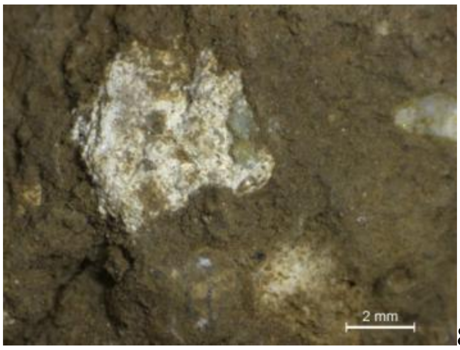

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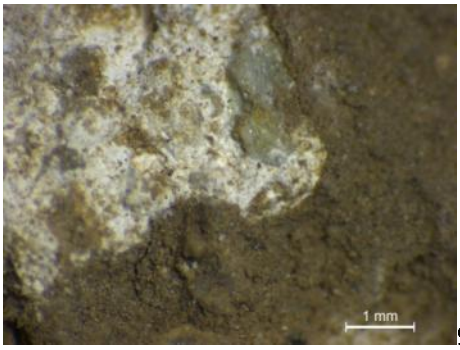

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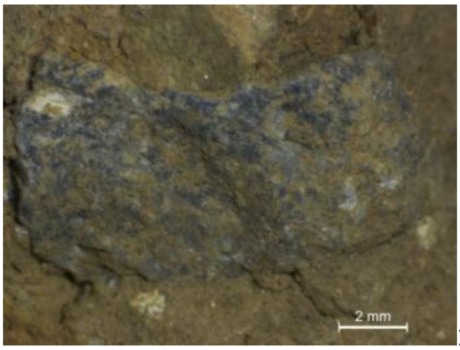

11

Larger regions of secondary crystalline structures and not only in fissures (P_07_6), evidence of excess of lime (P_07_08/9). In these secondary crystalline structures there

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are small aggregates possibly drifted (P_07_09) they do not seem to be part of the aggregate matrix.

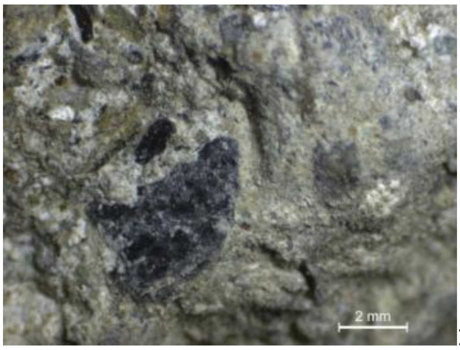
Larger rounded grains similar to schist (P_07_11). Large flakes of micas (sizes of 2mm, P_07_01/2).

AG.L.2

Gray colored samples and binder. (all photos).

Fissures (AG.L._02_01). Fracture surface following aggregate matrix relief, fissures delimit (follow the shape of) larger aggregates (AG.L._02_02).

Thick aggregate matrix / good grain gradation/ 0,5mm grains (AG.L._02_03/4) Presence of secondary crystalline formations.



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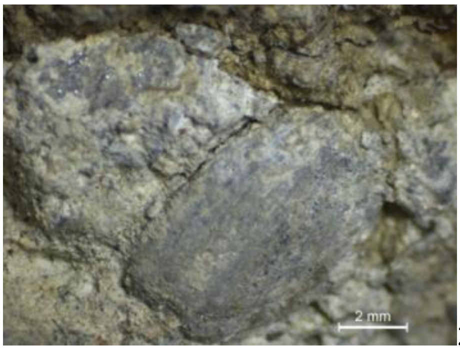

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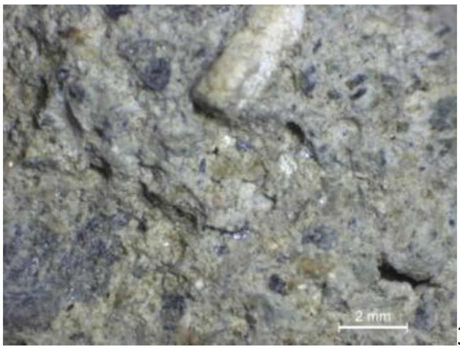

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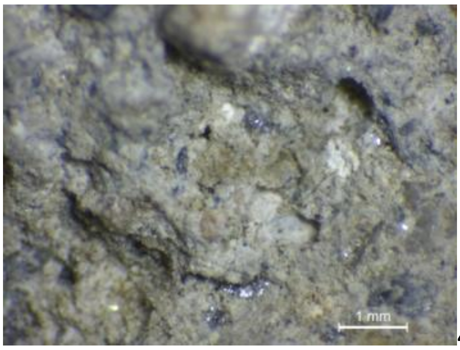

4

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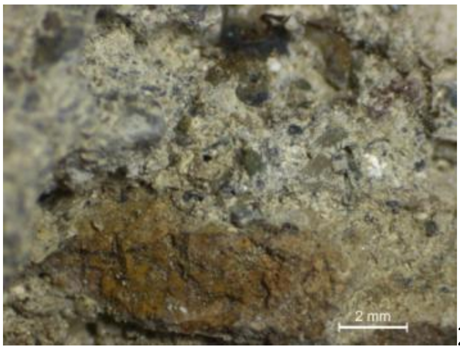
AG.L.9

Similar to AG.L.2, but with the presence of ceramics (AG.L._09_02) More fractures (AG.L._09_03) / darker, usually elongated aggregates (AG.L._09_04)



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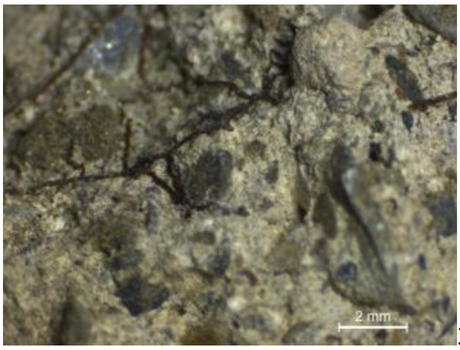

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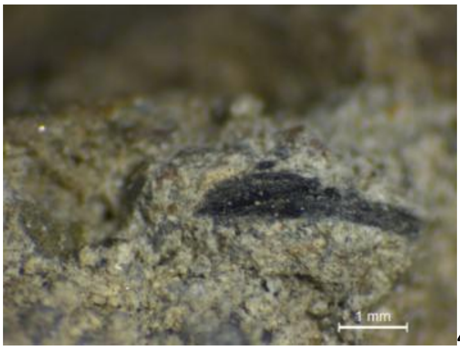
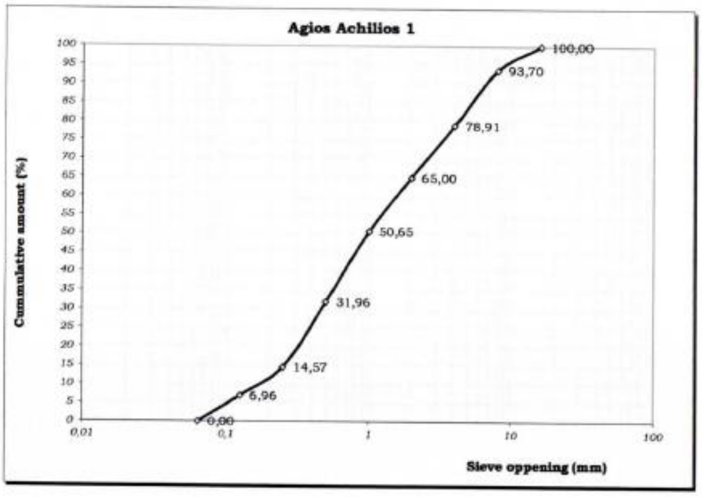
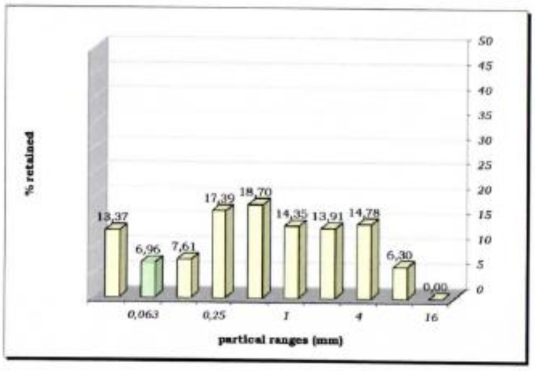


4

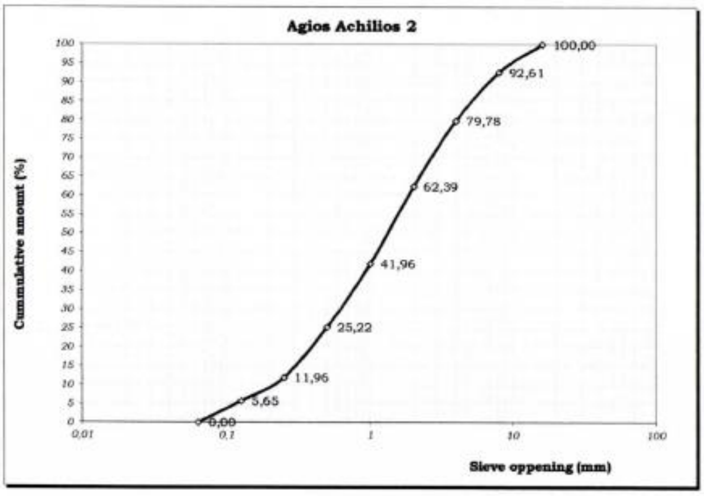
5.3 Grain size distribution

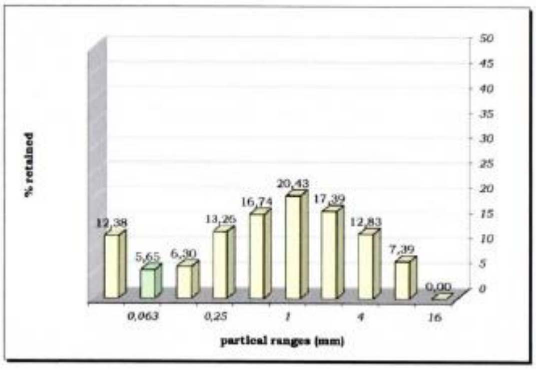
I.FOT.01



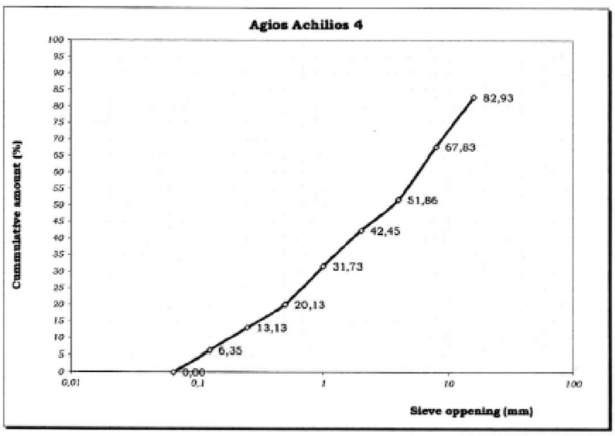


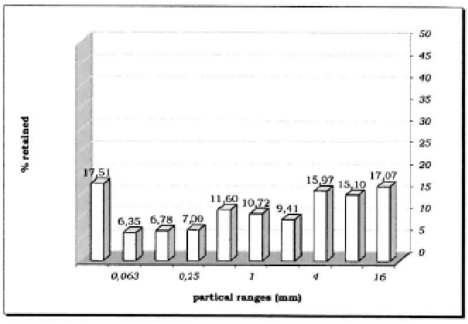
I.FOT.02





I.FOT.04





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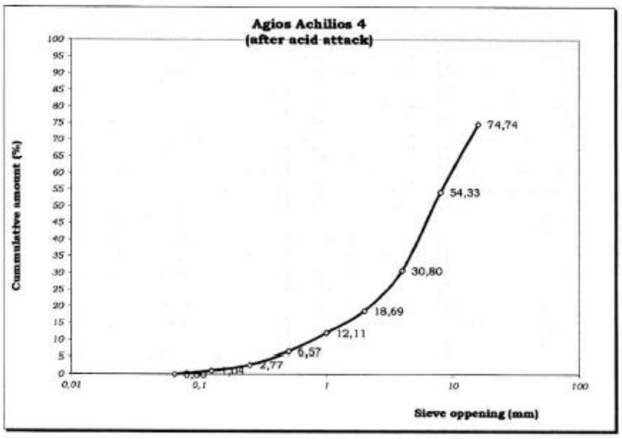
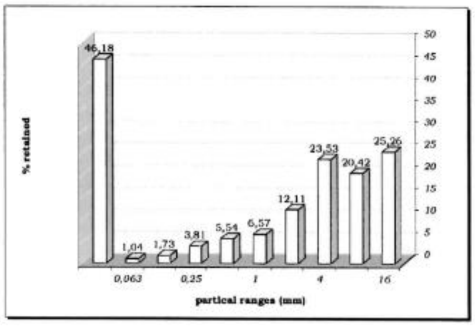
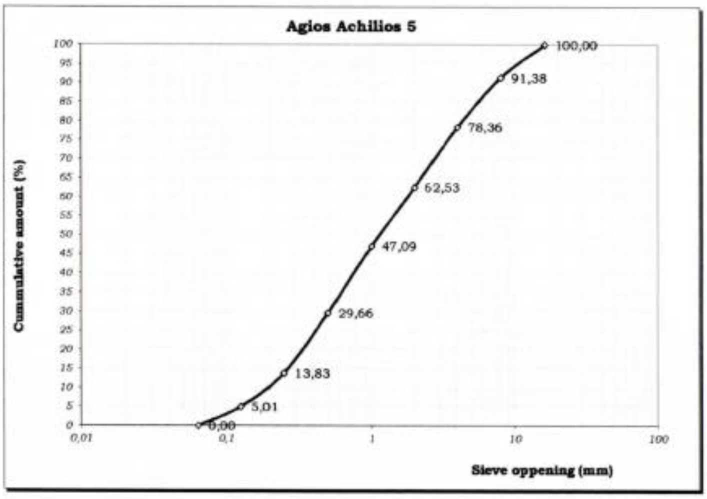
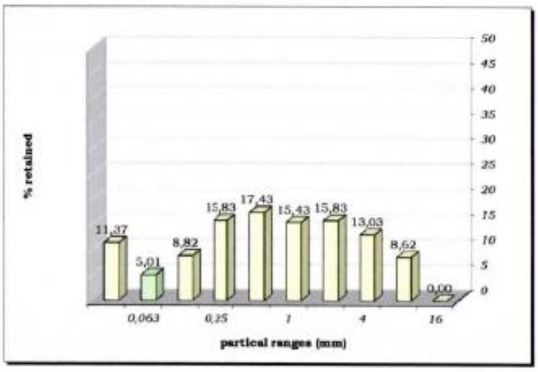
I.FOT.04



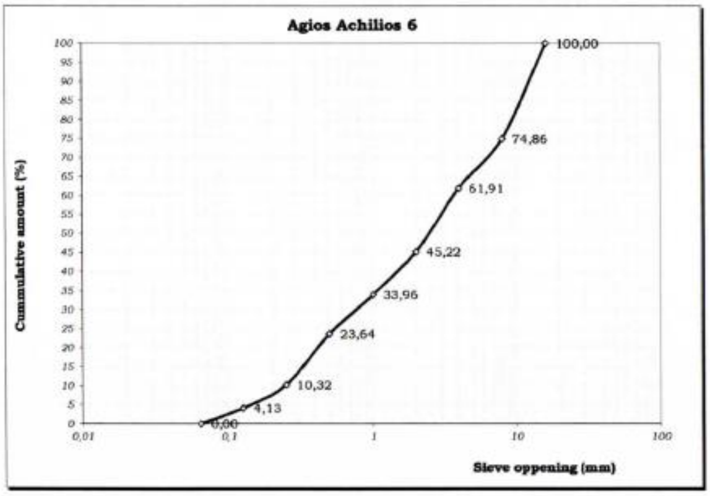


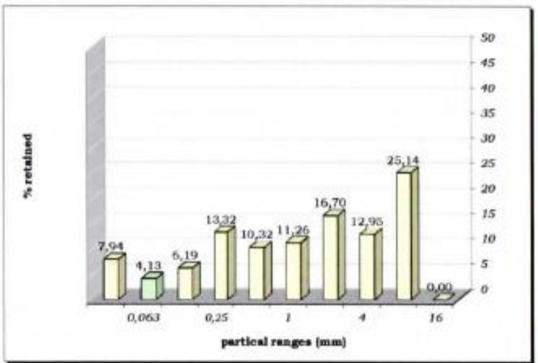
I.FOT.05



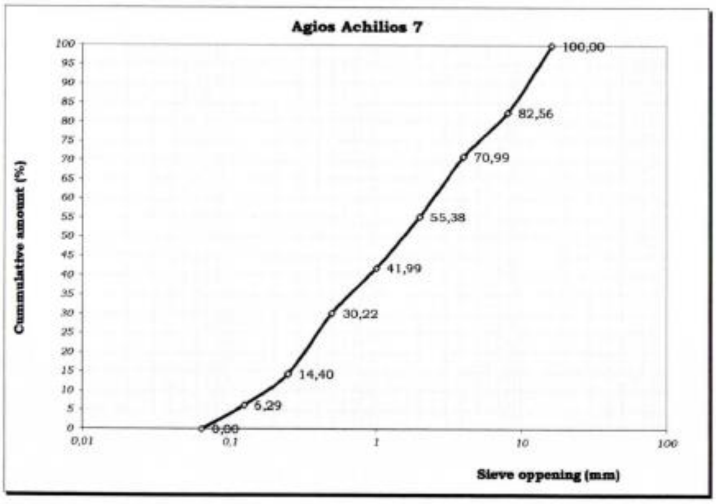


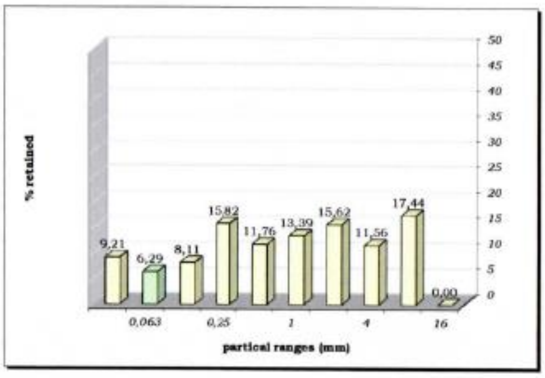
I.FOT.06



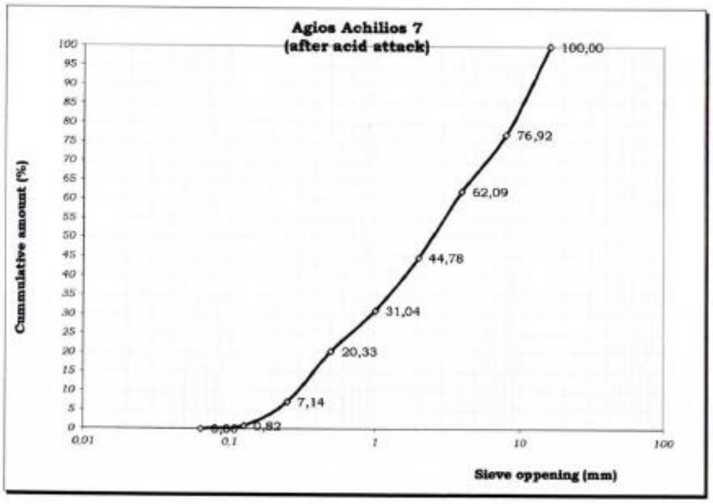


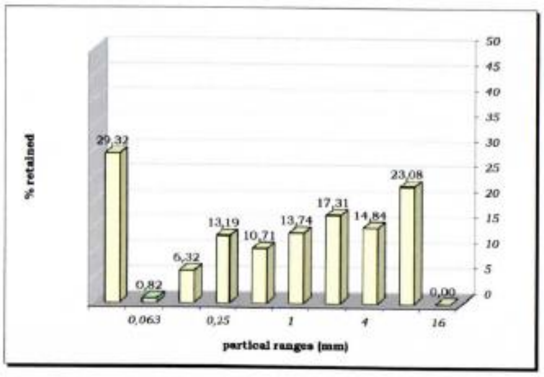
I.FOT.07



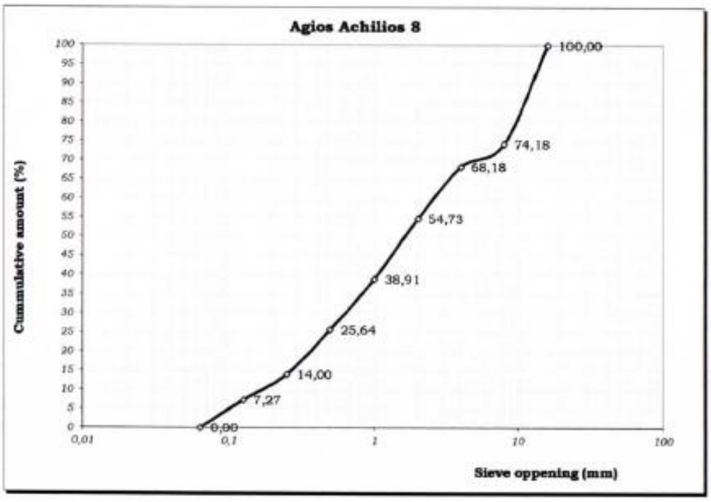


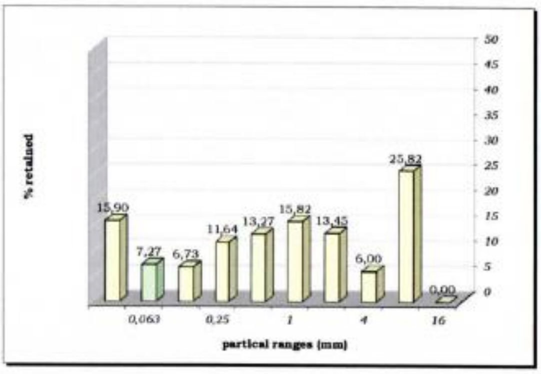
I.FOT.7 (after acid attack)





I.FOT.08





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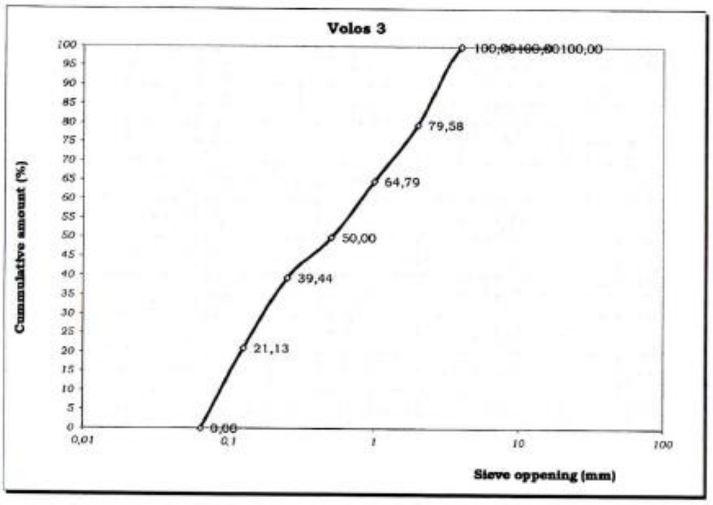
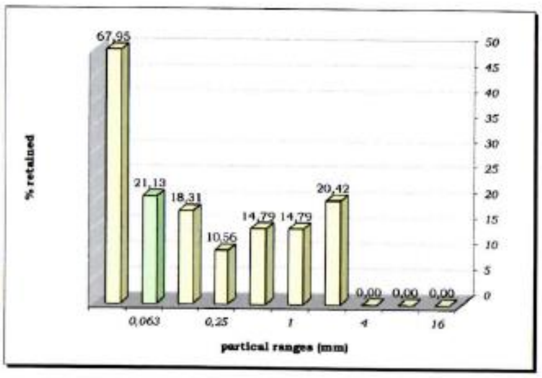
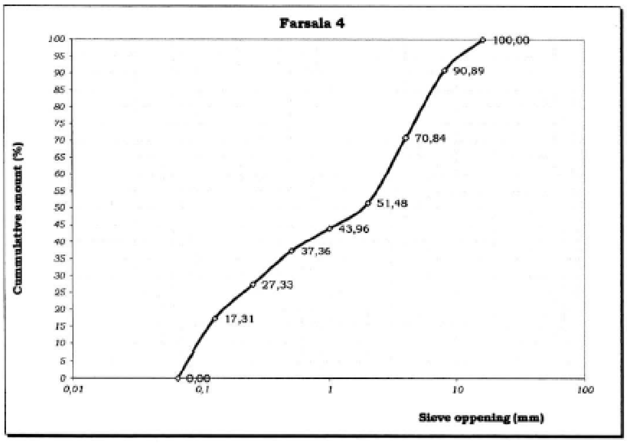
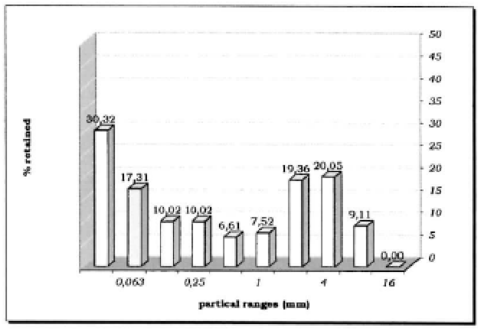
I.FOT.09



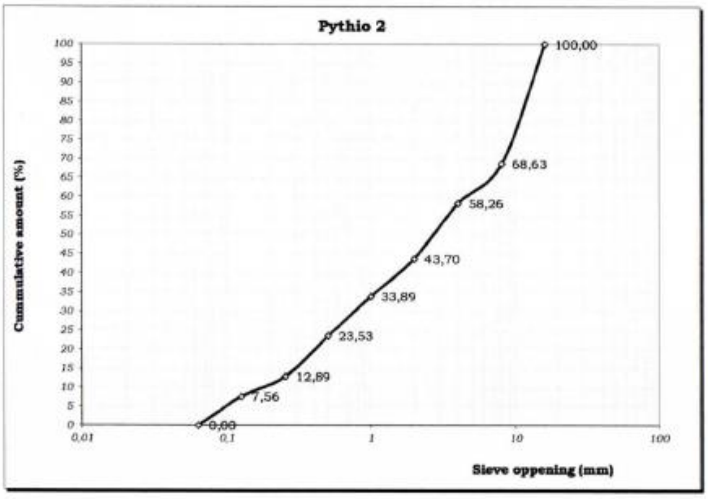


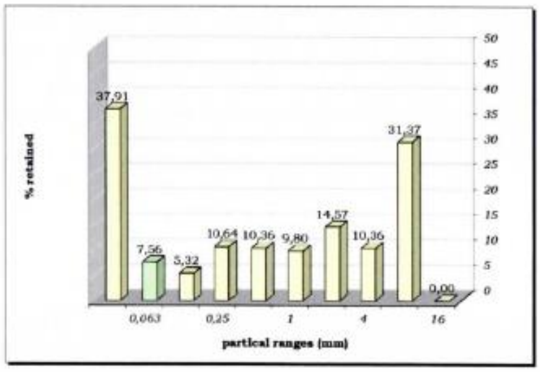
I.FOT.10



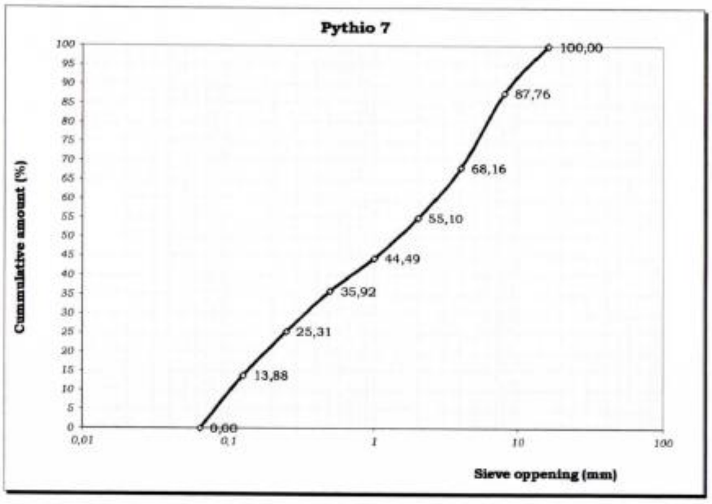


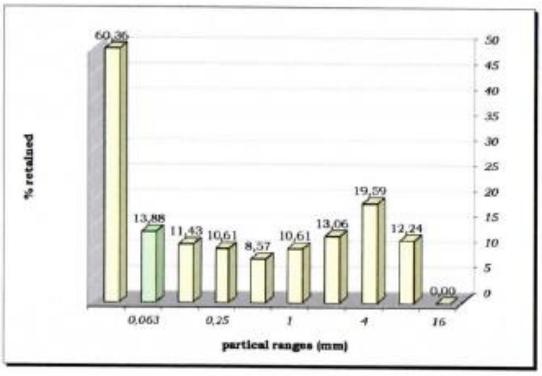
I.FOT.11



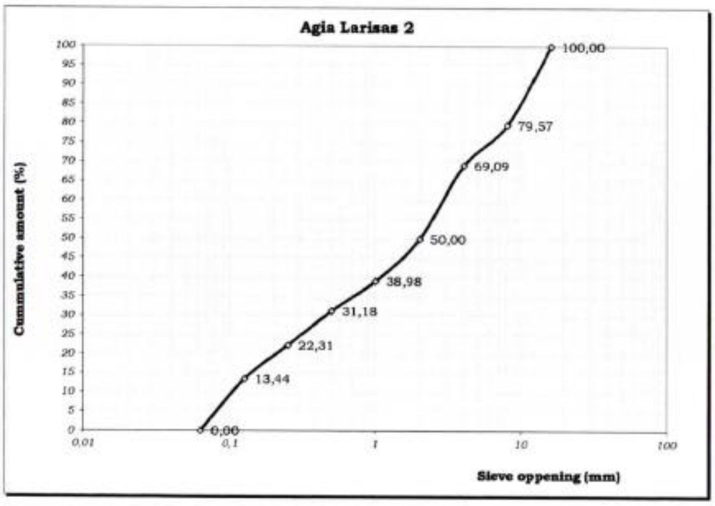


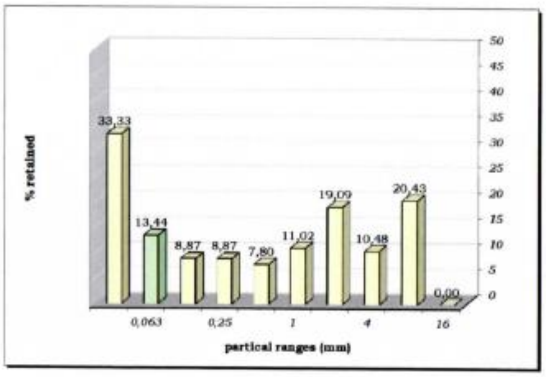
I.FOT.12



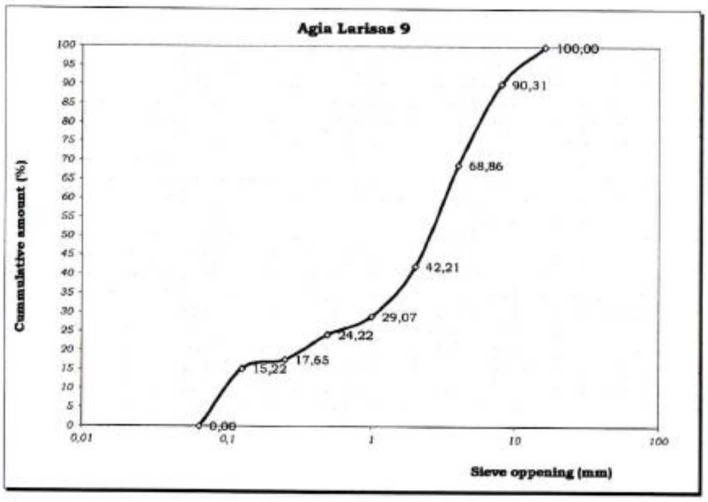


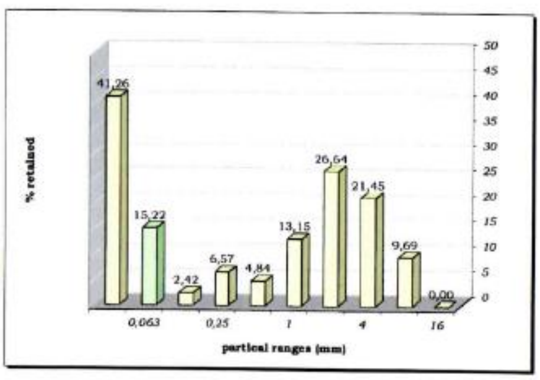
I.FOT.13





I.FOT.14

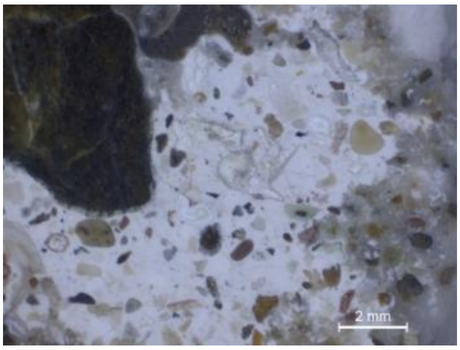


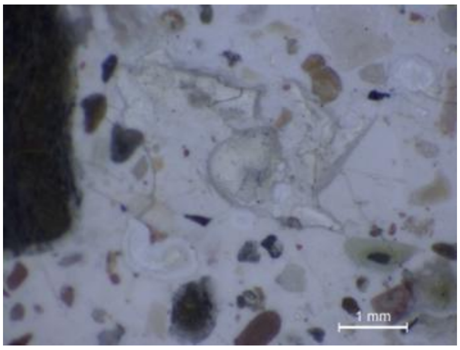


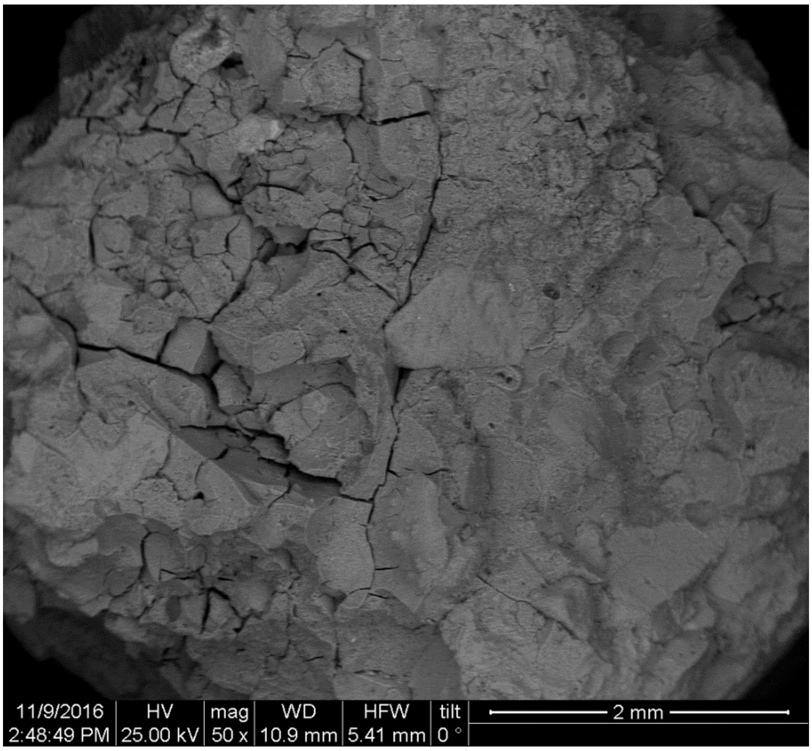
5.4 SEM (EDX)

I.FOT.01 – Agios Achillios 1

Light colored (almost white) lime mortar with dense structure. It is rich in binder and fine grained aggregates (pictures) It contains natural aggregates, mostly lime stones with no sharp edges. Maximum grain size 1,0 – 1,8 cm. It is characterized by low mechanical stress values and presence of several large pores. Examination in SEM reveals a rather mixed binder, with presence of alumino-silicate constituents.







Macroporosity revealed in backscatter

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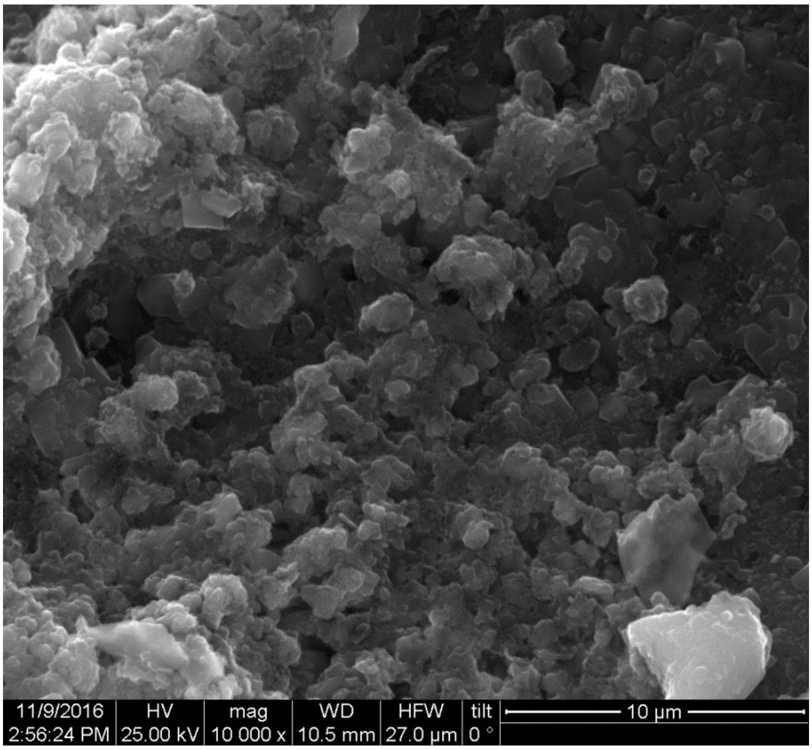
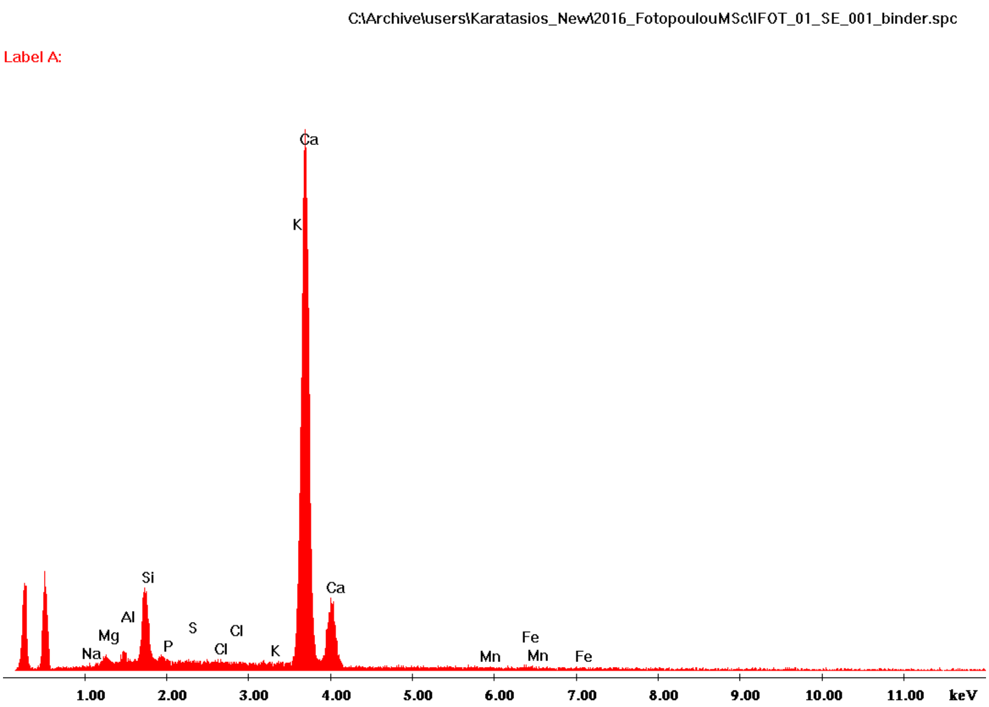
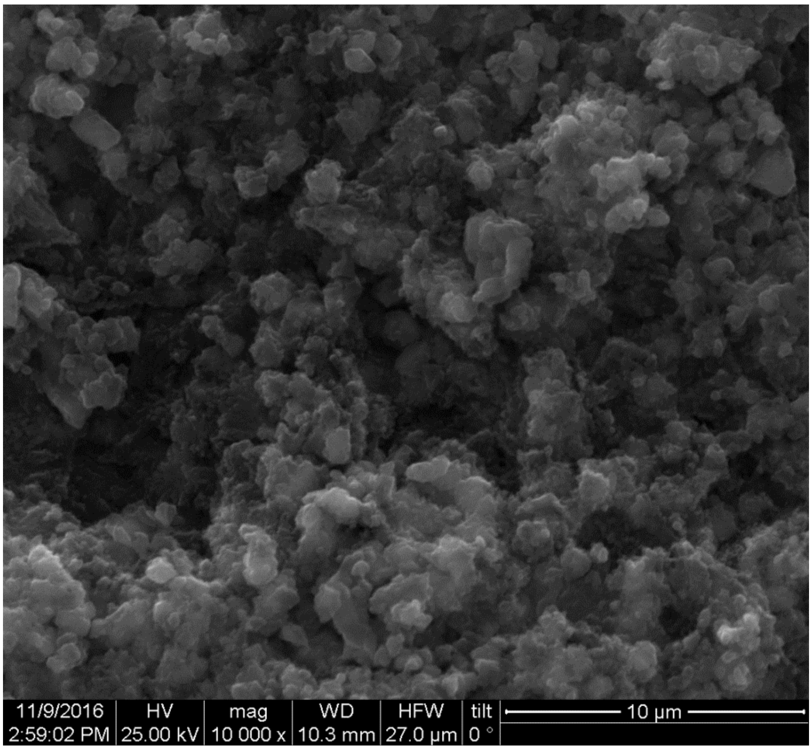


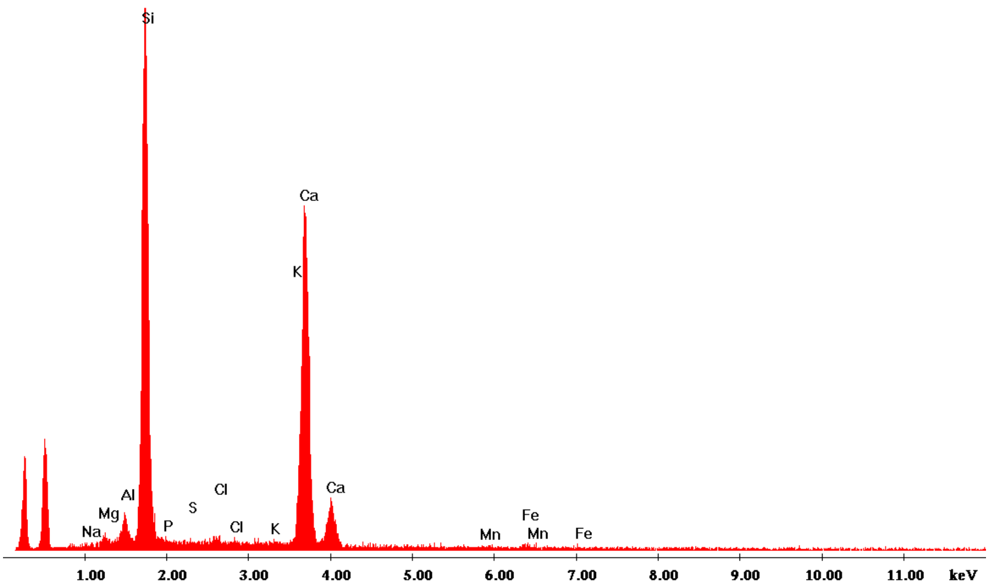


Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd) suggests non hydraulic character.



C:\Archive\users\Karatasios_New\2016_FotopoulouMSc\IFOT_01_SE_002_binder.spc

Label A:



Binder microstructure (1st picture) and corresponding SEM/EDX analysis in another spot of the same sample: Increased presence of Si proves presence of a mixed binder.

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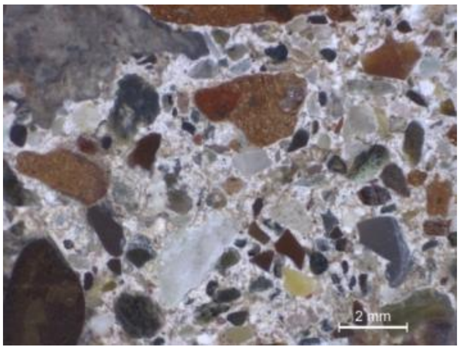
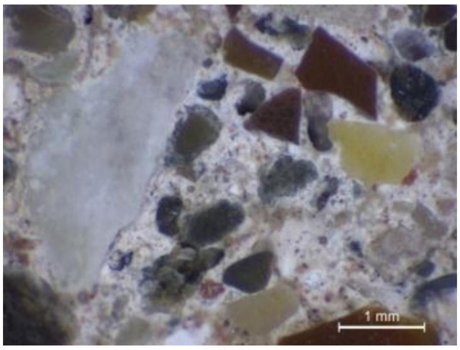
I.FOT.02 – Agios Achillios no 2

Lime mortar contained crushed ceramics and mixture of aggregates (crushed ceramics natural stones with max.grain size of approximately 2cm). The consistency is medium to strong. Presence of large lime lumps. SEM examination reveals a rather mixed character, slightly hydraulic.





In all above pictures in stereoscope the microstructure can be observed: Solid structure of lime binder in mixture of ceramic powder, small presence of ceramics as aggregates along with natural light colored limestone grains and small presence of lime lumps.

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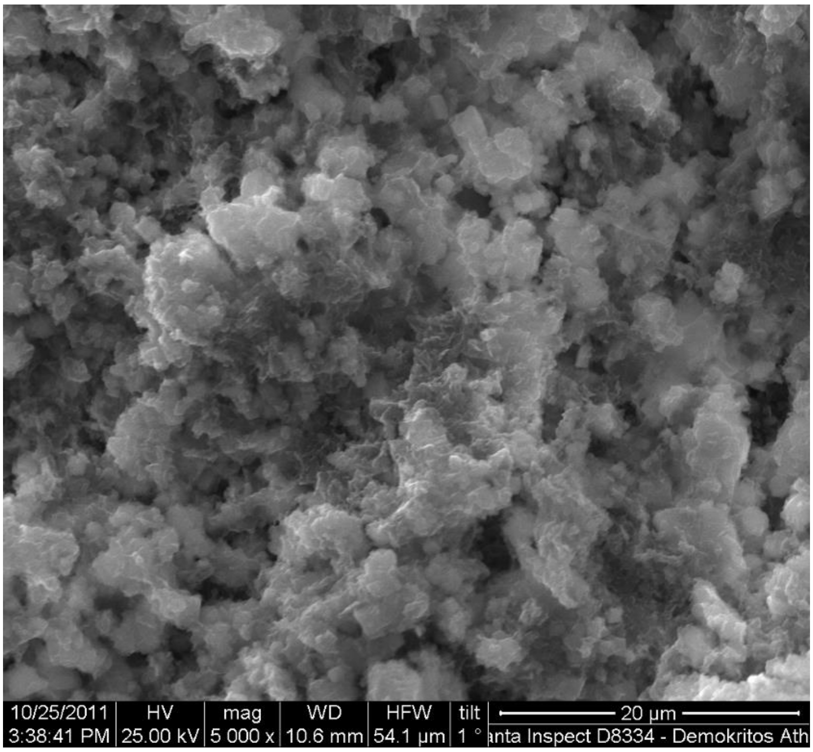

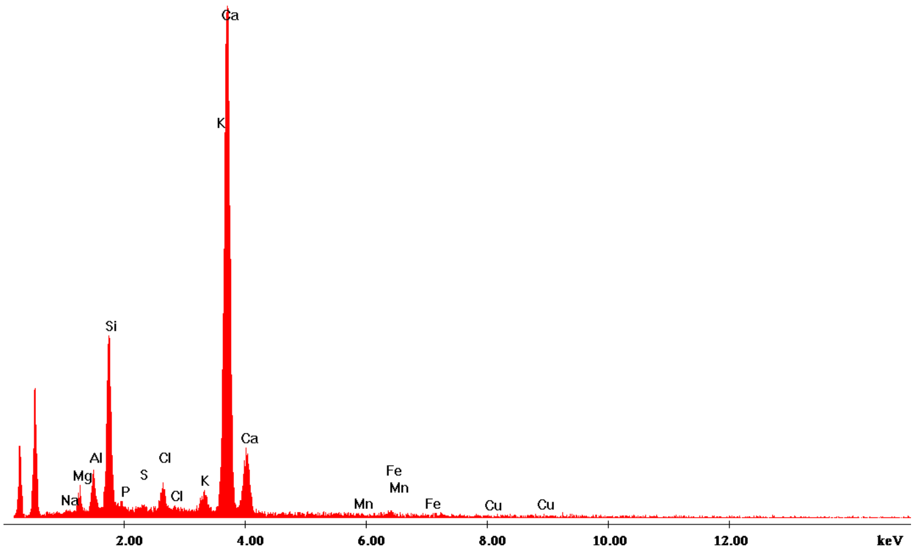

Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): mixed binder character with small percentage of hydraulic phases.

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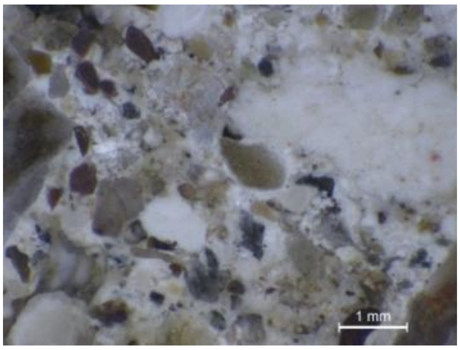
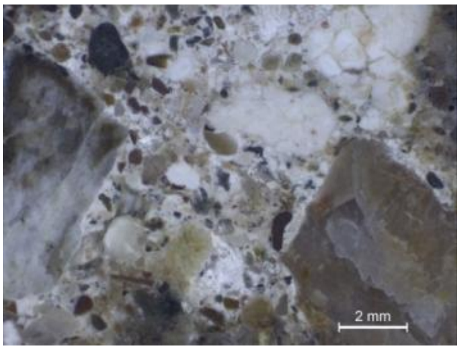
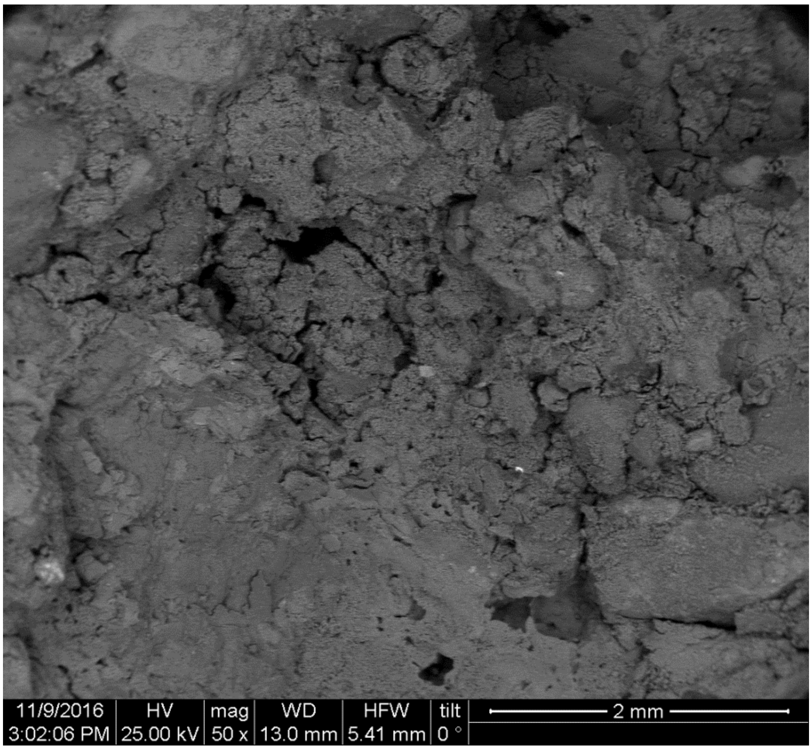
I.FOT.03 – Agios Achillios 3

Light colored grayish mortar with solid structure and grain size up to 2mm. Presence of larger grains up to 2cm is noted. Systematic presence of lime lumps is observed; binder having a greenish-gray hue. SEM examination proves a high hydraulic character of the binder with recognizable presence of hydraulic phases.







Even in this structure, micro cracks are evident.

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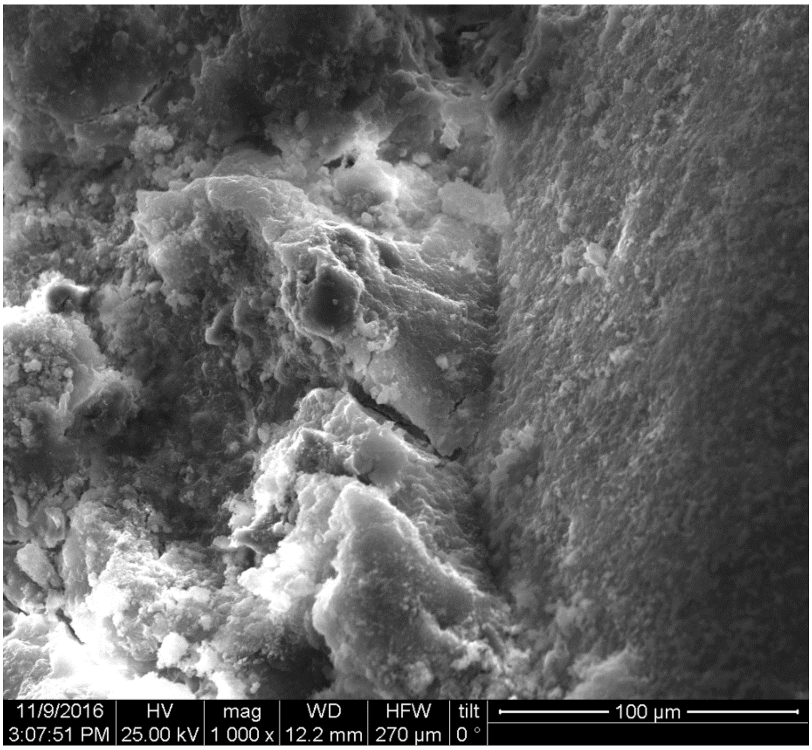

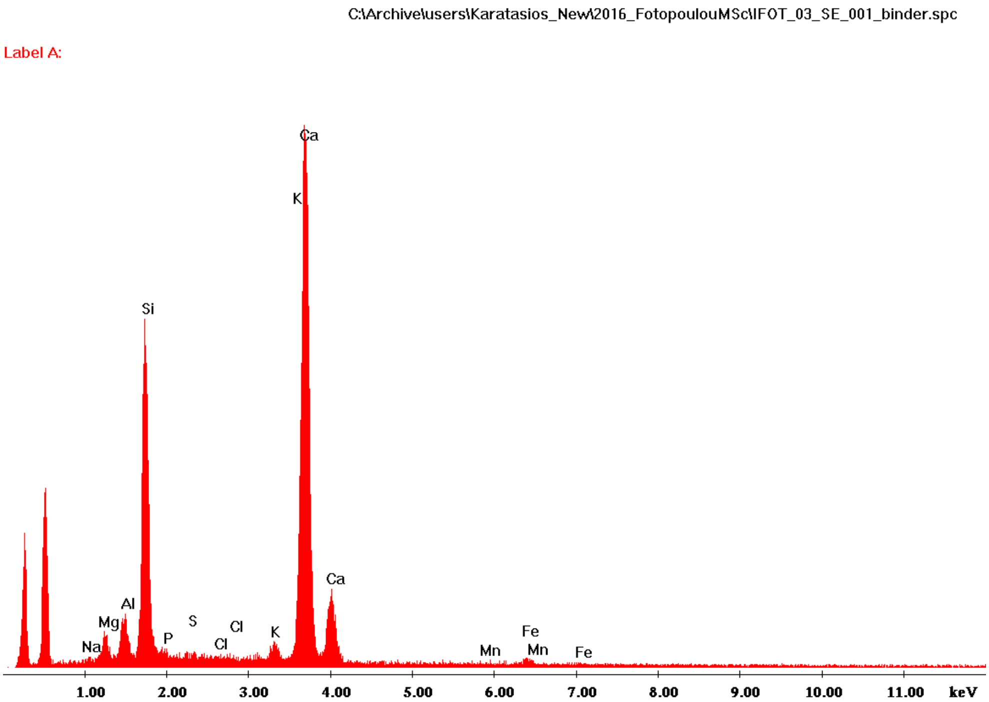

Binder microstructure (1st picture and the one's following this page) and corresponding SEM/EDX analysis (2nd): Presence of binder with strong hydraulic character.

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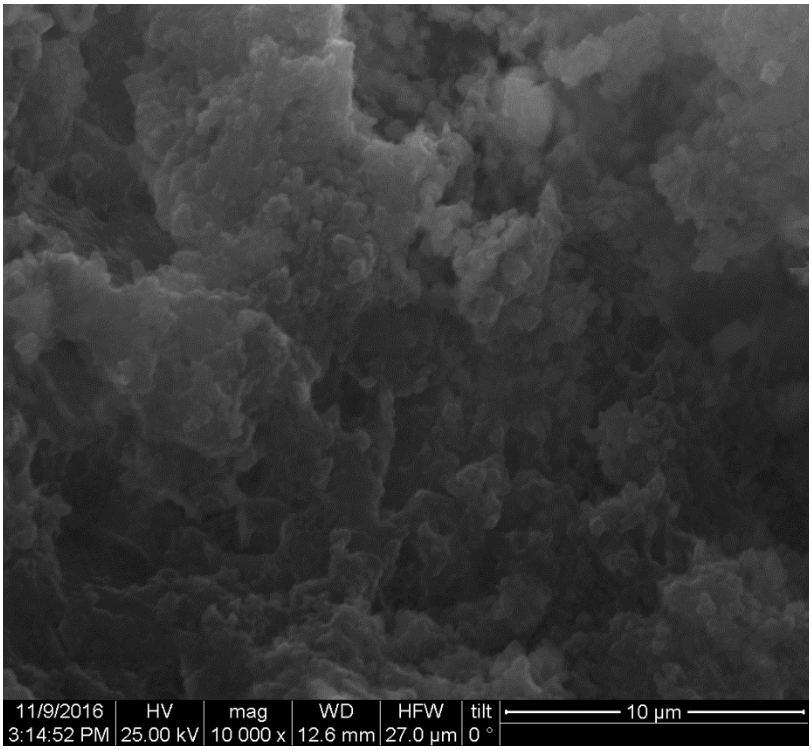
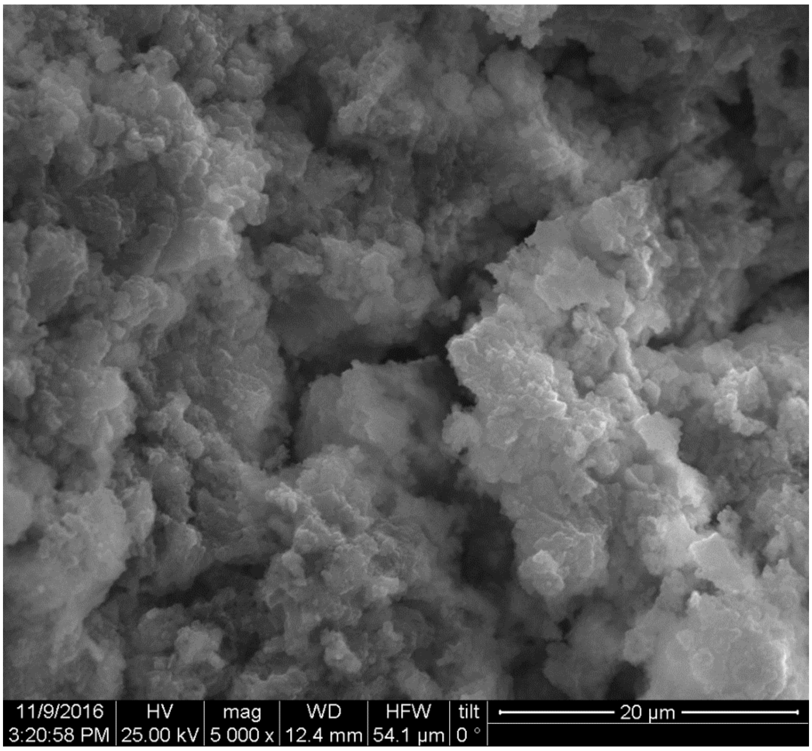
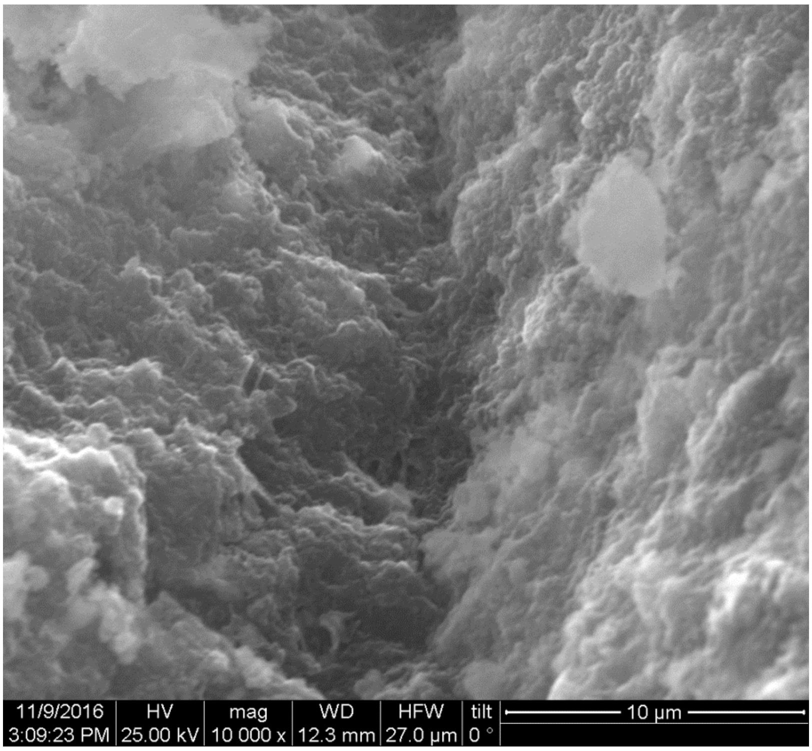

11/9/2016 3:14:52 PM
HV 25.00 kV
mag 10 000 x
WD 12.6 mm
HFW 27.0 µm
tilt 0 °
10 µm


11/9/2016 3:20:58 PM
HV 25.00 kV
mag 5 000 x
WD 12.4 mm
HFW 54.1 µm
tilt 0 °
20 µm

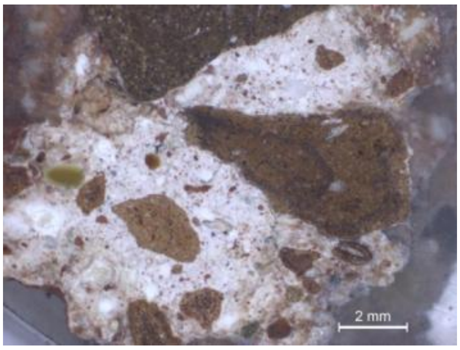
`

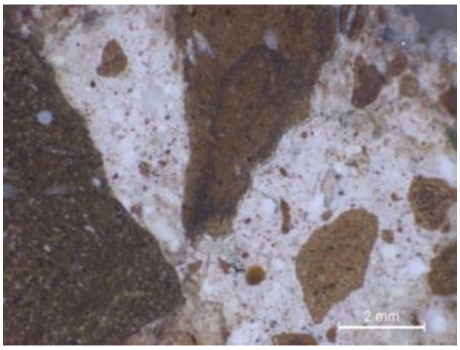

11/9/2016
3:09:23 PM
HV
25.00 kV
mag
10 000 x
WD
12.3 mm
HFW
27.0 µm
tilt
0 °
10 µm

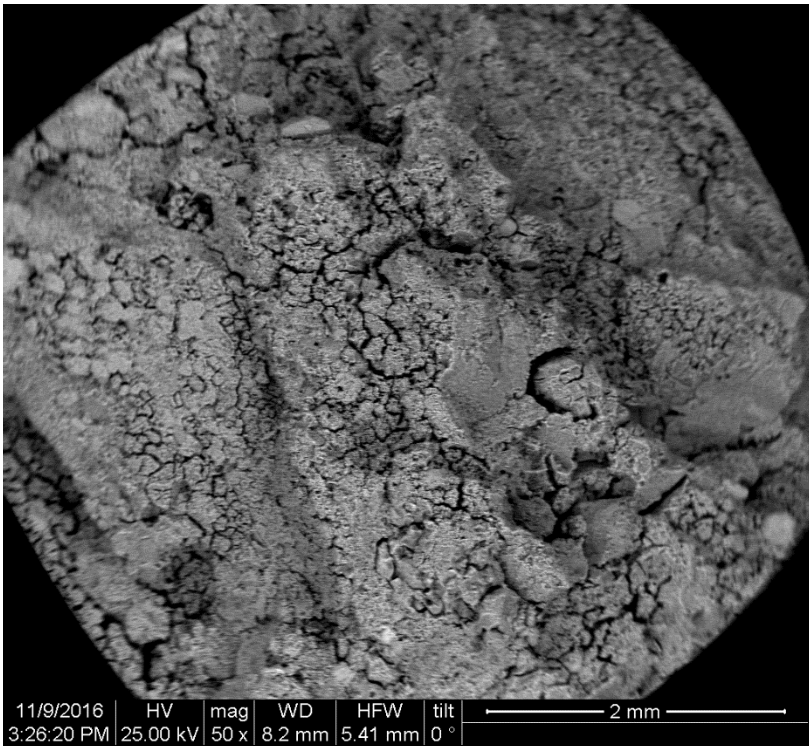
`

I.FOT.04 – Agios Achillios 4

Lime mortar with graded ceramics, rich in binder and exclusive presence of ceramics as aggregates. Maximum grain size 1,0-1,5cm. It has medium to strong consistency and strong presence of lime lumps (maximum size of 1-2mm). Mortar mass is cohesive. SEM examination reveals a strong hydraulic character.







Fractures revealed in backscatter.

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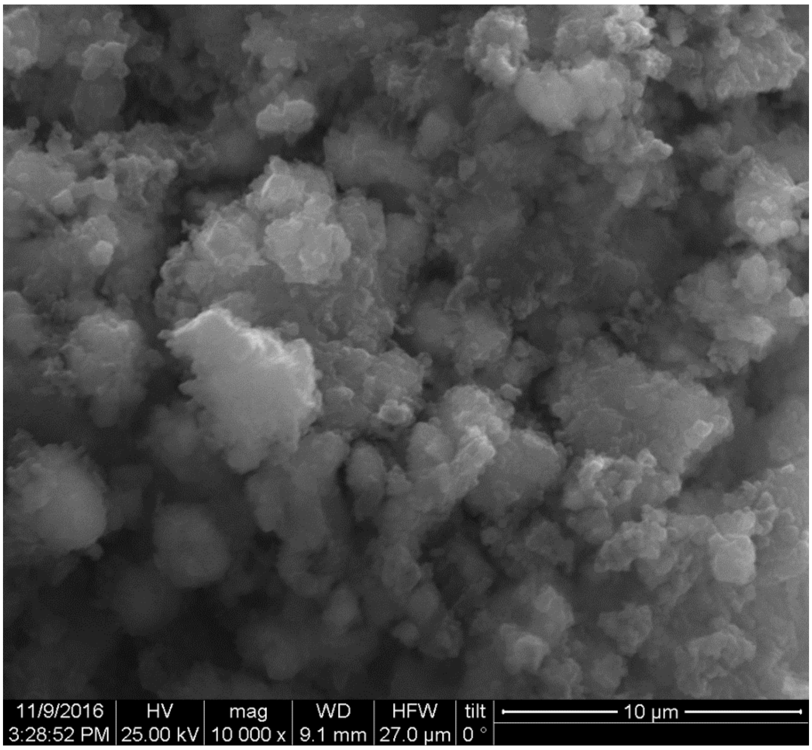
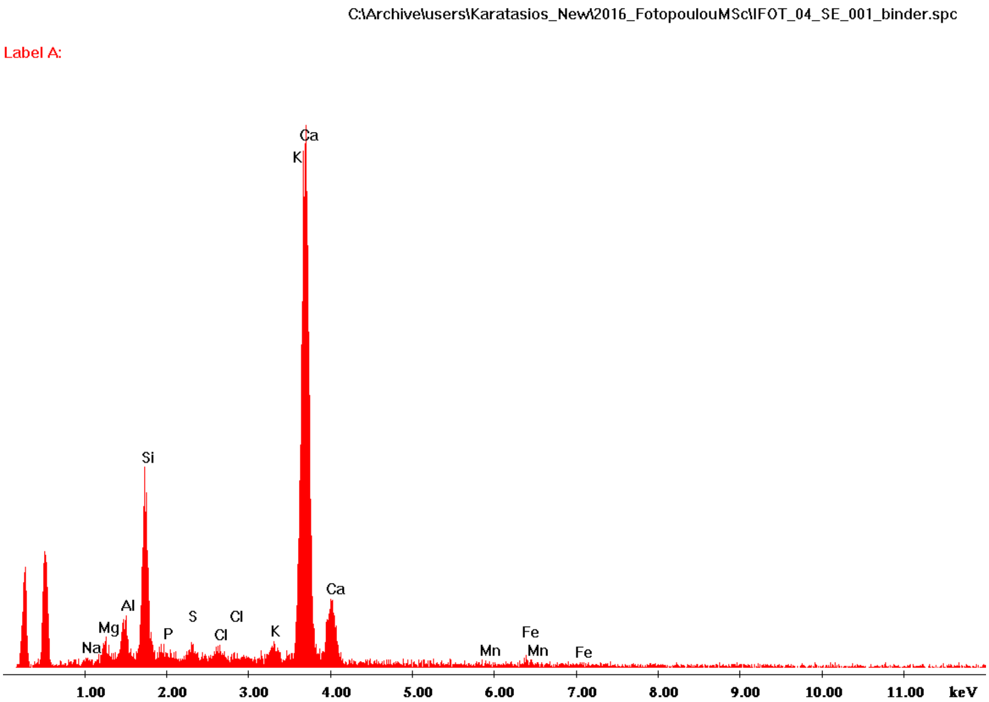
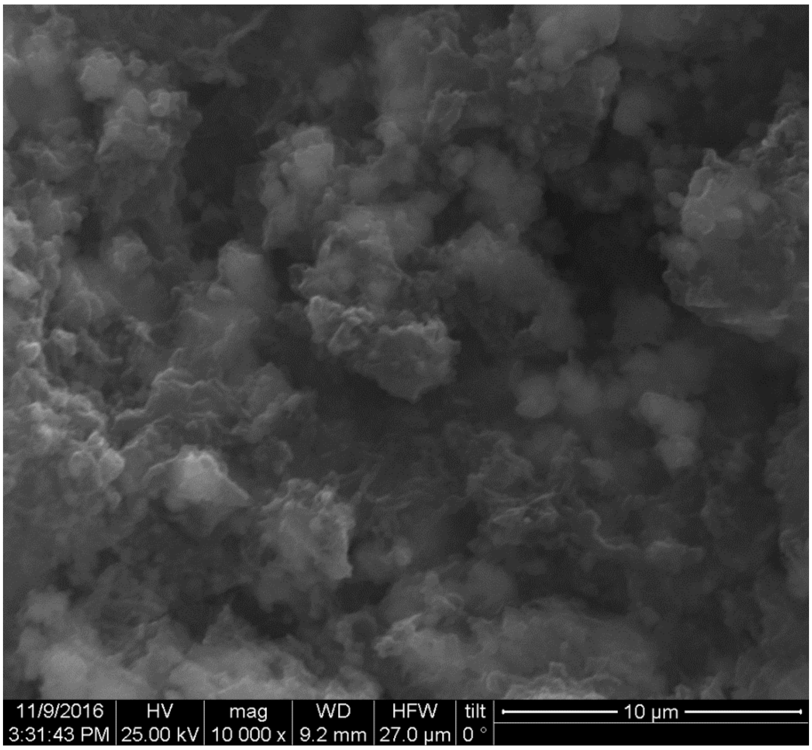
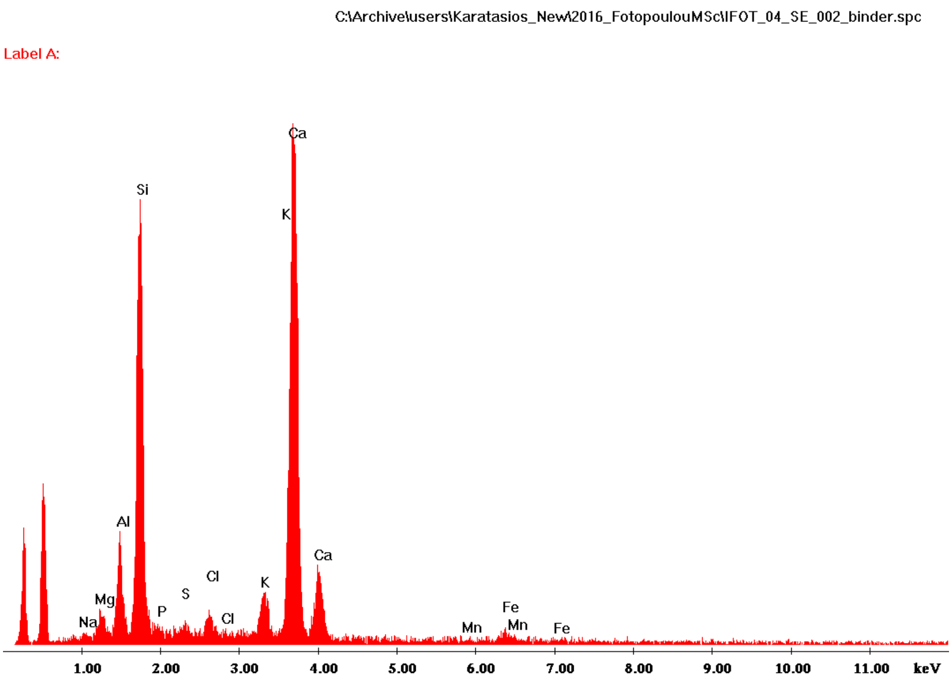




Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): Presence of binder with strong hydraulic character.





Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd) in another spot: An even stronger hydraulicity of the binder is indicated.

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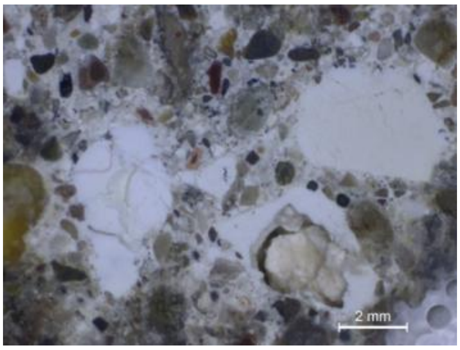
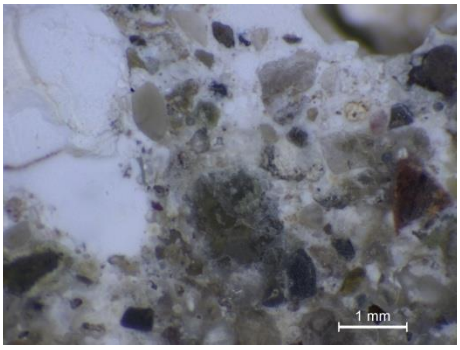
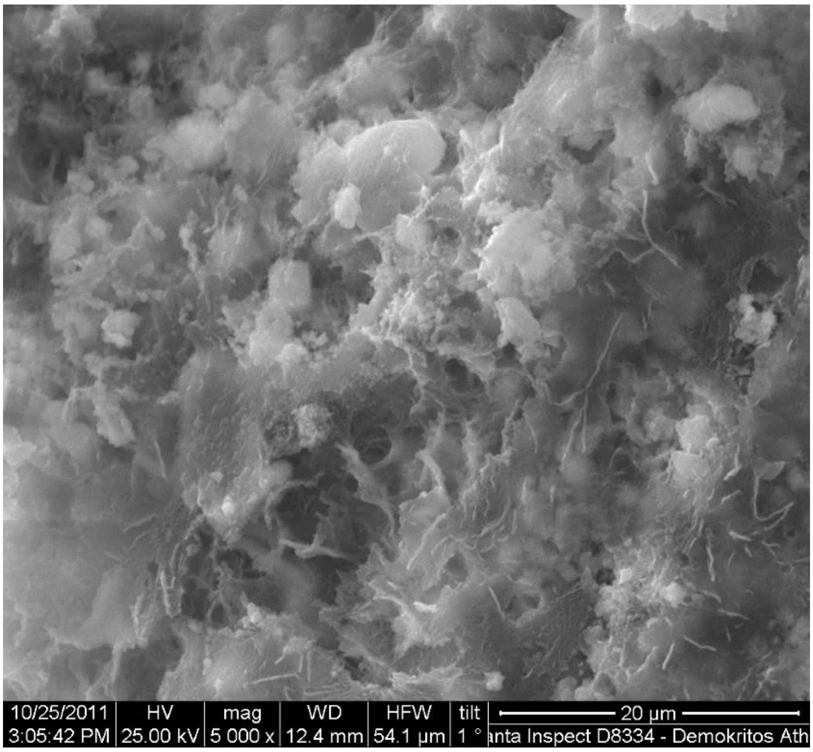
I.FOT.05 – Agios Achillios 5

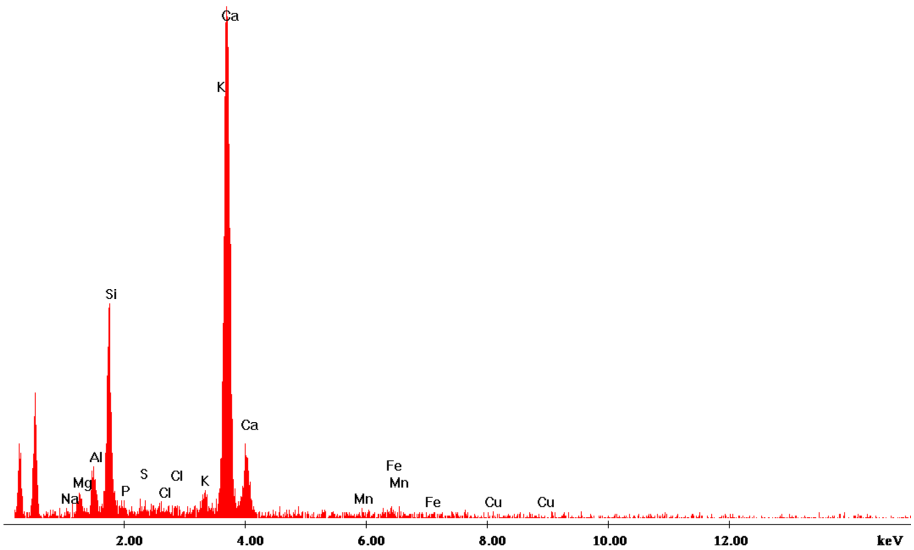
Light colored gray mortar with cohesive microstructure, rich in aggregates up to 3mm and considerable amount of larger natural grains and breccias up to 3,00-4,00cm maximum size. Systematic presence of lime lumps is observed. Considerable amount of binder, of green grayish hue. SEM examinations suggests strong hydraulic character with recognizable hydraulic phases.





Mortar microstructure: cohesive structure and high percentage of well graded natural aggregates.





Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): The strong hydraulic character of the binder is best indicated by the microstructure.

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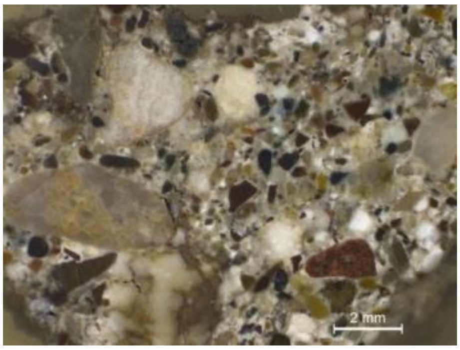
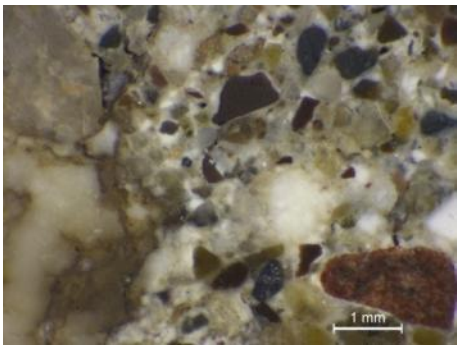
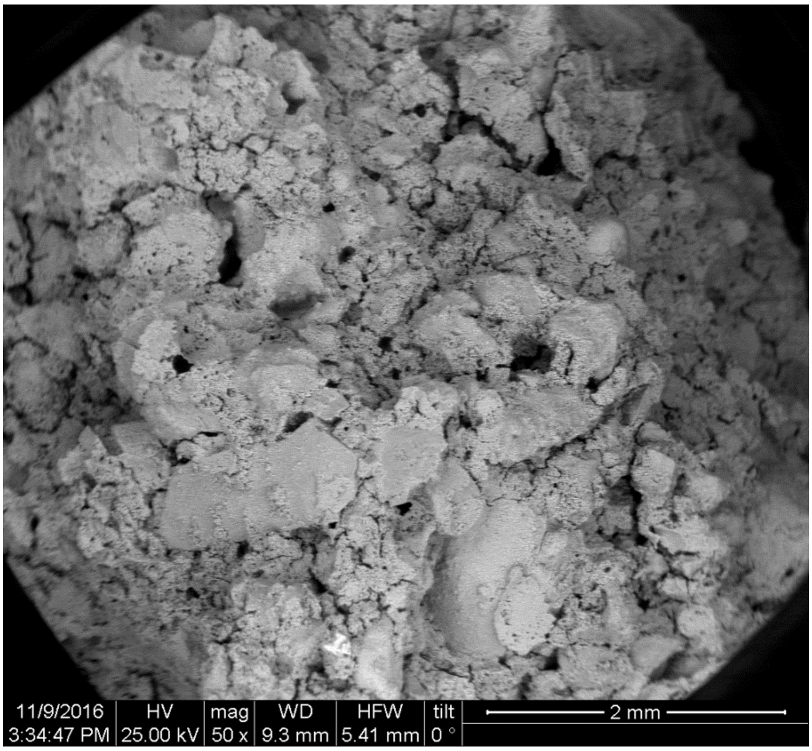
I.FOT.06 – Agios Achillios 6

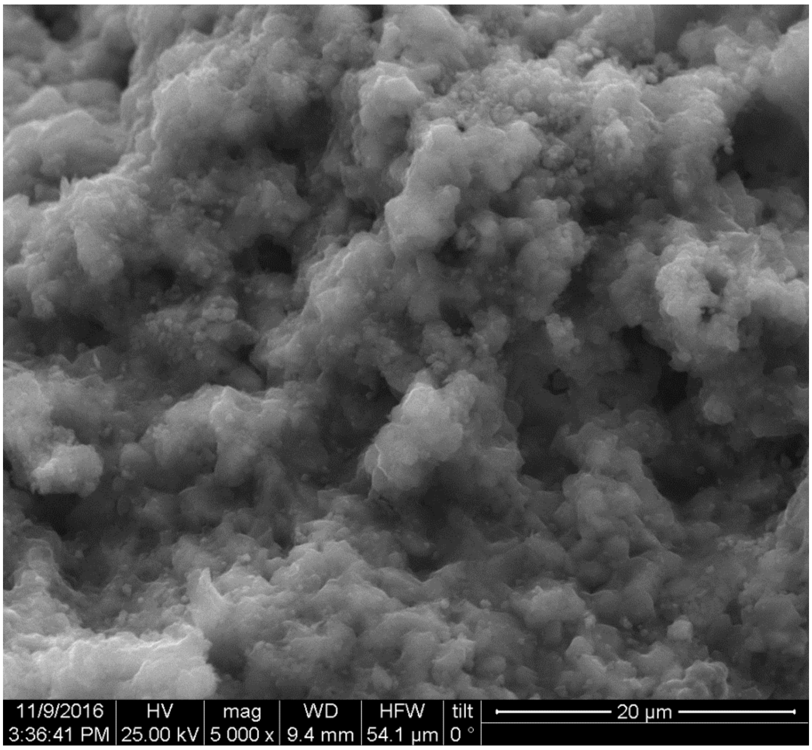
Light colored gray mortar with cohesive microstructure and basically angular aggregates (maximum grain size: 4,0cm). Systematic presence of lime lumps is observed. Green grayish binder hue. SEM examinations suggests non-hydraulic character with small presence of aluminosilicate admixtures.

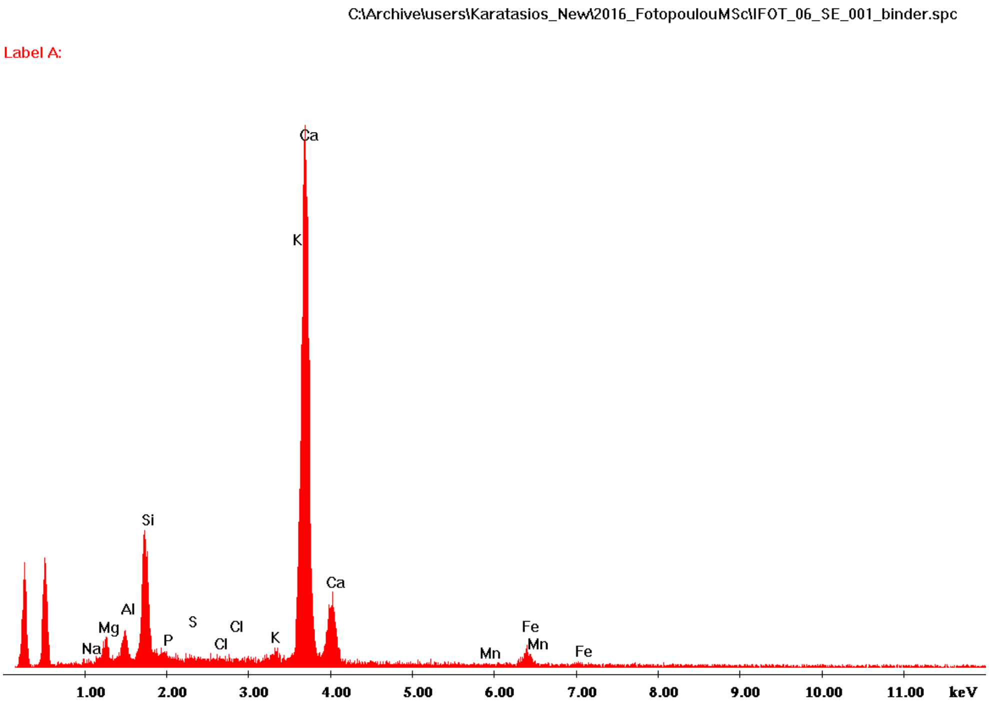






Small presence of fractures.





Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): Non hydraulic binder with small presence of aluminosilicates.

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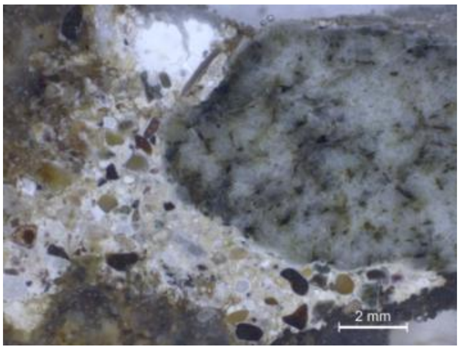
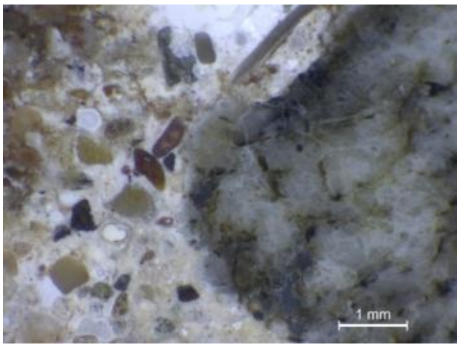
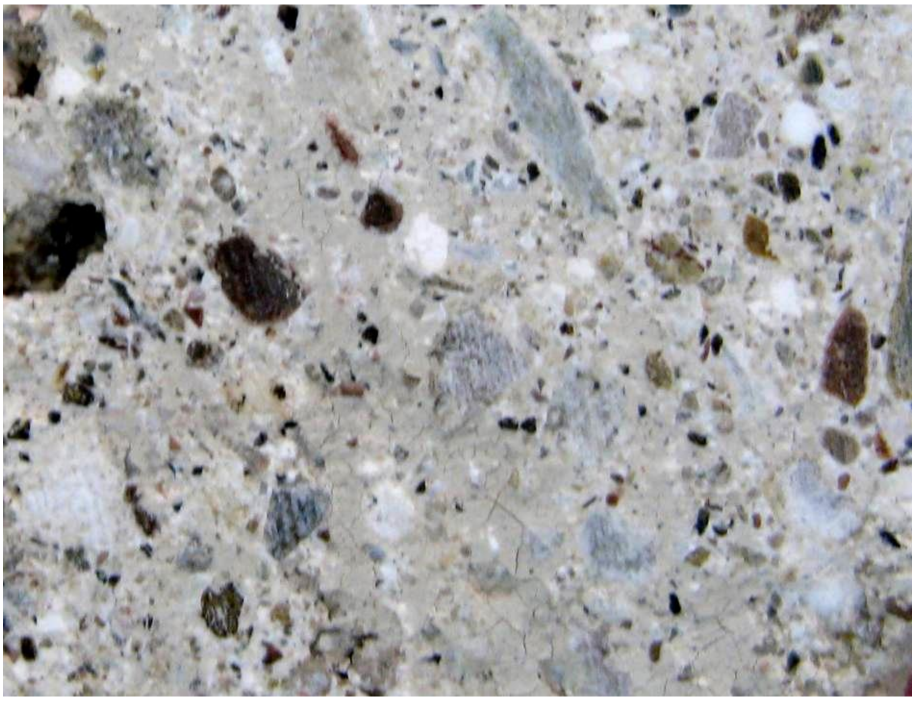
I.FOT.07 – Agios Achillios 7

Light gray colored mortar with very cohesive microstructure, rich in binder and aggregates of maximum size of 1,0-2,0cm. Small presence of lime lumps is observed. Binder has a greenish gray hue and small presence of macro porosity. SEM examination suggests hydraulic character with considerable amount of silicoaluminate admixtures.







Strong presence of multi colored aggregates inside the cohesive structure of the mortar.

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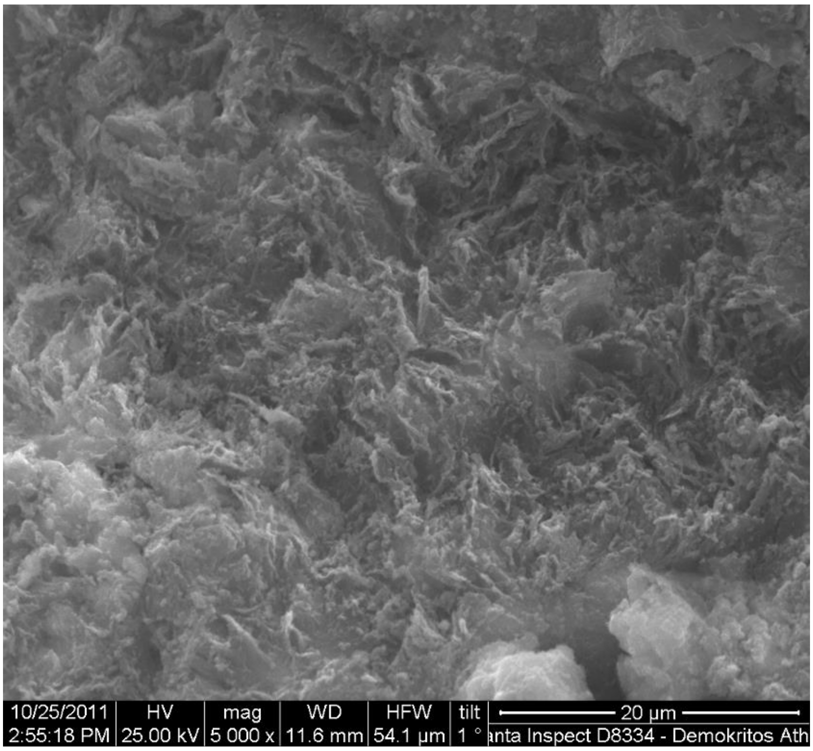

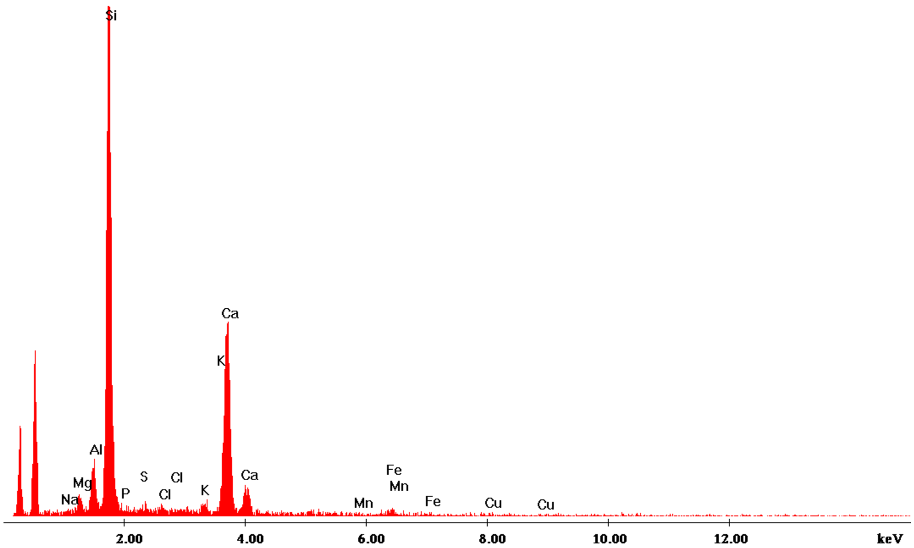

Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): Hydraulic binder and strong presence of aluminisilicate admixtures.

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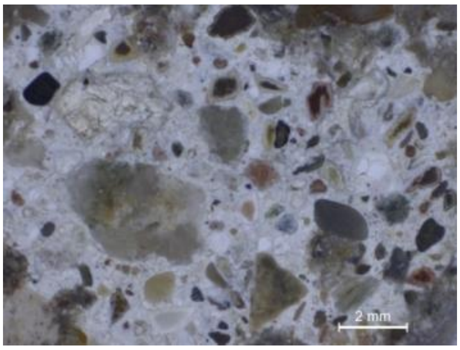
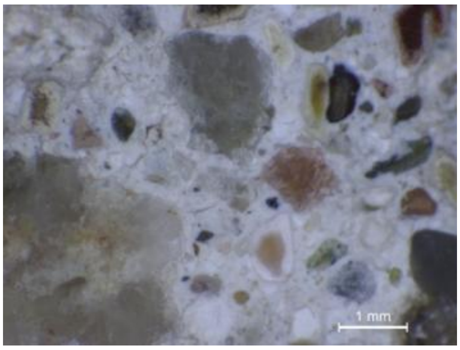
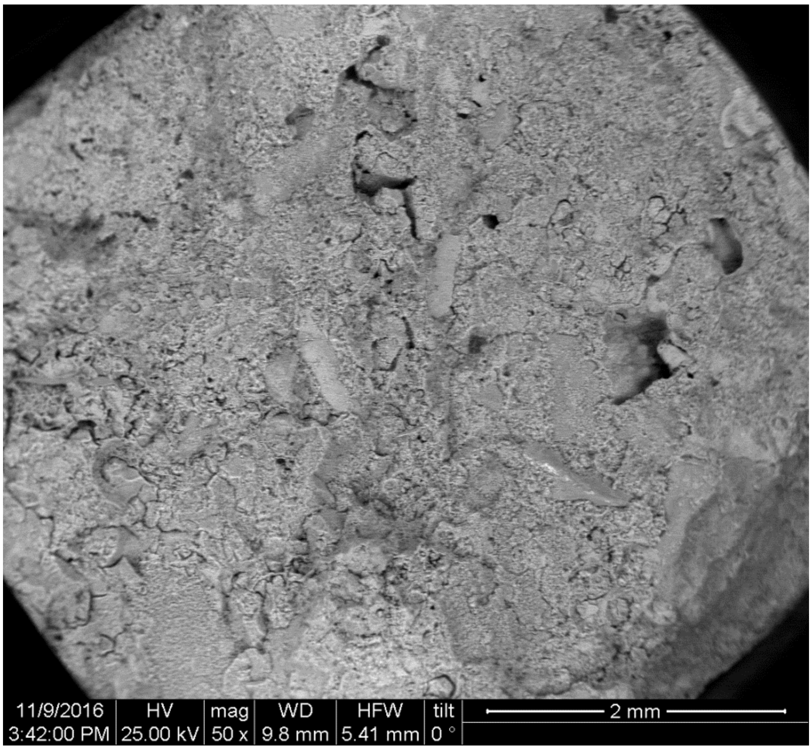
I.FOT.08 – Agios Achillios 8

Light gray colored mortar with very cohesive microstructure, rich in binder and aggregates of maximum size of 1,0-2,0cm. Small presence of lime lumps is observed. Binder has a greenish gray hue and small presence of macro porosity. SEM examination suggests hydraulic character with considerable amount of silicoaluminate admixtures.







Very cohesive microstructure

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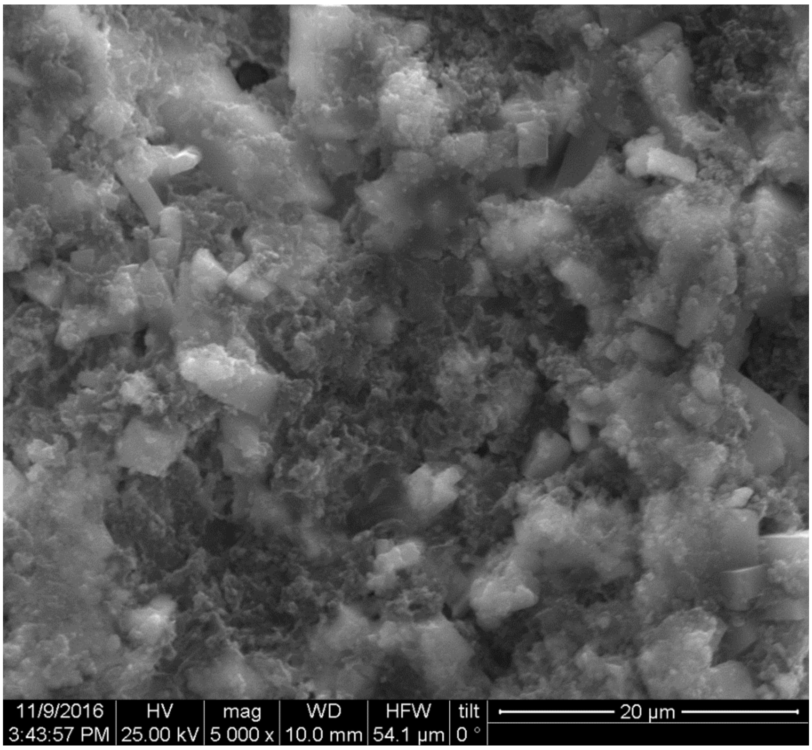

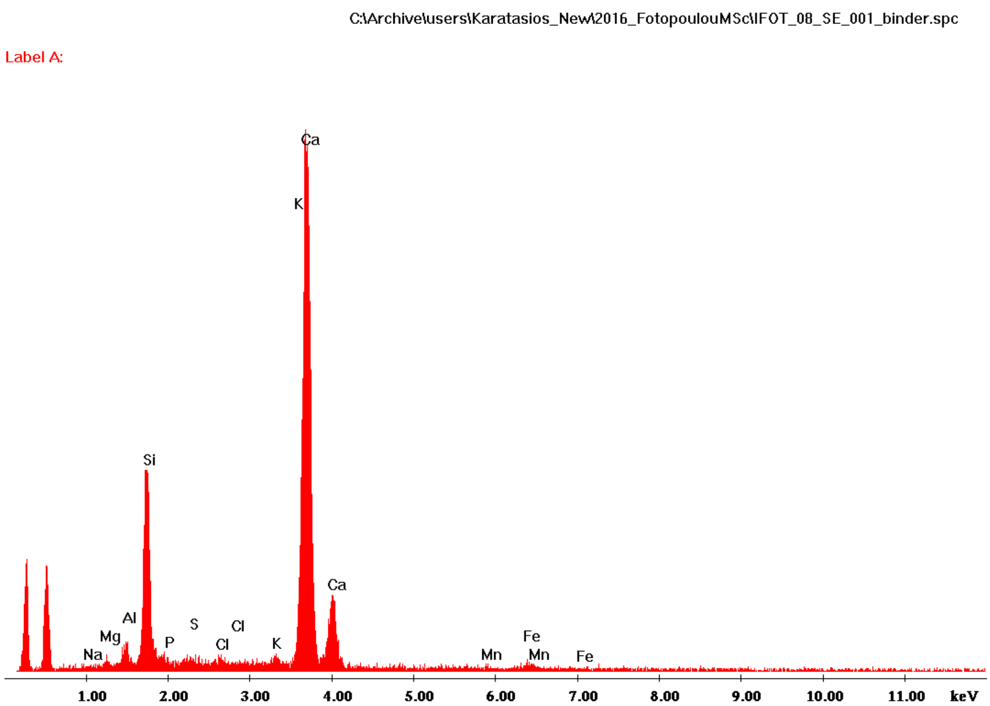

Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): Hydraulc character of the binder.

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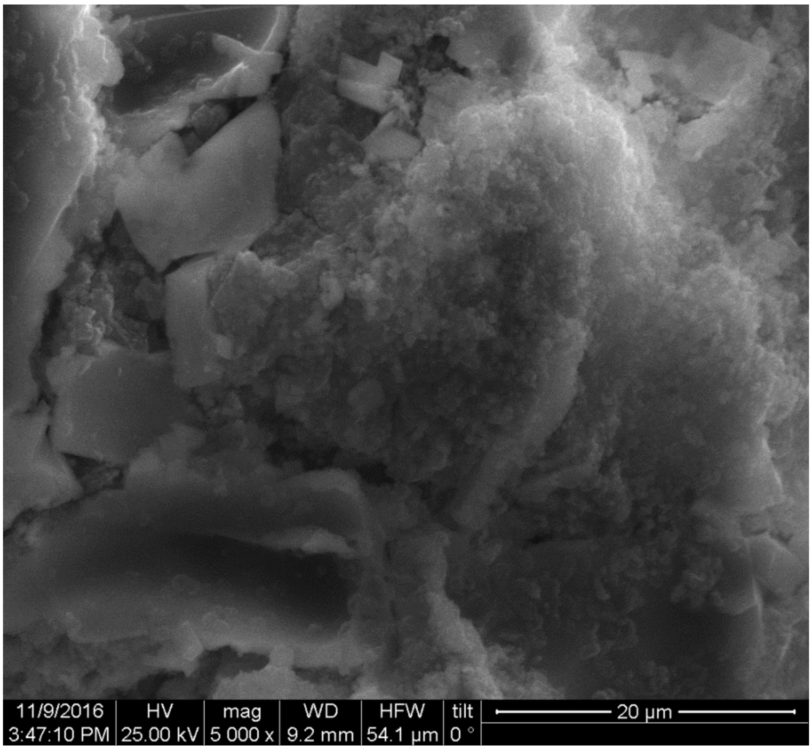

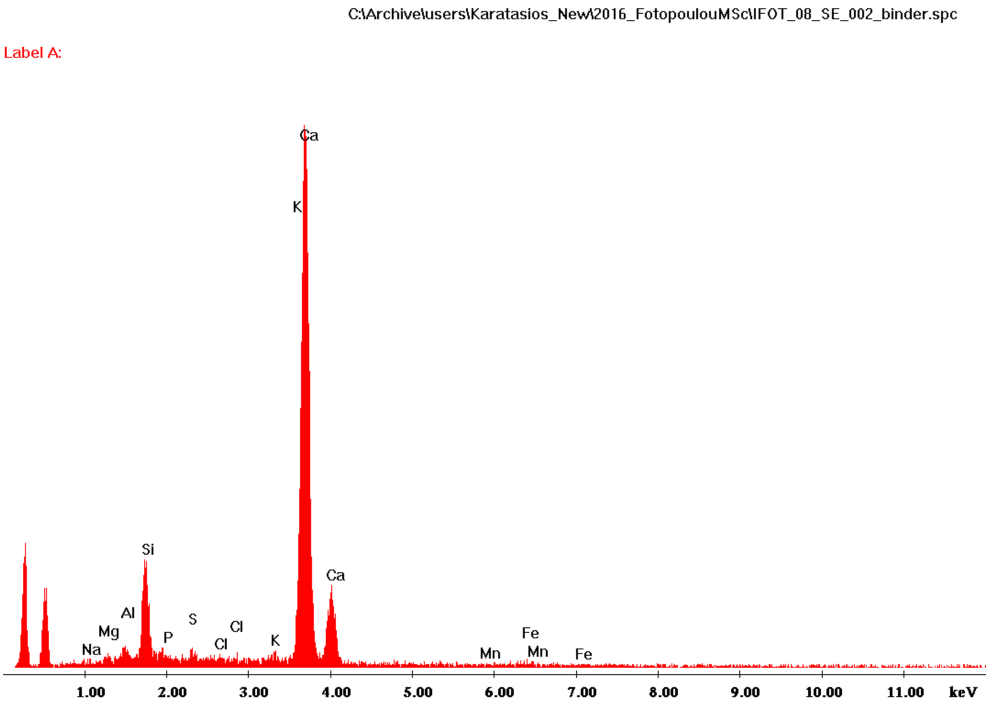

Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): Hydraulic character of the binder (the same with previous page).

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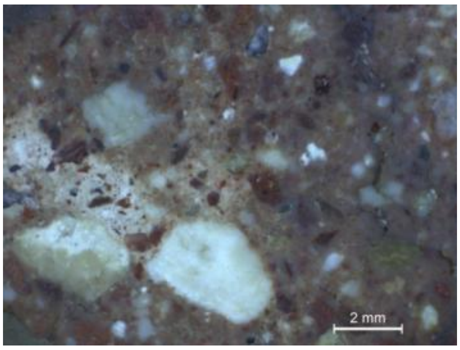
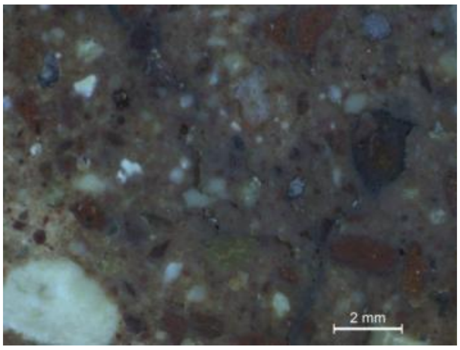
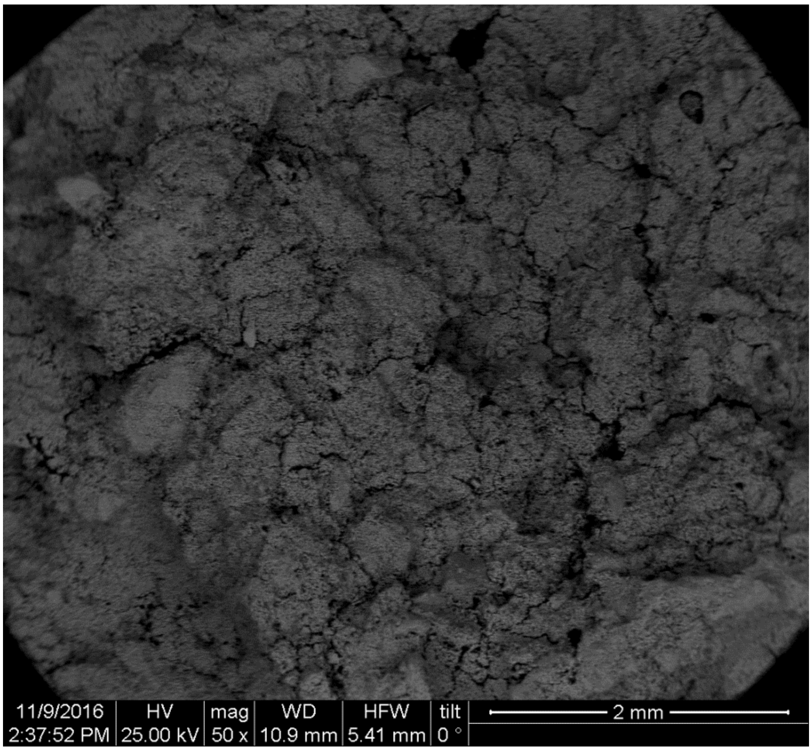
I.FOT.09 – Palaion Castle, Volos 3

Lime mortar with graded ceramics, containing almost exclusively ceramics as aggregates. It is very cohesive, with small percentage of macroporosity.Maximum grain size: 1,00-1.50cm. Several lime lumps are recognized. SEM examination suggests an almost non hydraulic character.







Also very cohesive sample, minor fractures.

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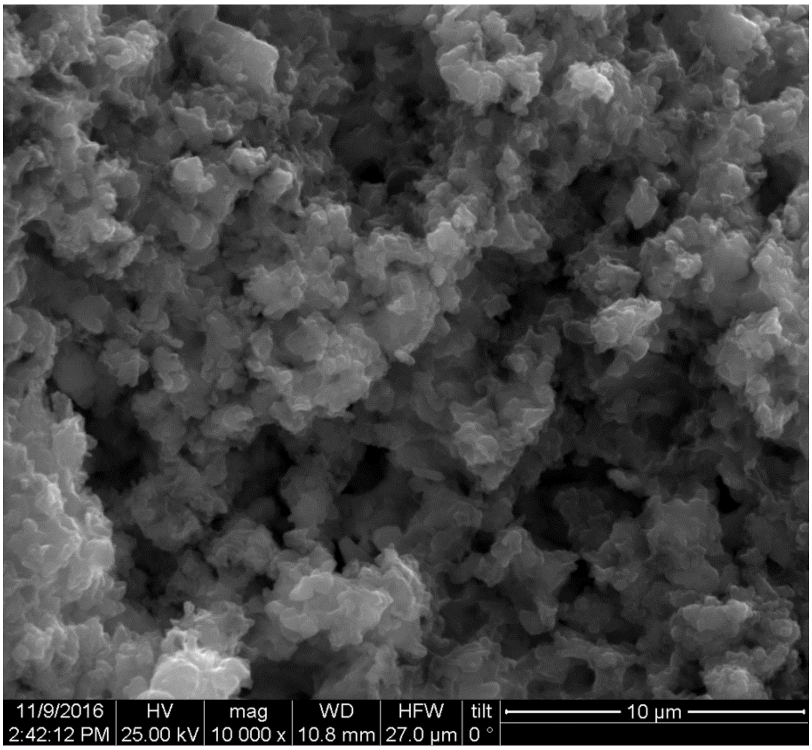

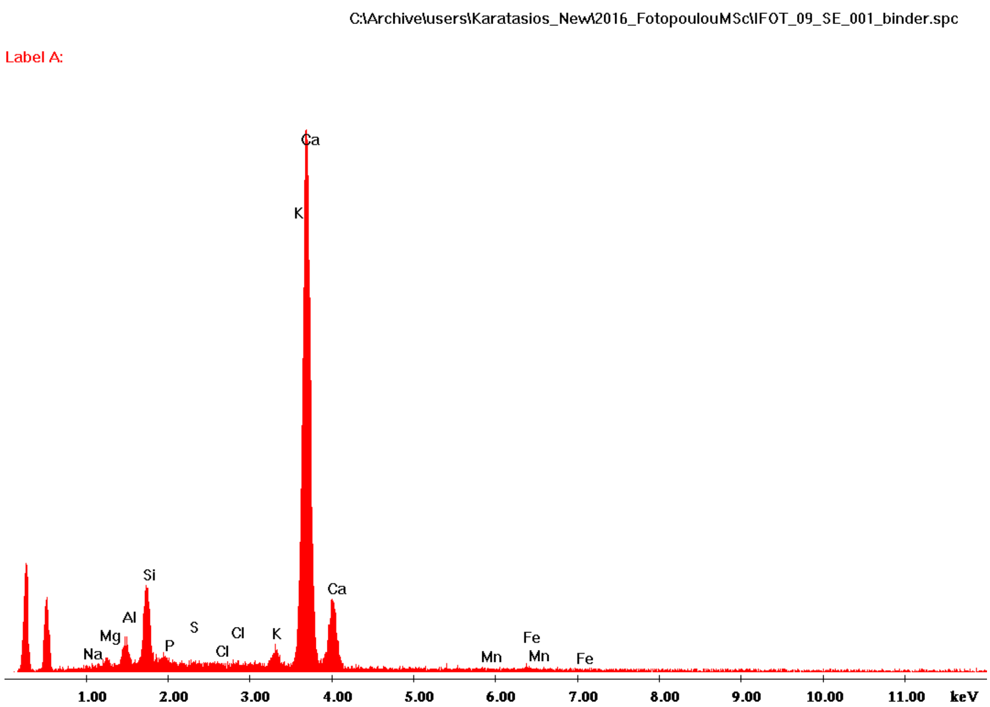

Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): Non hydraulic binder.

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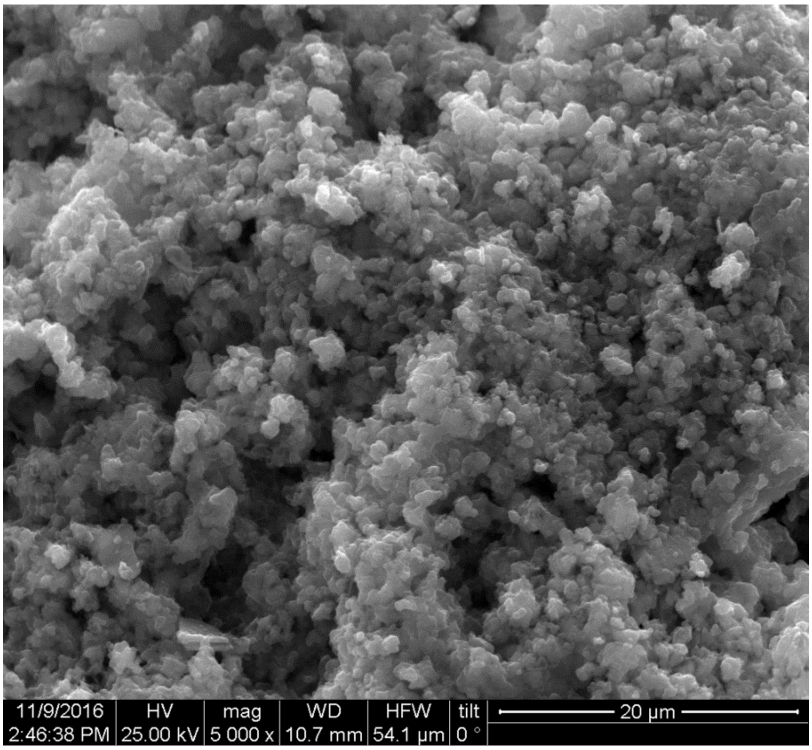

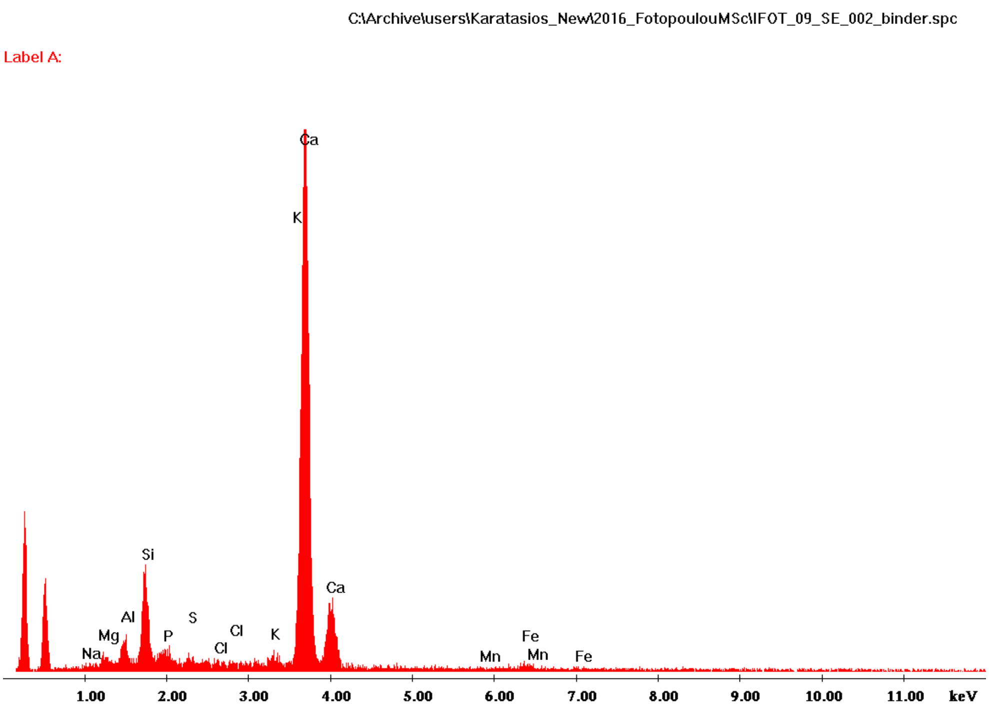

Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): Non hydraulic binder, small percentage of aluminosilicates.

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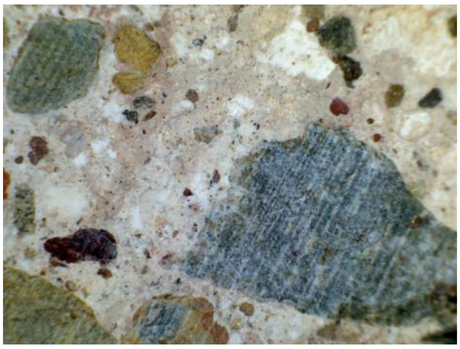
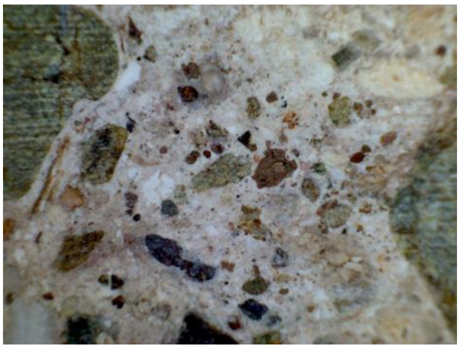
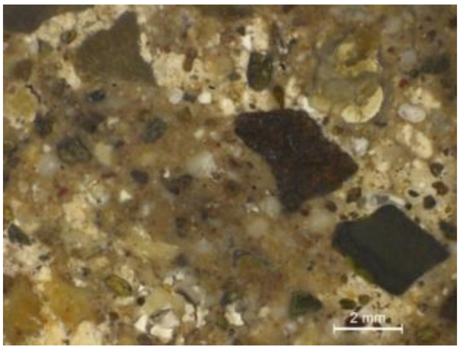
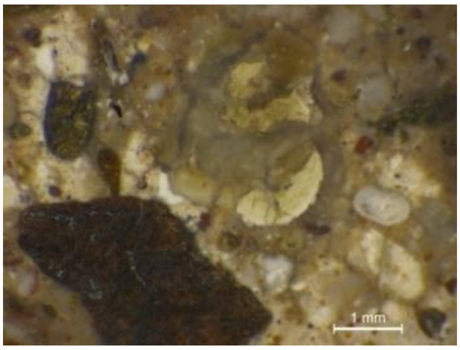
I.FOT.10 – Farsala 4

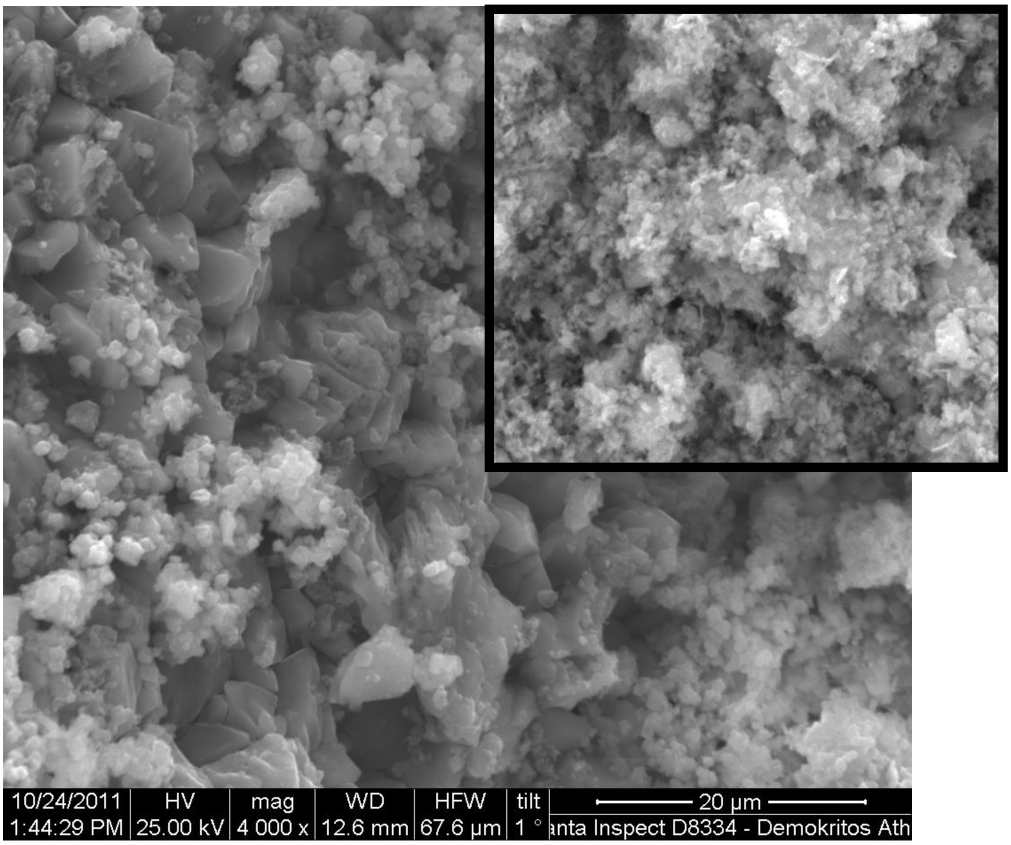
Light colored mortar, with very cohesive structure and small macro porosity.
Maximum grain size between 1-1,5cm (very few up to 3-4cm. Lime lumps are recognized and light colored ceramics. SEM examination suggests a mixed but feeble hydraulic character with small presence of aluminosilicate phases.

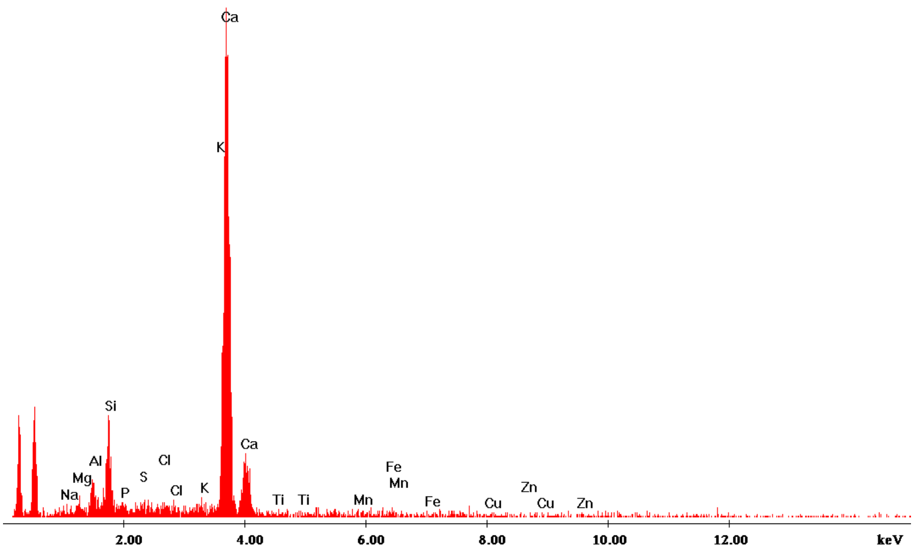







Intense presence of dark colored aggregates in the microstructure.
Also small brown-red spots that could indicate the presence of ceramic powder.

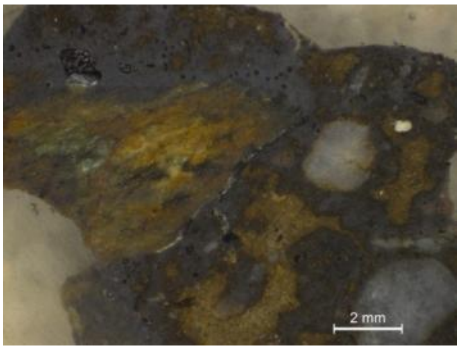


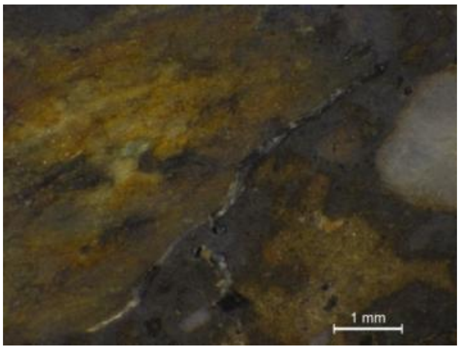


Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): Mixed binder character / small percentage of hydraulic phases / considerable amount of aluminosilicate admixtures.

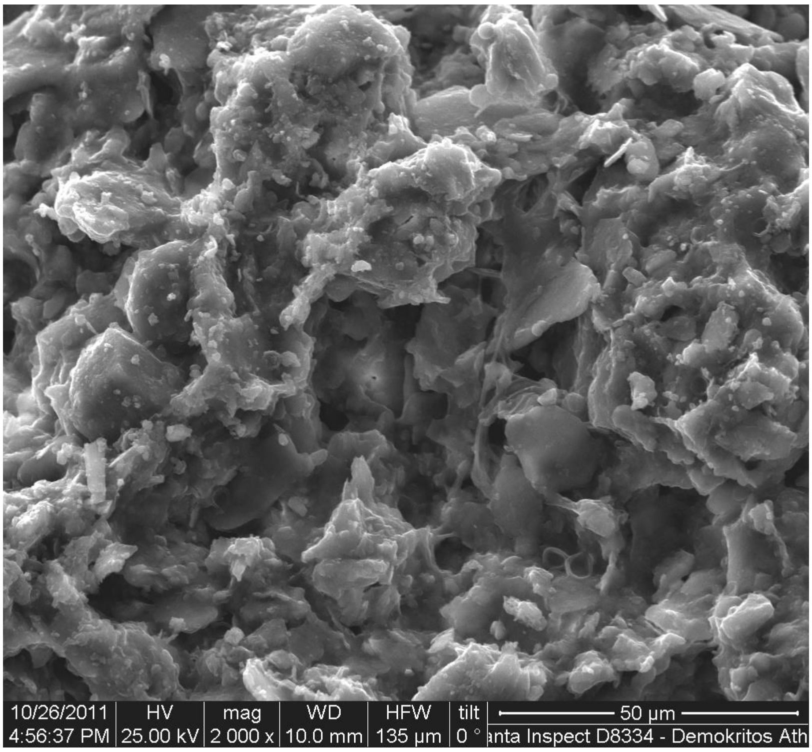
I.FOT.11 – Pythio 2

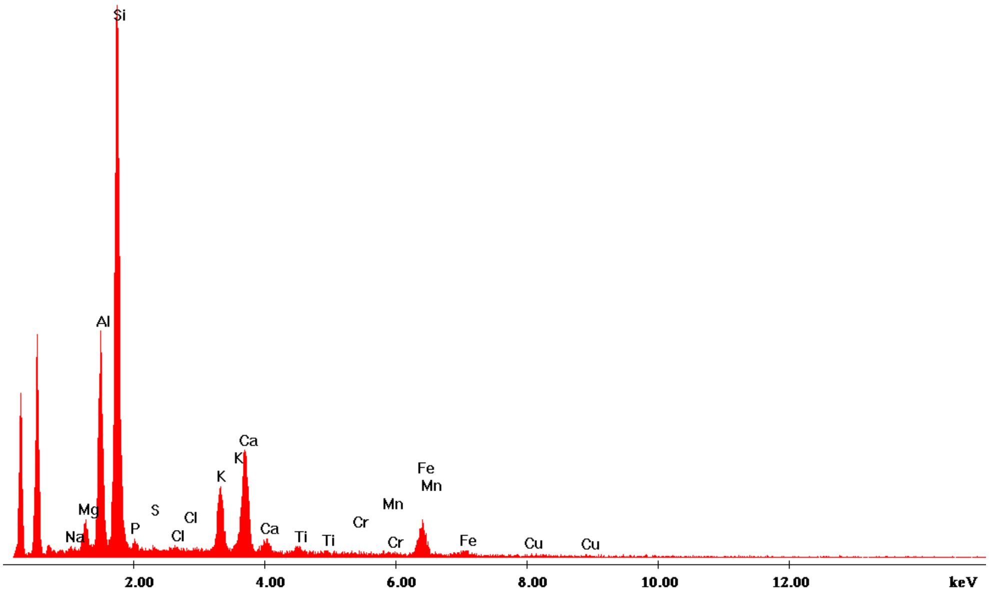
Brown clay mortar with angular aggregates (limstones and aluminosilicates). Maximum grain size of 1,0-1,5cm. Mortar has medium to very light consistency and no evident presence of lime. SEM examination suggests a loose structure of binder containing clay. No systematic use of organic or plant fibers.





Loose mortar microstructure is observed along with the presence of natural aggregates and a lot of discontinuities and macro porosity.
The result of the latter is the almost fully resin saturated samples observed in the last two pictures (samples prepared for SEM examination).





Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): Loose structure of Ca containing clay without the addition of lime.

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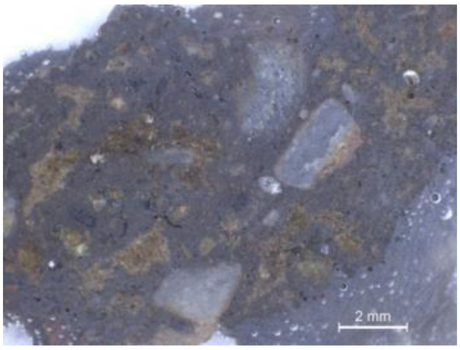
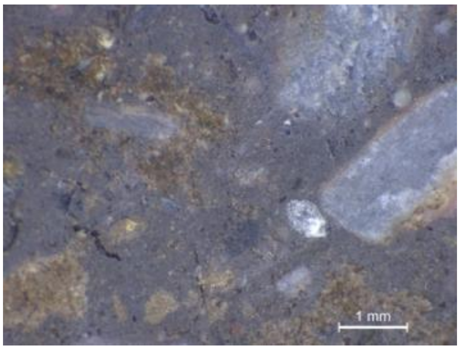
I.FOT.12 - Pythio 7

Brown colored clay mortar with angular aggregates and considerable aluminosilicates as aggregates. Maximum grain size 1,2 -2,0cm, but also with considerable amount of breccia of 3 -4cm minimum size. It has very small coherence. No presence of lime is recognized. SEM examination suggests a loose structure of Ca containing clay. No systematic use of plant or organic fibers is observed.





In above stereoscope pictures the loose microstructure can be observed along with natural aggregates and presence of micro cracking. In the last two pictures saturation of resin is also evident.

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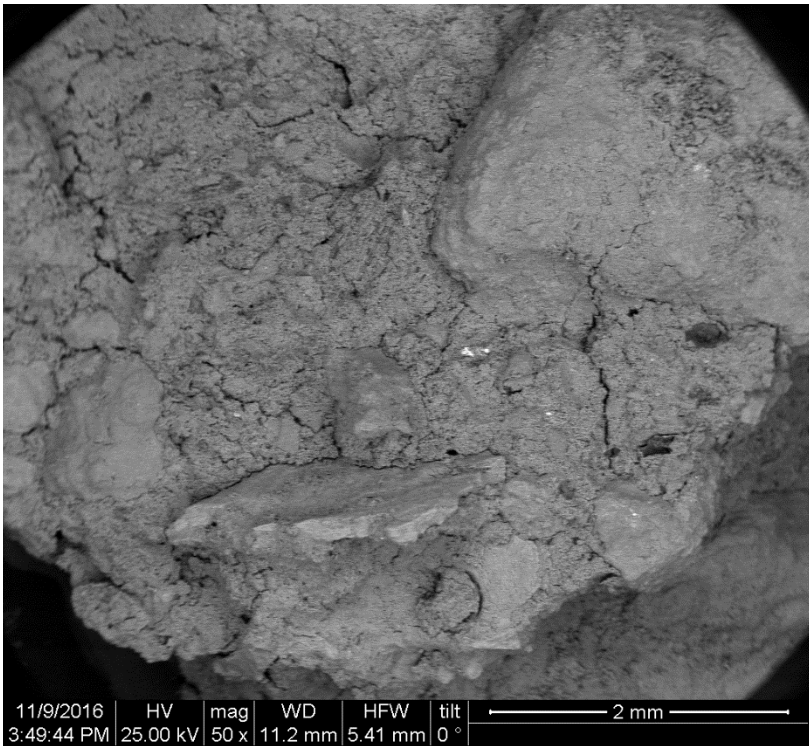

The light clay matrix

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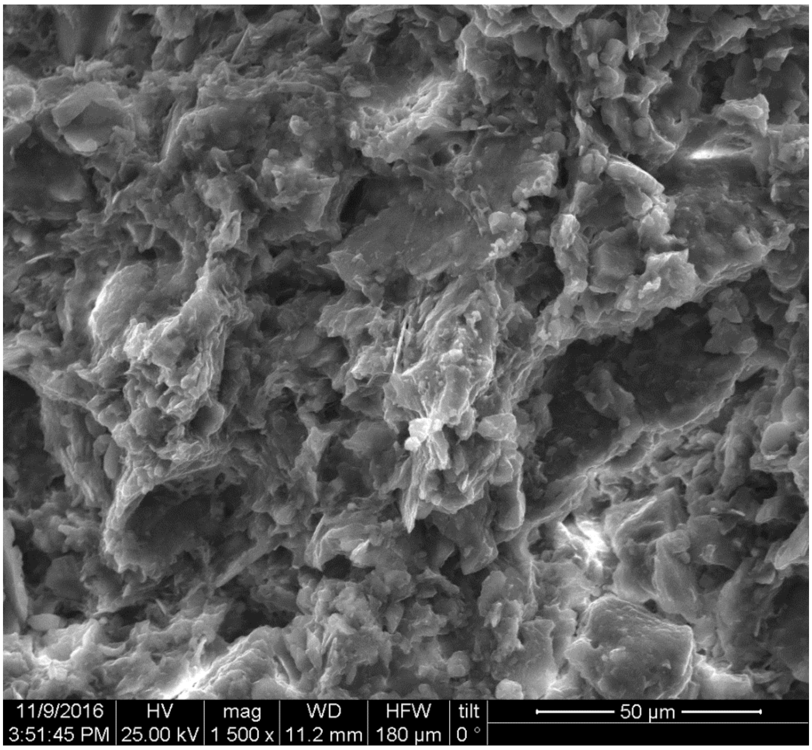
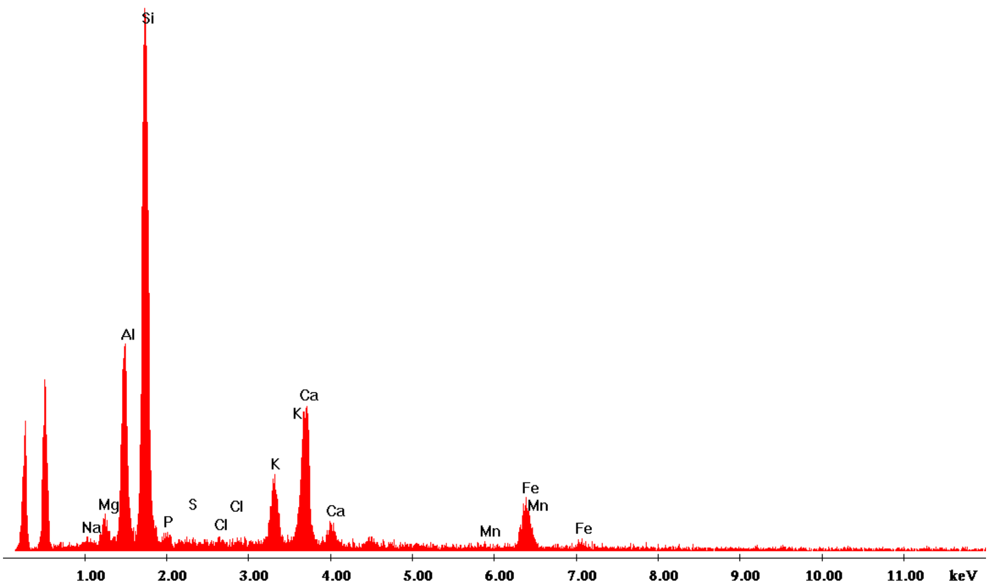


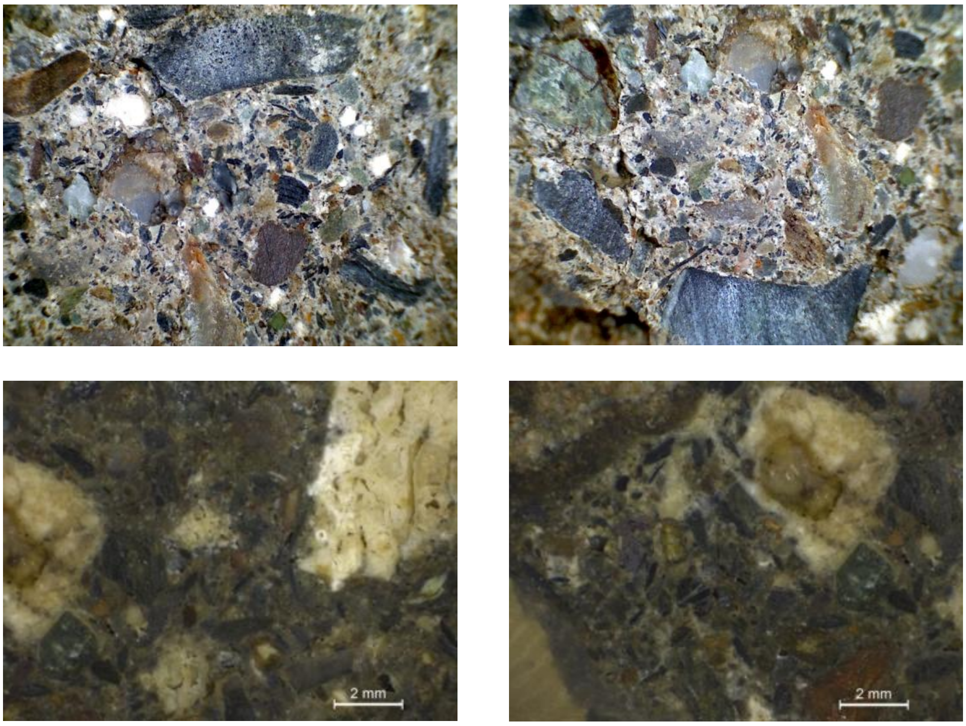
C:\Archive\users\Karatasios_New\2016_FotopoulouMSc\IFOT_12_SE_001_binder.spc

Label A:



Binder microstructure (1st picture) and corresponding SEM/EDX analysis (2nd): Loose microstructure, typical of raw clay. Presence of binder, such as lime, is not recognizable.

I.FOT.13 – Agia Larisas 2



Mortar microstructure in stereoscope (1st raw): Loose microstructure with dense aggregate network and small fissures. In second raw SEM samples are saturated in resin.

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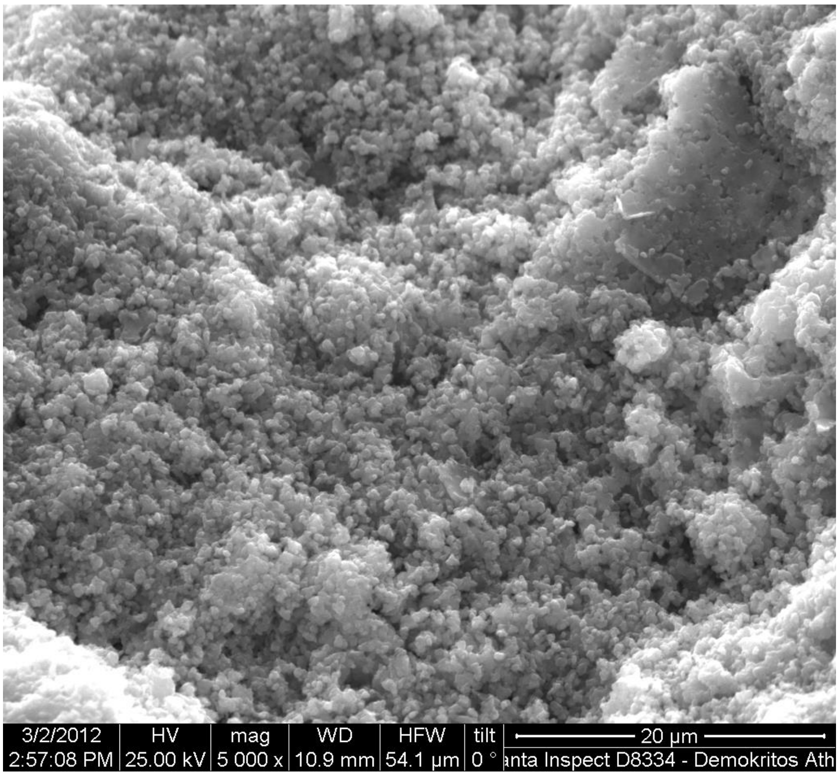

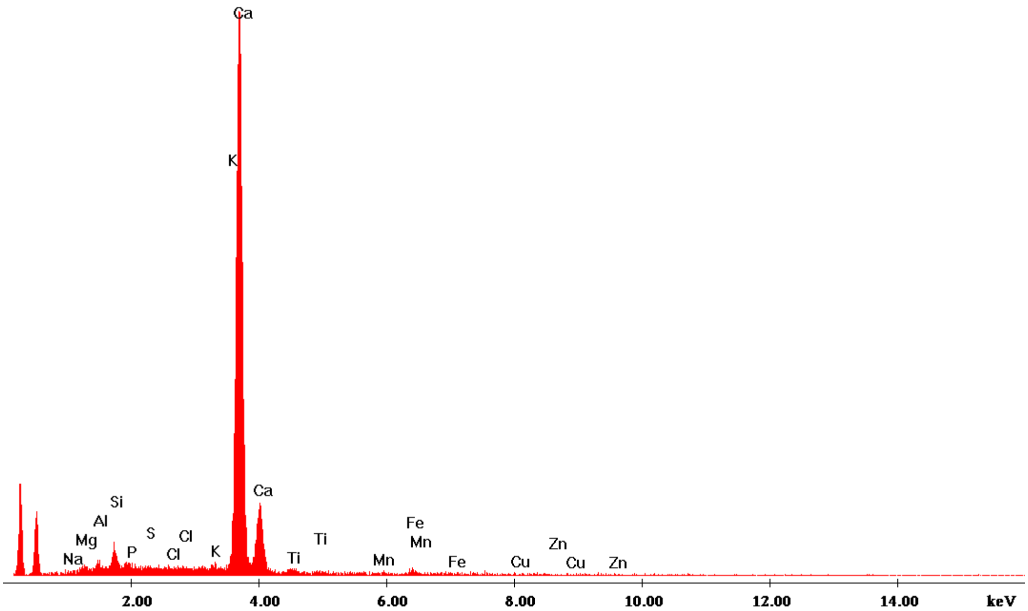

Binder microstructure (1st picture) and corresponding SEM/EDX analysis suggests non hydraulic character.

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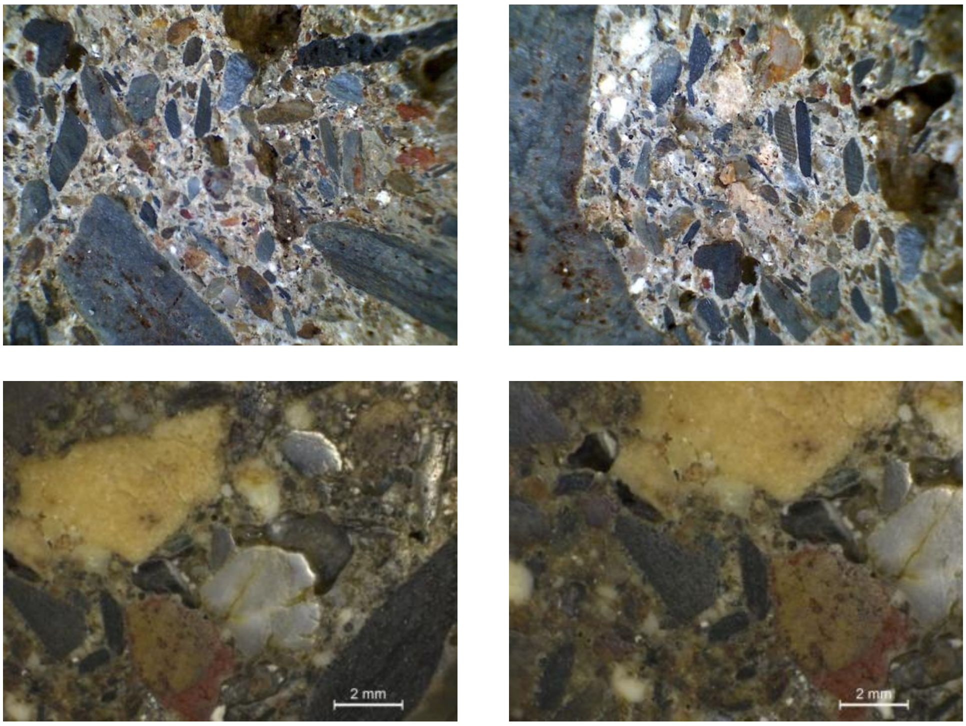
I.FOT.14 – Agia Larisas 9



Mortar microstructure in stereoscope:

1st raw: Relatively cohesive microstructure with macro porosity and small lime lumps.

2nd raw: SEM Samples fully saturated in resin. Intense relief.

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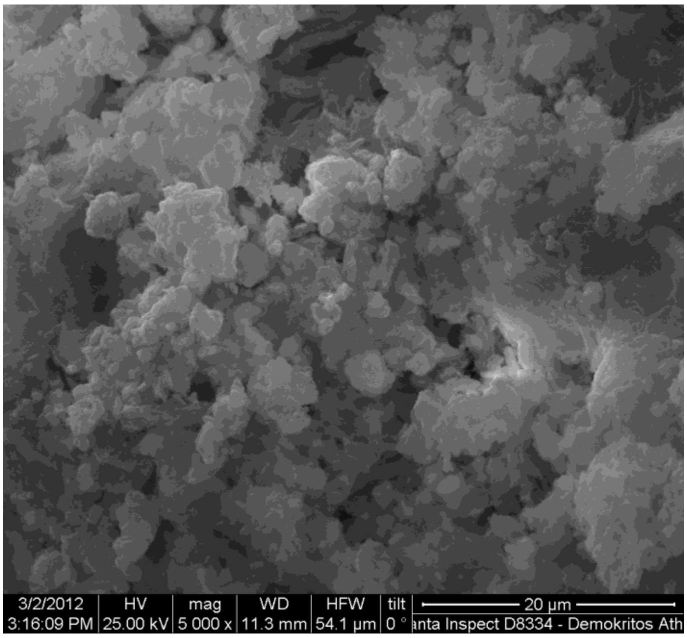

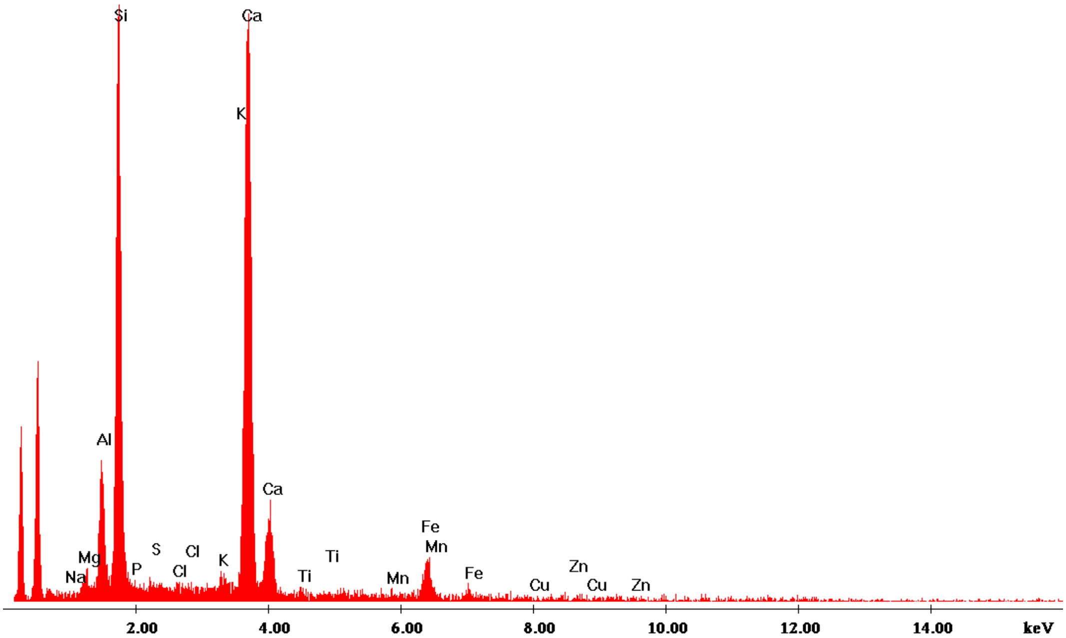

Binder microstructure (1st picture) and corresponding SEM/EDX analysis suggests non hydraulic character and significant amount of aluminosilicate admixtures.

6 Discussion

Based on the analytical results presented in the previous chapters the mortars can be grouped firstly according to binder:

1. Clay mortars (no11/Pythio2 and no12/Pythio7)
2. Lime mortars

Lime mortars can further be grouped in those containing powder ceramics (no2/Ag.Achillios2 and no4/Ag.Achillios4)[1]

Another distinction can be made according to aggregates:

1. Containing ceramics exclusively (no4/Ag.Achillios 4 and no9/Palaion Castle,Volos3) or along with natural aggregates (no2/Ag.Achillios2 and no 10/Farsala4)
2. Containing shale as aggregates (no13/Agia Larisas2 and no14/Agia Larisas9)
3. Containing dark elongated grains. This category includes the previous two mortars and no10/Farsla4
4. The rest lime mortars, all belonging to the monument of Agios Achillios that contain mostly light colored natural aggregates, besides:
5. Sample no1/Agios Achillios1 presents distinctive differences (absence of lime lumps, bright white color in stereoscope, high percentage in fine white aggregates, high percentage of binder and very low compressive strength[2]).

[1] There are other two mortars containing ceramics (no9/Palaion Castle, Volos3 and no10/Farsala4) but in those cases ceramics are not fine grained and mostly considered as aggregates only. Low hydraulicity and the absence of hydraulicity confirms it.
[2] It is at the same level as clay mortars

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All above differences can indicate chronological and technological differences (e.g. presence of ceramics / absence of lime lumps) as discussed in chapter 1.1.

The differences between aggregates have already been illustrated. One observation remains, that of the presence of rounded aggregates, especially in sizes that can be described as breccias (no12/Pythio7)

The main differences between binder microstructure are presented between clay (low and very low cohesive / loose microstructure) and lime mortars[3]. On the other hand, cracks and fissures are more evident on lime mortars.

The differences on porosity are generally small with the exception of samples no9/Palaion Castle, Volos 3 (around 40%) and no4/Agios Achillios 4 (around 50%), that is the two samples that contain ceramics as aggregates.

Mortars of the same monument exhibited similar characteristics in terms of binder (Pythio / clay mortars) and aggregates (Agia Larisas / shale). Most differences can be distinguished to the monument of Agios Achillios due to the large number of samples compared to other monuments (8 samples).

[3] They are more cohesive and have been described in four gradations: very cohesive, medium/strong, cohesive, medium/low cohesive.

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7 Conclusions

The first categorization after examining samples under a stereoscope, proved very satisfactory, giving information on almost all main differences between the main types of mortars. Besides pointing out extreme differences in binder (the clay mortas), gave a adequate distinction between aggregates and made possible the distintion between different construction techniques and phases.

Most other analytical methods used, just proved this preliminary categorization (eg porosity, grain size distribution etc)

The most illuminating technique of all proved to be SEM giving not only quality but, with EDX also qualitative results. It illustrated differences in binder and structures easily.

XRD analysis in the other hand, gave evidence of mistqakes in mortar characterization.

The potential of hand-handled pXRF on the study of mortars did not give promising or easy results during this study. It just gave a first evaluation of the problems encountered.
The comparison between traditional chemical analysis and pXRF, for instance could have given different potentials.
One should consider making the first steps through known samples, not with historical ones. For example, binder – aggregate ratio, an essential factor for evaluating XRF measurements in hardened mortars proved difficult to

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estimate. Even with samples of known consistency and binder – aggregate ratio, XRF surface mortar measurements could have been difficult to process.

Field measurements, heaving to deal with erosion and decay of surface layers, are another issue.

Nevertheless, the potential of such a use make the decision easy. It should be further studied.

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