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**DIPLOMA THESIS:**

«The Niokastro of Pylos: Conditions Survey through Microscopy,  
Imaging and Computing Technologies»

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The topic selection (The Niokastro of Pylos: Conditions Survey through Microscopy, Imaging and Computing Technologies) aroused from my need to accomplish in practice ones that I was taught from the curriculum in relation with the possibilities and knowledge provided via the analytical techniques on the manufacture, characterization and provenance of ancient and historical materials, in combination with the benefits offered from new technologies through computer programs for the management and visualization of the outcomes. The survey on the Niokastro of Pylos was conducted in cooperation with the Ephorate of Antiquities of Messinia.

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## Abstract

In the present study, structural condition survey of the castle of Pylos, (Niokastro castle), a historical monument dated in 15<sup>th</sup> century conducted. Stone and mortar samples from the masonries of the monument have been analyzed for the identification of their preservation state, physic-chemical characteristics, their manufacture techniques, and their provenance via microscopy, imaging techniques with the application of new technology computing program (ArcGIS).

Fifteen historical mortar and sixteen building stones samples were collected from eight regions of the monument (perimetrical). The specimens include mortars from different construction phases of the monument. Optical microscopy (LED), grain size distribution analysis (in mortar samples), Scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDS), X-ray diffraction (XRD) technique, were performed in castle's stone and mortar samples. In order to examine the provenance of the construction materials of the monument, samples PLs, Ptk, KsKd originated from Pylos, examined by SEM/EDS and XRD analysis.

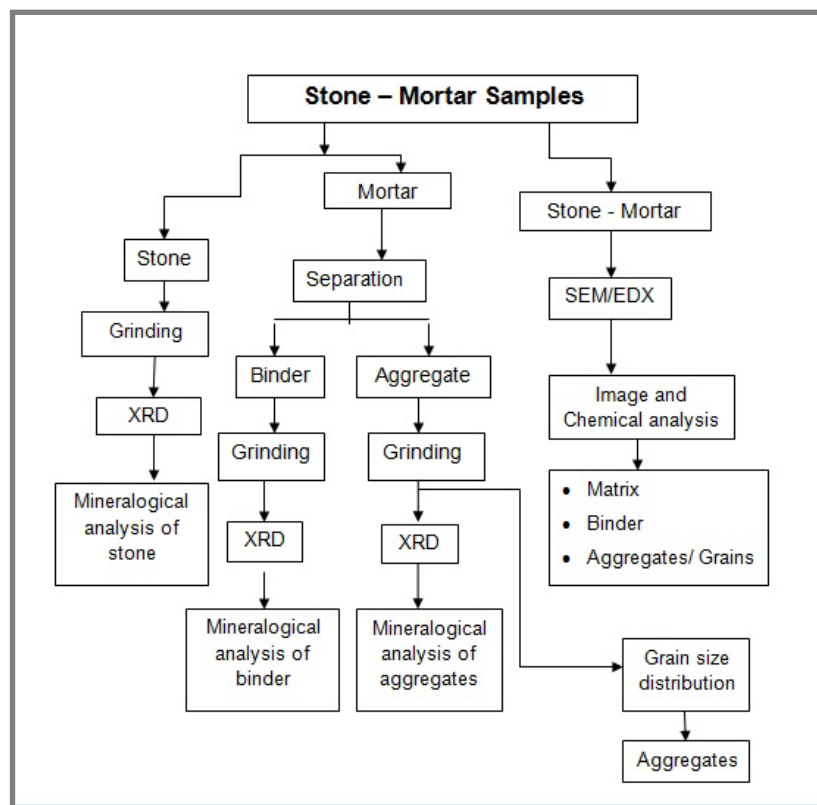
The obtained data reveal that the castle is mainly made of two types of local stones the gray limestone and the yellow sandstone. Between the two types of stones sandstones introduced in a more eroded state than lime-stones. Historical mortar samples are classified in five categories according their application (structural, structural for sandstone blocks, forehead-structural, renderings, and structural reconstruction mortars). Mortar samples that appear more contaminated are from the areas of initial gate of the monument, the western wall, the reconstruction mortars and these that belong to the external sides of the monument.

Calcite is the most abundant mineral in the stone and mortar samples, was identified by XRD. Sulfur oxides presented in elemental composition mainly of mortar samples is due to dry and wet deposition of atmospheric SO<sub>2</sub> and aerosol. Its reaction with the calcium carbonate constituting the binding component of the lime mortar, leads to the formation of gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O), as confirmed by the XRD data.

The microscopic, mineralogical, chemical and physical data, collected on the bulk mortar and their binder material show the constant use of a high-quality lime. From the grain size distribution analysis, the binder aggregate ratio (B/Ag) was identified,

range from 1/2 to 1/3. The most conspicuous differences between mortar samples lie in the aggregate content, that have similar mineralogical composition, but the granulometry is different, depending on the mortar function in the monument and the construction phase to which they belong. The coarser aggregates with grains up to 1.960mm have mostly siliceous composition and the finer grains are of calcareous composition both derive from local origins.

Three thematic maps via computer mapping software (ArcGIS) to emerge the process and the outcomes of the research were created. The implementation of GIS achieves the goal, where a document remains usable and useful after its initial creation. Datasets used should meet four criteria: (1) that the dataset remain accessible by more than one person (2) that it can integrate with other types of data (3) that it is easily updated with future research, and (4) that it results in the creation of accompanying documentation.



**Figure 1: Flowchart illustrate a scheme for the chemical and mineralogical characterization of historical stone and mortar samples from the castle of Pylos, Niokastro, Messenia.**

## Introduction

In the Niokastro, the castle of Pylos (Ottoman period), a coastal monument, a continuous sequence of constructions, interventions and adaptations of existing buildings to different uses is readable on architectural surfaces. Niokastro is an important monument from both historical and technological points of view, especially regarding the comparison between construction materials employed in the original structure and in the following centuries.

Ottoman period followed the traditional techniques and construction materials depend on locally available raw materials. In this period was usually used pure lime, although the quality of materials and constructions distinguished by a trivial character (Papayianni, 1997)(Papayianni & Stefanidou, 1997).

Over the last decades, there has been an increased interest in the preservation of valuable ancient and historical monuments, which tend to deteriorate both naturally and due to anthropogenic vandalism. The deterioration of a coastal stone monument is often due to a combination of many factors, including: mechanical wave erosion, daily wet-dry tidal cycling, salt weathering, bio-corrosion and other biological influences, frost and related mechanism and alterations.

The historical masonry is, a composite system whose durability is related both to the nature of the single constituents and to the particular interaction between mortar and stone. In order to find a suitable compatible material with the old one, it is necessary to know the exact chemistry, mineralogical composition and technology but also the deterioration processes of the original material. The employment of interdisciplinary approaches like chemical, geological and physical analytical techniques in the study of historical buildings is a common practice (Panda, et al., 2013). While, managing of archaeological scientific data with geographical information systems (GIS) is rarely addressed in archaeological literature. The usage of such structure, permits researchers to create datasets that are accessible, integrative, updatable, and documentable.

# I. THEORETICAL PART

## 1. Niokastro (Castle of Pylos)

The word castle<sup>1</sup> comes from the Latin *castrum* used by the Romans to describe any kind of military installation and camps.

In Messenia, Peloponnese, Greece, the fortress of Niokastro or New Navarino (Greek: Νέο Ναυαρίνο, Turkish: Anavarin-I cedid) is built on a small hill above Pylos and is considered, along with Palaiokastro or Palaio Navarino (a 13<sup>th</sup> century Frankish fortress on the hill of Koryfasio), the guard of the passage of the natural port of Pylos (Καρποδίνη & Δημητριάδη, 1990/1993). Niokastro is an Ottoman fortification. Ottoman Turks kept it under their control for almost three centuries with small exceptions (Davis, 2008)(Andrews, 1953/1978). Niokastro constituted a new fortified city, built at the entrance of the largest natural harbor in Western Peloponnese (Papathanasopoulos & Papathanasopoulos, 2000)(Bennet, et al., 2005). The great strategic importance of the fortress for the control of the passage in the entrance of Navarino led to numerous occupations of the area by various major powers during the centuries. The history of the monument formed through the centuries in relation to the conquests that took place at the monument imprinted in the *table 1* below: Nowadays the castle is a significant Archaeological site of cultural heritage open in public that hosts important museums exhibitions and renovated monuments.

**Table 1: Historical periods and important facts of Niokastro, castle of Pylos.**

<b>Period of conquest</b>	<b>Historical Fact</b>
<b>1573 - 1686:</b> 1 <sup>st</sup> Ottoman	Inhabitation of Turkish population (Wolpert, 2005)
<b>1686 – 1715:</b> 2 <sup>nd</sup> Venetian (Morosini)	Niokastro is the capital of Messinia (Papathanasopoulos & Papathanasopoulos, 2000)
<b>1715-1821:</b> 2 <sup>nd</sup> Turkish	Inhabitation by the expelled Turks, and repair of the fortifications (Kontogiannis N. D., 2012)

<sup>1</sup>Castle: walls that fortified village, town or place that had strategic importance (*Dictionary Manolis Triantafyllides*)

<b>1770:</b> Russians (Orloff)	Explosion of the ammunition stores and the fortification (Bees & Savvides, 1993)
<b>1821-1827:</b> Greeks	Liberation (Bakalopoulos, 1975β)
<b>1827-1828:</b> Ottoman/Egyptian (Ibrahim Pasha)	Naval battle of Navarino (Nikolaou, 2007)
<b>1828-1829:</b> French (Maison)	Rebuild and restore the castle (Davis, 2008)
<b>1829-1842:</b> French	Military base ( <i>Grigoropoulou &amp; Sakkari, 2008</i> )
<b>1841-1938</b>	Use as a prison ( <i>Papathanasopoulos &amp; Papathanasopoulos, 2000</i> )
<b>1939-1945</b>	Second World War (Italian and German armies) ( <i>Grigoropoulou &amp; Sakkari, 2008</i> )
<b>1947-1949</b>	Use as a prison (Papathanasopoulos & Papathanasopoulos, 2000)

## 1.1 Architecture of Niokastro

Niokastro was built in an era when the invention of gunpowder (14<sup>th</sup> c.) and the ensuing spread of firearms (second half of the 15<sup>th</sup> c.), played a catalytic effect on the layout, form, design and construction of defense works. The new type of fortresses had to respond to the new methods of waging war and new fortification technology, the ideal principles for the design of fortresses based on the bastion system (fronte bastionato) (Georgopoulou, 2008).

Only little is known about the initial phase of construction of Niokastro, during the 1<sup>st</sup> Turkish rule period (1460/1500 - 1685). According to the Ottoman traveler Evliya Celebi (1668-1671), Niokastro at this time consisted of the outer citadel, that is, the settlement within the fortress walls, and the inner citadel, what is known today as the acropolis (Celebi, 1994).

Niokastro covers circa 70,000 sq. m, it consists of a large enclosure containing the settlement and linked to a second, smaller enclosure, the citadel, which was strongly defended and reinforced by a moat, and a glacis (sloping embankment). Masonries built of rubble, bricks and tiles and a strong mortar compounded of lime. The gates,

the corners of the buildings, the frames and all the decorative parts of the fortress, are made mainly of squared blocks of porous stones. K. Adrews mentioned that the Niokastro is characterized of homogeneity in the way of building and in the structural materials have been used (Savvidis, 1991).

The fortress has two entrances. The original entrance to the settlement was at the northeastern corner of the fortress, known as the “Zematistra Gate”. It was a portal consisting of a system of three successive gates and is protected by an adjacent semicircular tower. Today only the first gate preserves its wooden door and its iron dressing (Grigoropoulou & Sakkari, 2008). The modern entrance to the fortress from the Pylos side is in the middle of the north wall of the enclosure and consists of an apsidal gateway in which successive building phases can clearly be seen. It is made of porous stone masonry mounted by a semicircular arch (Grigoropoulou & Sakkari, 2008).

The hexagonal citadel at the highest point of the fortress is entered by a monumental gateway on its west side. The gate is a structure of porous stone the exterior of the gate is surrounded by a rectangular frame, which probably dates to the second period of Venetian rule (Kontogiannis, 2001). The citadel was guarded by six pentagonal bastions, at the corners, of which five survive today (Andrews, 1953/1978)(Grigoropoulou & Sakkari, 2008)(Papathanasopoulos & Papathanasopoulos, 2000).

The walls of the citadel, which are over 8 m. high and 2.50 m. thick, are tough and solid, and are surmounted by battlements with cannon emplacements and long, narrow loop holes (Papathanasopoulos & Papathanasopoulos, 2000).

The so-called Hebdomos Bastion (“Evdomos”, seventh) at the south-west corner, called Bateri de marini or Forte Santa Barba by the Venetians, is the start of the south wall of the fortress, which ends at one of the strong bastions of the citadel Santa Maria at the north-west corner (bastion III), though it does not communicate with it. Hebdomos is particularly important and powerful because its artillery batteries control the spout of the bay of Navarino, and is the oldest part of the fortress, which was operated independently and subsequently incorporated into the rest of fortification (Kontogiannis, 2001)(Papathanasopoulos & Papathanasopoulos, 2000).

In addition to the Hebdomos and the Santa Maria, there are three more bastions in the large enclosure, which are circular in plan and take the form of a truncated cone. One is near the Zematistra in the north-east of the enclosure. A second to the west,

known as the Makriyannis bastion and the third round bastion is in the south side, the “Vergas Bastion” (the wall on the south side). These bastions have hemispherical roofs built with large tiles, whereas the roofs of the bastions at the citadel moat are vaulted.

With Niokastro reinforcing the south-west edge of the Ottoman Empire in the Mediterranean, the Turks had a large, secure bay in which they could station their fleet, and a safe base for naval operations that enabled them to bring supplies from Egypt (Papathanasopoulos & Papathanasopoulos, 2000).

## 1.2 Reconstruction & Restoration Works at Niokastro

According to the Davis New Navarino or Niokastro is one of the best preserved castles in Greece (Davis, 2008). Today it is quite difficult to distinguish the different building phases of the monument. This is because of its structural complexity, of the lack of information, of the incomplete study of the monument, as well as of the large number of the disasters, the interventions and, the reconstructions, take place of the beginning of its construction during the centuries. We tried to combine and summarize the collected information in a table chronologically (*table 2*). The understanding of the different construction phases of studied monument is particularly useful as it provides information for the proper selection of the samples (mortars and stones) and is basic for the identification and documentation of the results of analyzes.

**Table 2: Construction, Reconstruction and Restoration works in Niokastro**

<b>Period</b>	<b>Construction - Reconstruction - Restoration works</b>
<b>1573 - 1686:</b> 1 <sup>st</sup> Ottoman Period	<ul style="list-style-type: none"> <li>• The original entrance to the settlement was at the northeastern corner of the fortress, known as the “Zematistra Gate”.</li> <li>• Hebdomos bastion is likely to be constructed a little earlier than the rest of the wall, however, as part of the same building phase (Andrews, 1953/1978).</li> <li>• West bastion (bastion VIII) belongs to the initial construction phase of the Castle (1573).</li> </ul>
<b>1686 - 1715:</b> 2 <sup>nd</sup> Venetian	<ul style="list-style-type: none"> <li>• The gate of the citadel probably dates to the second period of Venetian rule (Kontogiannis, 2001).</li> </ul>

<p>Period</p>	<ul style="list-style-type: none"> <li>The sixth pentagonal bastion of the citadel was destroyed by an explosion in 1686 (Andrews, 1953/1978)</li> <li>To the south and east, the citadel is defended by a moat inside of which are constructed small pentagonal earthworks situated between the bastions, the constructions are probably date to the second Venetian period (<i>Venetian map in the Grimani archive</i>) (<i>Grigoropoulou &amp; Sakkari, 2008</i>).</li> </ul>
<p><b>1715-1821:</b> 2<sup>nd</sup> Turkish Rule</p>	<ul style="list-style-type: none"> <li>Megali Verga Bastion constructed at the same period with Megali Verga Wall in the 17<sup>th</sup> century. (<i>Technical report, Construction fencing of the damaged circular bastion of Megali Verga, June 1999</i>)</li> <li>Outer fortress: the walls on the side of the gate right and left side are ruin, the bastion (tabya) above the gate, in ruin on the one side, the bastion on the left corner of the gate (L.9 x W8) and the bastion in the right corner of the gate, half ruined: (L8xW8)(Zarinebaf, 2005).</li> <li>A description of the Inner fortress: the wall next to the gate: 105 zira's of which 30 are in ruin. The bastion on the top of the gate, in ruin, two bastions attached to the left of the gate, in ruin. The bastion at the left corner of the wall in ruin (<i>Tapu Tahrir 880, 1716</i>)(Zarinebaf, 2005).</li> </ul>
<p><b>1770:</b> Russian Expeditionary force</p>	
<p><b>1821-1827:</b> Greek Revolutionaries</p>	<ul style="list-style-type: none"> <li>In the siege of 1825, the Forte Santa Barba was blown up in an explosion of the ammunition store (<i>Grigoropoulou &amp; Sakkari , 2008</i>).</li> </ul>
<p><b>1827-1828:</b> Ottoman/Egyptian forces</p>	<ul style="list-style-type: none"> <li>Entire north wall of the citadel with two bastions and the main gate depicted as corrupt. (<i>Kontogiannis, 2012</i>).</li> </ul>
<p><b>1828-1829:</b> French Occupation (Maison)</p>	<ul style="list-style-type: none"> <li>Entire north wall of the citadel with two bastions and the main gate - this part was rebuilt by the French engineer corps after 1830. (<i>Blouet, 1831</i>) (<i>Kontogiannis, 2010</i>)</li> <li>Hebdomos was the bastion that sustained most of the fire of enemy ships attempting to enter Navarino. Restoration works of the bastion from the French under General Maison.</li> </ul>

	<ul style="list-style-type: none"> <li>The citadel is shown almost in its present form, while the battle stations for firearms (batterie) appear on all points, both the city and the citadel (<i>Kontogiannis, 2010</i>).</li> </ul>
<b>1841-1948:</b> Prison	<ul style="list-style-type: none"> <li>In the Second World War the fortress was used as a base for the Italian and German armies. Many of the buildings in the settlement were used as kitchens, baths and barracks for the occupying forces</li> </ul>
<b>1941-1944:</b> Garrison Headquarters	<ul style="list-style-type: none"> <li>The round bastion in the south side, the “Vergas Bastion”, exploded during the Second World War.</li> </ul>
<b>1982-1986</b>	<ul style="list-style-type: none"> <li>Extensive restoration works were carried out during that period. Conservation was undertaken on the walls and bastions of the fortress, as well as the so-called “Maison building”, but also on the “Makrigiannis Bastion” and on the arches of the citadel. Restoration works were carried out inside the citadel, once it was detached from the enclosure walls of the courtyard used by the prison.</li> </ul>
<b>1988-2011</b>	<ul style="list-style-type: none"> <li>Restoration of S-W wall, precinct, and battlements.</li> <li>Restoration of “Hebdomos” bastion.</li> <li>Restoration N-W coastal bastion.</li> <li>Restoration N - E entrance of the fortress (current).</li> <li>Restoration of the initial fortress gate (<i>Zematistra</i>).</li> <li>Reconstruction of the bastion of “Megali Verga”.</li> <li>Reconstruction work of ruin parts of Niokastro, on the fortress walls, commenced and continues to the present day.</li> </ul>

## 2. Structural Materials

### 2.1 Ottoman Building Constructions & Materials

Despite its lack of complex drawing technique, but thanks to standard detailing conceptions and tradition of stonecutting, Ottoman architecture had an empirical and rational mentality that was reflected in its methods of design and composition. They were of a very simple nature from the point of view of architectural theory, but quite articulate when applied to building practice (*Cerasi, 2016*).

Ottoman period followed the traditional techniques and materials are depending of locally available raw materials. Usually used pure lime, but in special structures where high durability needed moisture observed adding crushed ceramic and natural pozzolan. The quality of materials and constructions is distinguished by usually trivial character (Papayianni & Stefanidou, 1997)(Papayianni, 1997).

Usual configuration of forehead mortars has been used characterized by the role of structural mortar in the construction. In the case where the resistance of mortars with respect to the remaining components (stones, bricks) is lower, typically created by a recess in the front of the joints. The morphology was found in isodoma systems where mortars act primarily as an adhesive stones in rubble flying coatings or simple masonry construction worthless. Found in all historical periods from prehistory to the 20th century (Pachta, 2011).

According to the study of Stefanidou et al., 2012, different types of inclusions were observed in Ottoman structural mortars, as calcite lumps, charcoal, wood chips and shells have been recorded in a significant number of samples. The calcite lumps occurred in 1.0–1.5% w/w of binder, charcoal in small grains, proportioning at less than 1% w/w of binders, and was strongly connected to the binder, chips of wood were found in 1.0–1.5% w/w of binder (Stefanidou, et al., 2012).

## 2.2 Stones

Rocks or stones are the morphologically distinct heterogeneous structural units with specified mineral composition of which consist the solid crust of the Earth. Stones according to their formation are classified in three basic categories, the igneous, the sedimentary, and the metamorphic (Misopolinos, 1990). Each type of rock or stone is composed of one or more minerals<sup>2</sup>. The properties and behavior of a particular type of stone are influenced by their formation process and by the physicochemical properties of the minerals consist of (Robertson, 1982).

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<sup>2</sup> Inorganic substances with particular chemical composition, physical formed and they have a specific internal structure, and stable physical properties (Misopolinos, 1990).

**Table 3: Type of stones, formation processes, and physical properties**

<b>Stone</b>	<b>Formation</b>	<b>Species</b>	<b>Physical Properties</b>
Igneous	Under the earth's surface with coagulation of magma fluid	Granite, Obsidian, Pumice, Basalt	Porosity Permeability Density Thermal
Sedimentary	Transport, deposition and adhesion of disintegration products of underlying rocks	Limestone, Chalk, Dolomite, Sandstone	Mechanical Optical
Metamorphic	Physical and/or chemical transformation under pressure of igneous and sedimentary rocks	Marble, Phyllites, Gneiss, Schist	Electrical Magnetic

Based on literature it is considered that historical monuments and especially for the construction of castles the use of limestone and sandstone were more frequent than the use of other rocks (Misopolinos, 1990). This was due to the abundance of these materials in Greece<sup>3</sup> and their easy processing.

Limestone, contain at least 90% calcite and up to 10% dolomite, common components in smaller proportions are also quartz, feldspars, clay minerals, pyrite, siderite, aragonite, travertine, and siderite. They are formed from organic or inorganic processes and can be clastic, chemical or biogenic, crystalline or recrystallised. Crystals of calcite, quartz, dolomite or barite may line small cavities in the rock. The depositional environment is important, because it determines the size, shape and purity of the carbonate granules. When conditions are right for precipitation, calcite forms mineral coatings that cement the existing rock grains together or it can fill fractures. Limestone grain size is variable, clastic texture consist of clast of all sizes, its smooth is rough to touch, and generally is a hard material (Jackson, 1997).

<sup>3</sup> The 75% of Greece is covered by sedimentary and metamorphic rocks(Tsirampidis, 1996)

Limestone formed in areas with strong sea currents contain very small amount of non-carbonaceous components and are considered as a source of high purity material. Their color varies from pure white to gray (Misopolinos, 1990)(Tsirampidis, 1996).

Sandstones are clastic sediments. Depending on the predominant mineral component, or the type of adhesive or type of filling material designated as quartzite, calcitic and aluminate. Color is typically light gray, yellow or reddish brown, reflecting the variation in mineral content and cement. Their texture is grainy and rough. Sand consists of limestone fragments form from the cementation of sand and/or mud by calcite (clastic limestone)(Pettijohn, et al., 1987).

In addition to framework grains, sandstones also consist of much smaller silt- or clay-sized clasts known collectively as matrix and a mineral matter between the grains that holds them together. This is known as cement. The cement is usually either carbonate (calcite and dolomite are very common) or silica (chemically precipitated material identical in composition to quartz grains). Silica cemented sandstones is very durable and hard while calcite cemented sandstones is subject to acidic dissolution and is more easily eroded (Pettijohn, et al., 1987)(Jackson, 1997).

Sandstones can be further divided according to: clast size-fine (0.006 – 0.2mm), medium (0.2-0.6mm) coarse (0.6-2mm)<sup>4</sup>. Sandstone comprising a mixture of clast sizes is poorly sorted, while sandstone comprising mostly clasts of the same size is well sorted. Hardness is variable through soft to hard, dependent on clast and cement composition. The main mineral components are calcite, quartz, feldspar (orthoclase, plagioclase), and iron oxides, are usually accompanied by small amounts of other minerals known as heavy minerals (Natural, 2016)(Jackson, 1997).

### **2.3 Mortars**

Mortar mixture generally called every of one or more binder with aggregates and water. Mortars are among the oldest and most common building materials, due to the plasticity and the ability to demonstrate to adapt to the needs of morphological structures (Stefanidou, et al., 2012).

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<sup>4</sup>Grain size: (0.6-2mm), clasts visible to the naked eye, often identifiable.

Further it is an artificial accumulation cement binder, inorganic fillers, water and optionally organic impurities, in proportions that impart adequate workability to the mix, when fresh, and acquire the physical, chemical and mechanical properties and durability when cured (Papagianni & Oikonomou, 1997). Although mortars seem to be simple materials, it is actually complex, multiphase systems consisting of crystalline and amorphous phases.

**Table 4: Main properties of mortars**

<b>Properties of Mortars</b>	
Fresh Mortars	<ul style="list-style-type: none"> <li>• The coagulation and hardening (two successive phases of the same phenomenon)</li> <li>• Workability (the most important advantage of a fresh mortar-good adhesion with the other materials)</li> <li>• Plasticity (to cover all surfaces of building materials, even those with high relief, without destroying its consistency)</li> </ul>
Hardened Mortars	<ul style="list-style-type: none"> <li>• Porosity (affects the strength and sturdiness over time)</li> <li>• Mechanical properties (determine the behavior of materials under stress due to load or environmental influences)</li> <li>• Elasticity (is related to the crystal structure)</li> </ul> <p>Permeability (is defined as the property that characterizes the rate of fluid resources transfer through solids)</p>

**Table 5: Classifications of historical mortars**

<b>Classification of historical mortars</b>	
According to their usage:	<ul style="list-style-type: none"> <li>- <i>Structural mortars</i>: to connect the building materials such as stones and bricks, to fill the gaps on the order of layers and as grouts</li> <li>- <i>Rendering mortars</i>: to invest the construction elements. The investment made for precautionary reasons, insulation and aesthetic appearance. These mortars are called coatings and are essential for the quality and the duration of the structure</li> <li>- <i>Decorative mortars</i>: for work with plaster, stucco, mosaics and</li> </ul>

	wall substrates ( <i>Moropoulou, et al., 2005</i> )
According to the type of the binder:	<ul style="list-style-type: none"> <li>- Lime mortars (lime paste or powder)</li> <li>- Cement mortars (with binder cement)</li> <li>- Cement - lime mortar (mixed mortar)</li> <li>-Pozzolanic mortars (lime binder with pozzolan admixture material)</li> <li>- Hydraulic mortar ( hydraulic lime binder)</li> <li>- Gypsum mortar (gypsum binder)</li> <li>- Clay mortar (clay binder)(<i>Moropoulou et al., 2005</i>)</li> </ul>
According to the amount of the used binder:	<ul style="list-style-type: none"> <li>- <u>Dim:</u> where the use of less than the normal quantity of binder leads to less resistance and results in brittle surfaces</li> <li>- <u>Normally:</u> contain as much binder is needed to fill the gaps of sand</li> <li>- <u>Thick:</u> rich powder thus characterized by considerable shrinkage due to drying that causes cracks on the surfaces (<i>Moropoulou, et al., 2000</i>)</li> </ul>

### 2.3.1 Binder materials

As binder named the material which, when mixed with water acquire plasticity and develop adhesive properties. Initially pulp is formed, which allows the formulation adhesion and bonding with aggregates. Then the pulp is solidified, to form a hard, compact mass with remarkable strength.

Binders are divided into two main categories, depending on the setting and hardening process:

Non-hydraulic binders: are undergoing coagulation, hardening and acquire mechanical strength in the air and maintained in the environment. In this category are the clay, lime, gypsum and magnesia cement. They characterized as poor water resistance even in wet environments.

Hydraulic binders: are those which undergo thickening, hardening and acquire their mechanical strength in the water or in a humid environment. In this category,

belongs the cement, the pozzolanic binders and the hydraulic lime (Tsimas, 2001)(Papagianni & Oikonomou, 1997)(Taylor, 1983).

Most common binders found on the monuments are:

- *Clay* is the first binder in man-made structures. Clays exhibit various mineralogical compositions but the basic components are silicon ( $\text{SiO}_2$ ) and aluminum ( $\text{Al}_2\text{O}_3$ ) oxides and, secondary are oxides of calcium ( $\text{CaO}$ ), magnesium ( $\text{MgO}$ ), of alkali metal ( $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ) and iron ( $\text{Fe}_2\text{O}_3$ ). Main mineralogical component of clays are the kaolin (Orlandos, 1955-1958)(Koroneos & Poulakakos, 2006).
- *Gypsum*: produced by roasting of natural gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  selenite). In nature always found with impurities eg  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ . The percentage of impurities should be less than 20%. In historical times, the gypsum used in building construction for wall coatings and decorative reliefs such as cornices (coronae)(Orlandos, 1955-1958)(Bakolas, 2002).
- *Lime* ( $\text{CaO}$ ): As raw material for the manufacture of the lime can be used all the calcareous rocks containing an important proportion of calcium carbonate ( $\text{CaCO}_3$ ). When the lime is exposed to air, due to high affinity with water, it absorbs moisture, swells and by the influence of air carbon dioxide is converted to calcium carbonate.

Types of lime with respect to the impurities content:

- *Calcitic lime* or normal lime, exist when the active calcium oxide ( $\text{CaO}$ ) contained in a proportion exceeding 85%.
- *Magnesian lime* contains 80%-90% calcium oxide ( $\text{CaO}$ ) and magnesium oxide, must not exceed 10% -20% ( $\text{MgO}$ ).
- *Dolomitic lime* is called the one containing a percentage of magnesium oxide ( $\text{MgO}$ ), greater than 20% (Balen, 2003)(Tsimas, 2001)(Orlandos, 1955-1958).
- Hydraulic lime differs from the hydrated lime (air lime) because it has the capacity to solidify not only in air but also under water. It is formed by firing marly limestone containing from 10 to 20% aluminum, silica and small rates, iron and magnesium oxides. The proportion of alumino-silicate compounds contained in the hydraulic lime depends on the initial concentrations of aluminum and silicon oxide in

the raw material, and affects the degree of the hydraulicity of the lime (Tsimas, 2001)(Koroneos & Poulakakos, 2006).

**Table 6 : Lime classification according to the hydraulicity index (Vicat):**

Hydraulicity index (i): $(Al_2O_3 + SiO_2 + Fe_2O_3) / (CaO + MgO)$	
i = 0,00-0,10	Air lime
i =0,10-0,16	Lime with low hydraulicity
i =0,16-0,32	Lime with medium hydraulicity
i =0,32-0,42	Hydraulic lime
i =0,42-0,50	Lime with high hydraulicity

### 2.3.2 Aggregate materials

The powders are rarely applied pure, for economic and technical reasons. Binders needed to be mixed with a certain amount of sand or other inert<sup>5</sup> in different grain sizes and proportions, except the necessary liquid.

Aggregates are typically inorganic materials, from physical partition or artificial fracture of natural stones. The natural aggregates come from various natural sources, such as rivers or coasts and from older deposits areas (mines) (silica sand, pumice etc.). This inert present rounded form. Artificial aggregates are of natural origin and are produced by crushing rocks solid or ceramics (Kourasani)<sup>6</sup>(Lamprou, 2016).

#### Description of the two main aggregates found in historical mortars:

- a. Siliceous sand: natural sand from rivers and seas, from the quartz (mineral of silicon,  $Si_2O$ ), has high hardness, due to the chemical inertness of the quartz product is timeless and does not influenced by atmospheric pollution.

<sup>5</sup>Inert: so-named because it does not participate chemically in clotting

<sup>6</sup> The kourasani known from antiquity is produced by crushing and grinding materials, in baked clay (bricks, tiles, etc. These materials which form hydraulic compounds reacting with  $Ca(OH)_2$ , in the presence of moisture(Papagianni & Oikonomou, 1997).

- b. Limestone sand: artificial sand by fracture (quarry). Limestone aggregates has the following composition: 51.3 % CaO, 41.6% CO<sub>2</sub>, 3.8 SiO<sub>2</sub>, 1.2 MgO, 1.0% Al<sub>2</sub>O<sub>3</sub>, and 0.4% Fe<sub>2</sub>O<sub>3</sub> (Papagianni & Oikonomou, 1997).

Inert materials, whether natural or artificial origin, in terms of grain size, divided into very fine, fine, medium, coarse, and very coarse. They may be further characterized as well-rounded, almost spherical, to very angular. Angular grains tend to interlock well, and when cemented, are desirable in masonry. Mentioned some common aggregates from the largest to the finest: Pebbles (rounded stone blocks), gravel, crushed gravel (more angular aggregates), sand (coarse sand (0.50- 1 mm), medium sand (0.25 to 0.50 mm), fine sand (0.10 - 0.25 mm), very fine sand: (0, 05 - 0.10 mm), sludge and clay.

The addition of aggregates in cement has been shown to provide technical advantages as well as contributing to the volume stability, durability and structural filling. Also, the volume contained in the mixture, the maximum size and its classification, affect the structure of the system binder – aggregate. The well graded crushed sand results in mortars with high strength, low permeability, good adhesion, low workability (rapid setting). The fine smooth sand gives the mortar high workability but lower strength. Generally good gradation means maximum volume density (Moropoulou, et al., 2000)(Biscontin, et al., 2002).

**Table 7: Properties of aggregates (Bakolas, 2002)(Aggelakopoulos, 2006)**

<p><b><i>The properties of aggregates can classified under their:</i></b></p> <p><u>Physical characteristics:</u> grain size (coarse, medium, fine, very fine), shape (cylindrical, spherical, tabular, ellipsoidal, irregular), roughness.</p> <p><u>Chemical and mineralogical composition:</u> strength, hardness, fineness measure and, content of harmful impurities (sulfur, nitrates, chlorides, lignite, coal, etc)<sup>7</sup>.</p> <p><u>Porosity</u><sup>8</sup>: specific weight, moisture absorption, resistance, hardness, modulus and toughness.</p>
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<sup>7</sup>For instant: Aggregates containing alumino-silicates should be avoided to use in binders containing alkalis because they generate soluble compounds (alkali aggregate reaction).

*Other additives in the ancient – historic mortars:*

The pozzolanic materials of historical mortars are silicates or clays of natural origin (action of volcanoes) or artificial (human technological activity). They mainly consist of silicon dioxide and, a small proportion of aluminum, iron, calcium and magnesium oxides. All the pozzolana materials contain glass substrates in varying amounts. In glass substrate may be contained mica illite, kaolinite, magnetite, plagioclase etc. The mineralogical compositions of Pozzolanic materials are the following:  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{SO}_3$ . The activity of the pozzolan constituent consists in having amorphous structure in the matrix, even in the absence of crystalline structure. Pozzolans are reacted with hydrated lime to form hydrated lime and calcareous aluminates compounds and exhibiting hydraulic properties (Aggelakopoulos, 2006), (Matias, et al., 2014)(Lamprou, 2016).

In historical mortars found organic materials. Common is the presence of various fibers such as wood chips, straw, and animals' hair, especially in coatings to improve the mechanical strength and to avoid cracking due to shrinkage during solidification. Characteristic is the presence of charcoal (Elsen, 2006)(Moropoulou, et al., 2005). All these materials are characterized as additives as they are in small amounts, usually not more than 2-3% by weight of binder and usually distinguished visually in the mortar matrix. Their small percentage may support the idea of do not affect the properties of the material. However, the presence of, appears to be associated with the mortar production technology and, its operation in manufacturing. In this sense can be defined as solid organic nature materials found in mortars, in an effort to enhance their properties (Stefanidou, et al., 2012).

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<sup>8</sup> Porosity indicative of standard aggregates are generally small, about 3-10%

## II. EXPERIMENTAL PART

### 1. Methodology

This study is concerned the detailed condition survey of the construction materials of the Castle of Pylos (Niokastro), starting with the history review of the monument, the in-situ visual observations of existing conditions and by testing of building materials. We aim to design the right criteria and definitions, for potential renovations. Specifically we analyze the stones, the mortars, and the coatings used in the construction of the monument to acknowledge and characterize the construction materials of the castle of Pylos. Finally, we also aim to determine the origin of the building materials, and to clarify the various construction phases of the individual parts of the monument.

Creation of the thematic maps of the sampling areas addressed with findings and recommendations are reported highlighting the usefulness of computer map program (ArcGIS). It is an innovative approach the usage of a new technological digitization tool for the study of cultural heritage monuments.

To achieve the objectives above, the experimental procedure is organized in the following steps:

- Creation of the ground plan of Niokastro on a map through ArcGIS program.
- Sampling of castle's stone and mortar construction materials.
- Sampling of reference stone samples from the region of Pylos.
- Positioning at the map of ground plan the sampled points, (to obtain specific coordinates).
- Description of the sample morphology through macroscopic observation.
- Preparation of the samples, for the analytical physicochemical analysis.
- Implementation of characterization techniques.
- Interpretation of results.
- Use ArcGIS program to up load results of laboratories analyses.
- Conclusions.

## 1.1 Sampling (application and documentation)

The sampling process is the first and perhaps the most important stage of a study, as should be documented as finest as possible by following all of the required steps.

Initially, before the basic process of sampling in situ, we created the ground plan of the castle on a map with the ArcGIS (Geographic Information System)<sup>9</sup> for positioning the sampling areas and finally to digitize<sup>10</sup> research's results.

In order to lay the right criteria for the selection of the sampling areas, gathering information about the historical route, the architecture and the construction phases of the monument have been necessary (*see table 1, and 2*).

### List of sampling criteria:

- Homogeneity, especially for the mortar samples. The samples should be in a good conservation state, homogenous and show no distinct layers. Is common practice in mortars to be constructed in layers. The result is that the layers may differ in composition and dating. Selected samples from the upper broken part of coatings (outer layers) and from the inner surface areas of the structural mortars, as to not be affected by external factors of erosion (Lamprou, 2016).
- Size samples: The size must be at least 50g to performed several different analytical techniques. It is not ethically to take larger samples as endangered the architectural integrity of the monument; we must cause as less damage as possible. Stone samples collected from broken stones and mortar samples from mortars that had low consistency with the stones.
- Localization of sampling positions: we attempted to cover all the major components of the monument. Namely, the castle walls, circumferentially (north, south, west), the two main gates of the castle (Central gate and “Zematistra”), and three bastions, two of them belong to the walls of the castle (NW Bastion and 7th Bastion) and the third belong to the citadel (Bastion I).

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<sup>9</sup>Computer program “for the management, analysis, and display of geographic information”

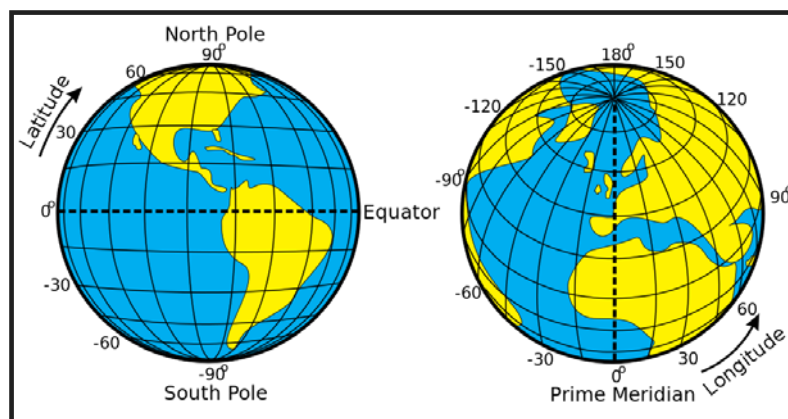
<sup>10</sup>Digitizing called the process through specific design programs create the information we need on our map.

### 1.1.1 Mapping Program (ArcGIS)

Geographic Information System (GIS) is a fast, powerful, interactive mean that helps in the analysis through the comparisons, the easy layering, the easy projection and the changes of projection. GIS is a computer-based information system that enables capture, modeling, manipulation, retrieval, analysis and presentation (Worboys, 1997).

GIS organizes geographic data so that a person reading a map can select data necessary for a specific project or task. ArcMap is the main component of Esri's ArcGIS suite of geospatial processing programs, and is used primarily to view, edit, create, and analyze geospatial data. There are numerous advantages to structuring GIS data in a geo-database environment. Some of the most important concern the structure of GIS data are the vector data including points, lines, and polygons are typically stored in shape-files referred to as feature classes.

A geo-database allows for the creation of feature data sets that enable coordinated relationships among feature classes (Tennant, 2007). The geographical coordinates are both latitude and longitude and serve to identify the precise location of sites on the surface of the Earth. Latitude represented by horizontal lines and, the vertical lines on a map is longitude<sup>11</sup>.



<sup>11</sup>There are two common types of coordinate systems used in GIS: 1. Global or spherical coordinate system (World Geodetic System of 1984 WGS 1984 – Google Earth). 2. Projected coordinate system provides various mechanisms to project maps of the earth's spherical surface onto a two-dimensional Cartesian coordinate plane.

In Greece, we use EGSA '87 (GGRS '87 Greek Grid Reference System '87) coordinate system. It offers a reference scale to all country and is being used by the public and the private sector in Greece.

They are two types of maps that it can be produced, the qualitative thematic maps or descriptive maps (include region, path, facility, and resource maps) and, quantitative thematic maps or statistical maps which use visual mechanism, such as color, to indicate the quantity of a data attribute at different locations on a map.

A feature on the map is not only the shape and geographical location but also a number of other characteristics that are not related to the geometry of the particular attribute. A thematic map has a table of contents that allows the reader to add layers of information to a base map of real-world locations. All of the descriptive characteristics of a layer are stored in a table (attribute table).

Specifically, the steps to create map using the ArcGIS program are the following:

- Load geospatial data into ArcMap (adding one or more layers)
- Create shape-files<sup>12</sup>
- Identify the features (point, lines, polygons) and attributes to present
- Define how to show the data
- Add maps components (map title, North arrow, scale bar, legend)
- Export maps

### *1.1.2 Sampling*

As the monument is not fully studied sampling was a difficult task. The representation of the whole region and each construction phase has not any documented sources in relation.







For the samples posting have been used hammer and small chisels. During the sampling process photographic documentation was carried out, a Canon EOS 600D camera, under natural light was used. The positions recorded in the ArcGIS map (castle floor plan), photographed, numbered and coded. The data are presented in *tables 8 (stone samples) and table 9 (mortar samples)*. The codification was done starting from the current main gate of the castle to the north: **1.**Main Gate **2.**North











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<sup>12</sup> Shape-file: the most commonly used geospatial data format.

wall 3.NW Bastion 4.West wall 5.7th Bastion 6.South wall 7.Bastion I (of citadel)  
 8.Zematistra gate. The codes indicate the origin, the number of the sample, the material (stone or mortar), and whether they are internal or external of the monument. For example sample **1.1.S.In**: **1**: Central Gate, **1**: first sample of the central gate, **S**: Stone, **In**: Internal phase.

**Table 8: List of stone samples (origin, usage, type, and photograph)**

<b>List of Stone Samples</b>			
<b>Sample/ Origin</b>	<b>Usage/Type</b>	<b>Photo of Sample</b>	<b>Photo Sampling Area</b>
<b>1.1.S.In Main Gate</b>	Structural Sandstone (blocks)		
<b>2.2.S.In North Wall</b>	Structural Lime-stone		
<b>2.2.S.Out North Wall</b>	Structural Lime-stone		

<p><b>2.3.S.Out</b> <b>North Wall</b></p>	<p>Structural Sandstone</p>		
<p><b>3.2.S.In</b> <b>NW Bastion</b></p>	<p>Structural Lime-stone</p>		
<p><b>3.4.S.In</b> <b>NW Bastion</b></p>	<p>Structural Sandstone (blocks)</p>		
<p><b>3.5.S.In</b> <b>NW Bastion</b></p>	<p>Structural Stone</p>		
<p><b>3.6.S.In</b> <b>NW Bastion</b></p>	<p>Filling Stone</p>		

<p><b>4.2.S.In</b> <b>West Wall</b></p>	<p>Structural Lime-stone</p>		
<p><b>5.3.S.In</b> <b>7th Bastion</b></p>	<p>Structural Sandstone (blocks)</p>		
<p><b>5.4.S.In</b> <b>7th Bastion</b></p>	<p>Structural Lime-stone</p>		
<p><b>6.2.S.In</b> <b>South Wall</b></p>	<p>Structural Lime-stone</p>		
<p><b>6.4.S.In</b> <b>South Wall</b></p>	<p>Filling Sandstone</p>		























<p><b>7.3.S.Out</b> <b>Bastion I</b></p>	<p>Structural Lime-stone</p>		
<p><b>7.5.S.Out</b> <b>Bastion I</b></p>	<p>Filling Stone</p>		
<p><b>7.6.S.Out</b> <b>Bastion I</b></p>	<p>Filling Sandstone</p>		
<p><b>8.1.S.Out</b> <b>Zematistra Gate</b></p>	<p>Structural Sandstone (blocks)</p>		






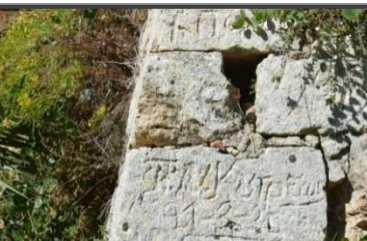




Table 9: List of the historic mortar samples (type, usage, and photography)

List of Mortar Samples			
Sample/ Origin	Usage/Type	Photo Sample	Sampling Area
<p><b>1.2.M.In</b> <b>Central Gate</b></p>	<p>Structural for Sandstone blocks Joint, thin layer</p>		

<p><b>2.1.M.In North Wall</b></p>	<p>Forehead - Structural<sup>13</sup> Thin - thick layer cover &amp; restrain stones</p>		
<p><b>2.1.M.Out North Wall</b></p>	<p>Forehead - Structural Thin - thick layer cover &amp; restrain stones</p>		
<p><b>2.4.M.Out North Wall</b></p>	<p>Structural Joint, deep</p>		
<p><b>3.1.M.In NW Bastion</b></p>	<p>Forehead - Structural Thin - thick layer cover &amp; restrain stones</p>		
<p><b>3.3.M.In NW Bastion</b></p>	<p>Forehead &amp; Structural Thin - thick layer cover &amp; restrain stones</p>		
<p><b>4.1.M.In West Wall</b></p>	<p>Structural Joint, deep</p>		

<sup>13</sup>Forehead – Structural mortar: structural mortar for limestone (main structural stones of the castle’s masonries) which covers the outer surface of the stones.

<p><b>4.3.M.In</b> <b>West Wall</b></p>	<p>Forehead- Structural Thin - thick layer cover &amp; restrain stones</p>		
<p><b>5.1.M.In</b> <b>7th Bastion</b></p>	<p>Rendering Thin layer cover stones</p>		
<p><b>5.2.M.In</b> <b>7th Bastion</b></p>	<p>Structural Joint, thick layer (reconstruction mortar)</p>		
<p><b>6.1.M.In</b> <b>South Wall</b></p>	<p>Forehead- Structural Thick layer in joints &amp; cover stones</p>		
<p><b>6.3.M.In</b> <b>South Wall</b></p>	<p>Rendering Thin layer cover stones (forehead arch)</p>		
<p><b>7.1.M.In</b> <b>Bastion I</b> <b>(Citadel)</b></p>	<p>Structural Thick layer</p>		

<p><b>7.1.M.Out Bastion I (Citadel)</b></p>	<p>Forehead- Structural Thick layer in Joints &amp; cover stones</p>		
<p><b>7.2.M.Out Bastion I (Citadel)</b></p>	<p>Structural Thick layer, deep</p>		
<p><b>8.2.M.Out Zematistra Gate</b></p>	<p>Structural Thin layer (restoration mortar)</p>		
<p><b>8.3.M.Out Zematistra Gate</b></p>	<p>Structural for Sandstones Thin layer, deep</p>		
<p><b>8.4.M.Out Zematistra Gate</b></p>	<p>Structural for Sandstones Thin layer</p>		





### 1.1.3 Reference Stone Samples

Reference stone samples, are included in our research to investigate the provenance of the construction materials of the castle of Pylos. For the sampling process of reference stones we consult the geological map of Greece, the relating sheet of Pylos, to identify the geological formations concerning the constructive materials of the monument. According to the geological map of Gavrovon – Pylos zone (Fytrolakis, 1980) the coarsening geological formations are:

Criteria for the selection of stone samples from the region of Pylos:

- a) Match in physical characteristics with the castle stones, b) to be unaffected by external corrosion agents, and c) as close as possible to the monument area, according to the transportation manner.

**Table 10: List of reference stone samples**

Sample	Type	Photography
<b>Pls</b>	Sandstone	
<b>Ptk</b>	Sandstone	
<b>KsKd</b>	Limestone	
<b>E-Pc.k</b>	Limestone	

Pl<sub>s</sub>

**Pls:** Pliocene (Astian), Marls, sandstones: in the lower and middle beds marls dominate, fine grained sandstones and sometimes clays. In the upper beds, coarse – grained sandstones and towards the margins of the basins conglomerates are dominant. In the middle beds lignite interstratifications are present, the most important outcrop is found in the area of Chomatero (Koroni).

Pl.k

**Ptk:** Porous Limestone, quaternary, Pleistocene

K<sub>s,k,d</sub>

**Ks.k.d:** Upper cretaceous, Limestone series: the lower parts are light – grey, thin – bedded limestones with Radiolites sp. (about 70m thick). Above this series, limestone banks occur in certain places with rhythmical sedimentary zones. Above this horizon, a series (about 10 m thick) mainly of black, thick – bedded dolomites occur. Thick – bedded limestones are following with Hippurites sp. and generally Rudist fragments. Total thickness: at least 300m.

E-Pc.k

**E-Pc.k:** Eocene – Paleocene, Limestones: thick – bedded, grey – white. Within the limestones black zones are often present. They have bituminous odor, when broken, and they alternate with dolomitic beds.



Figure 2: Geological map of Gavrovon – Pylos zone (Fytrolakis, 1980)

### 1.1.4 Map (sampling areas)

Geographical position, through the latitude and longitude we define the sampling points on the ground map.

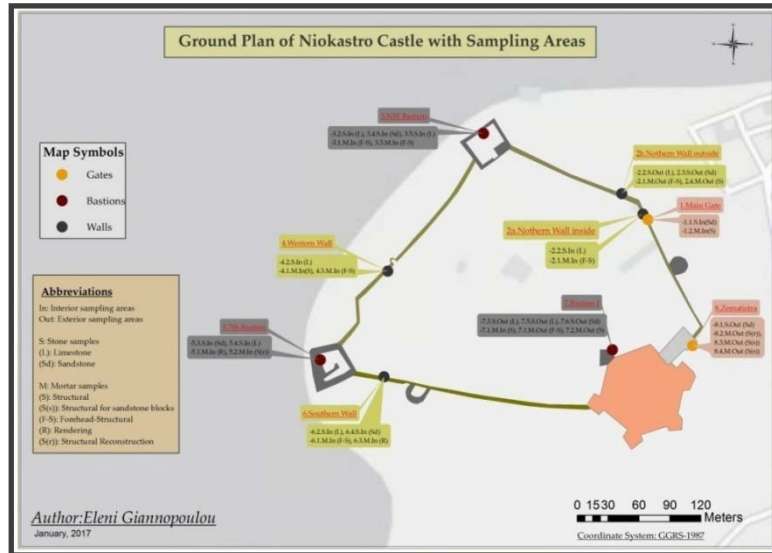


Figure 3: Sampling areas on the ground plan of the Niokastro Castle, Pylos, Greece (ArcGIS)

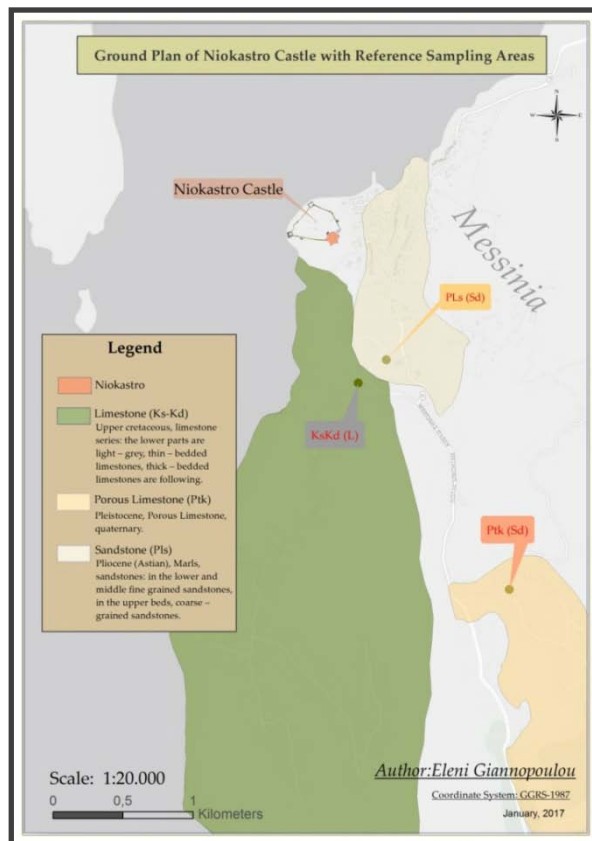


Figure 4: Sampling areas of the reference stone samples from the region of Pylos

## 2. Macroscopic Observation

### 2.1 Stone Samples

First approach of the studied materials was done by visual inspection of the samples in situ and in the laboratory.

For the construction of the castle have been used two basic types of stones, gray limestone in masonries (walls) and yellowish porous stones (sandstone rocks) for the formation of the gates (Zematistra gate, Main gate, 7<sup>th</sup> bastion gate and the gate of the Citadel), the same material has been used for the construction of various structural elements such as frames for the cannons or in the corners of the buildings.

Gray limestone is used extensively without any specific shape or size, crude stones, small fragments without any preparation first. Their preservation state is good, are observed limited material losses, micro-cracks, biological and salts deposits on the outer surface of the stones.

On the other hand porous stones (sandstone) are formed in plucked and large blocks. It is a rough, moderate porous material, without good cohesion. Also we observe differences between the sandstones, namely, they are materials rougher than others or with different mechanical properties or different binder. Their preservation state is considered moderate as extensive losses of the stone material are observed, combined with fractures, crushing and distortion. Expanded deteriorations attended at the lower parts of the sandstone masonries, this is due to the presence of the vegetation.

**Table 11: Macroscopic examination of lime-stone structural material of Niokastro**

<b>Macroscopic examination of lime – stone samples</b>			
<b>Sample</b>	<b>Type</b>	<b>Colour</b>	<b>Preservation state</b>
<b>2.2.S.In</b>	Lime-stone	Gray - Brown	Good, biological and salt deposits
<b>2.2.S.Out</b>	Lime-stone	Gray - Brown	Good, biological and salt deposits
<b>3.2.S.In</b>	Lime-stone	Gray - Brown	Good, biological and salt deposits
<b>3.5.S.In</b>	Lime-stone	White-Gray	Moderate, cracking, material loss
<b>3.6.S.In</b>	Dolomite	Black-Gray	Good
<b>4.2.S.In</b>	Lime-stone	Gray - Brown	Good, biological and salt deposits
<b>5.4.S.In</b>	Lime-stone	Gray - Brown	Good, biological and salt

<b>6.2.S.In</b>	Lime-stone	Gray - Brown	deposits Good, biological and salt deposits
	Lime-stone	Gray - Brown	Good, biological and salt deposits
	Lime-stone	Black-Gray	Good

Table 12: Macroscopic examination of sandstone structural material of Niokastro

Macroscopic examination of Sandstones			
Sample	Type	Colour	Preservation State
<b>1.1.S.In</b>	Sandstone	Yellowish	Moderate, friable, material loss
<b>2.3.S.Out</b>	Sandstone	Yellow	Moderate, friable, material loss
<b>3.4.S.In</b>	Sandstone	Yellowish	Moderate, friable
<b>5.3.S.In</b>	Sandstone	Yellowish	Moderate, friable, material loss
<b>6.4..S.In</b>	Sandstone	Yellowish	Moderate, friable, material loss
<b>7.6.S.Out</b>	Sandstone	Yellowish	Moderate, friable, material loss
<b>8.1.S.Out</b>	Sandstone	Yellowish	Moderate, friable, material loss

## 2.2 Mortar Samples

According to the in situ macroscopic examination of the mortar samples we separate them in five categories: a) **Structural mortars for the sandstone blocks (S(s))**, b) **Forehead - Structural mortars (F-S)**, c) **Structural (S)**, d) **Renderings (R)**, e) **Structural Reconstruction or Restoration mortars (S(r))**.

Mortar samples as heterogeneous materials, are consist of light colored binders, with only one exception a sample which has red terracotta color of binder (*3.3.M.In*) and of different kinds of aggregates. Aggregates are distinctly different shaped, are mostly angular, and light-pale colored. Also inside the binder in most of mortar samples are found a lot of calcite lumps and fragments of ceramic (mainly at S(s) and R mortar samples), both coarse and fine.

Furthermore, in a limited number of mortar samples we tracked down organic material (*7.1.M.In*, *7.1.M.Out*, *8.4.M.Out*) and charcoal (*1.2.M.In*, *3.1.M.In*, *4.3.M.In*), which their presence look like randomly. Some of the samples appear to have lost their bonding and their physicochemical properties while others presented hard enough and probably cohesive, confirmed by the attempt of fragmentation. Additional, on the surfaces but also within the mortar samples are observed deposits of biological origin, rootlets and dirt.

Table 13: Macroscopic examination of structural mortars for sandstone blocks (S(s))

<b>Macroscopic Examination of Structural Mortars for Sandstones (S(s))</b>			
<b>Sample</b>	<b>Colour</b>	<b>Comments</b>	<b>Preservation State</b>
<b>1.2.M.In S(s)</b>	Beige	Ceramic grains, charcoal, and granules of lime.	Good, hard material, good consistency between aggregates-binder, limited biological deposits
<b>8.3.M.Out S(s)</b>	Dark Beige	Coarse crushed ceramics, granules of lime	Medium, mild and friable good consistency between mortar-stones and medium between aggregates-binder, biological and salts deposits
<b>8.4.M.Out S(s)</b>	Beige	Coarse crushed ceramic grains, a lot of granules of lime, crushed sandstone, organic material.	Bad, mild and friable bad consistency between mortar-stones, a lot of biological and salt deposits, extensive loss of material.

Table 14: Macroscopic examination of forehead – structural mortars (F-S)

<b>Macroscopic Examination of Forehead - Structural Mortars (F-S)</b>			
<b>Sample</b>	<b>Colour</b>	<b>Comments</b>	<b>Preservation State</b>
<b>2.1.M.In</b>	Beige	Ceramic as aggregates, pellets of lime.	Medium, hard material, a lot of biological and salt deposits, change of out layer color, good consistency both between aggregates-binder and mortar-stones, loss of material
<b>2.1.M.Out</b>	Dark Beige	Thick mortar	Medium, hard material, biological and salt deposits, change of out layer color, medium consistency between aggregates-binder and good between mortar-stones, loss of material
<b>3.1.M.In</b>	Light Beige	Grains of crushed ceramic, coarse granules of lime and charcoal	Medium, hard material, biological and salt deposits, change of out layer color, good consistency aggregates-cement and mortar-stones

<b>3.3.M.In</b>	Light Terracotta	A lot of granules of lime, limited aggregates, weak mortar.	Medium, mild and friable, a lot of biological and salt deposits, change of out layer color, medium consistency aggregates-cement and good cohesion mortar-stones
<b>4.3.M.In</b>	Light Beige	A lot of granules of lime, (both fine and coarse), charcoal.	Medium, mild and very friable, soil inside, a lot of biological and salt deposits, change of color, medium consistency aggregates-cement, good consistency mortar-stones
<b>6.1.M.In</b>	Beige	Granules of lime.	Medium, hard, no friable medium consistency between mortar-stones and good between aggregates-binder, loss of material.
<b>7.1.M.Out</b>	Dark Beige	Plenty of lime granules, crushed ceramic, organic material, thick mortar.	Medium, hard, no friable, good consistency between mortar-stones and medium cohesion aggregates-binder, biological and salt deposits, loss of material.

**Table 15: Macroscopic examination of reconstruction – restoration mortars (S(r))**

<b>Macroscopic Examination of Reconstruction – Restoration Mortars S(r)</b>			
<b>Sample</b>	<b>Colour</b>	<b>Comments</b>	<b>Preservation State</b>
<b>5.2.M.In S(r)</b>	Dark Beige	Small granules of lime, not homogenous mortar.	Medium, mild and friable, good consistency between mortar-stones and medium between aggregates-binder.
<b>8.2.M.Out S(r)</b>	Beige - Gray	Granules of lime, thick mortar.	Bad, mild and friable, bad cohesion with stones, medium consistency aggregates-binder material loss, a lot of biological and salt deposits, change of out layer color.

**Table 16: Macroscopic examination of structural mortars (S)**

<b>Macroscopic Examination of Structural Mortars (S)</b>			
<b>Sample</b>	<b>Colour</b>	<b>Comments</b>	<b>Preservation State</b>
<b>2.4.M.Out</b>	Beige	Coarse lime granules, ceramic (fine grains), fine material.	Bad, very mild and friable, roots and soil inside the mortar, extensive material loss, medium consistency aggregates-binder and mortar - stones
<b>4.1.M.In</b>	Beige	Granules of lime, a lot of crushed ceramic grains.	Medium, mild and friable, a lot of biological and salt deposits, change of color, bad cohesion aggregates-binder and medium cohesion mortar-stones
<b>7.1.M.In</b>	Whitish	Granules of lime, organic material.	Good, no friable, good cohesion between mortar-stones.
<b>7.2.M.Out</b>	Whitish	Granules of lime.	Medium, mild and friable medium cohesion both between aggregates-binder and mortar-stones

**Table 17: Macroscopic examination of rendering mortars (R)**

<b>Macroscopic Examination of Rendering Mortar (R)</b>			
<b>Sample</b>	<b>Colour</b>	<b>Comments</b>	<b>Preservation State</b>
<b>5.1.M.In</b>	Dark Beige	Crushed stones, a lot of fine ceramic grains, is a thick mortar (enough inert), granules of lime.	Good, very hard material, good cohesion between aggregates-cement and mortar-stones, red color out-layer
<b>6.3.M.In</b>	Dark Beige	Coarse lime granules and crushed ceramics as inert material.	Good, hard, no friable, a lot of biological and salts deposits, Good cohesion between mortar-stones and between aggregates-cement, loss of material.

### **3. Methods of Examination (Introduction)**

For the physicochemical characterization of the historical samples of Niokastro we performed the following analytical techniques: Microscopic examination - observation (LED), for the determination of the microstructure of the samples (mortar and stone samples), granulometry for the grain size distribution, and for the identification of the proportion of binder/aggregates (only mortar samples). To identify the mineralogical features X-ray diffraction analysis (XRD) (mortar and stone samples) was carried out, and for the analysis of the chemical composition Scanning Electron Microscopy (SEM) SEM/EDX (mortar and stone samples) was conducted. These analytical techniques consider being the first basic steps for the characterization of inorganic materials such as mortar and stones.

#### **3.1 Optical Microscopic Examination (LED)**

A digital microscope is a variation of a traditional optical microscope that uses optics and a digital camera to output an image to a monitor, by means of software running on a computer.

A digital microscope has its own in-built LED light source, and differs from an optical microscope in that there is no provision to observe the sample directly through an eyepiece. Since the image is focused on the digital circuit the entire system is designed for the monitor image. The resolution of the image depends on the field of view of the lens used with the camera. The analytical technique of LED optical microscope is a non-destructive, portable technique, microscopic inspection of materials. The observation was conducted on the samples without any prior treatment.

#### **3.2 Grain Size Distribution (Granulometry)**

The grain size distribution is the process of measuring the different grain sizes in a granular material. This categorization allowing separation of the mortar into its components, and determines the percentage of each class of grain size contained in

the total amount of aggregates (*Maravelaki-Kalaitzaki, et al., 2003*) (*Silva, et al., 2006*).

For the grain size was used PVC sieves with stainless-steel grid, with standard sieves' hole diameters, specifically the diameters are: 1.940mm, 0.930 mm, 0.466mm, 0.263 mm, 0.122mm, and 0.062mm.

The technique was applied in 14 samples from the three categories of mortars (structural, forehead, and renderings). The samples used were unfortunately lightweight approximately 10gr, because the quantity of the samples did not allow us to have larger samples for the analysis. Generally an amount approximately of 50gr is considered intended for this analysis, as it allows a better evaluation of the material. Nevertheless we proceeded to the analysis to get more detailed determination for the aggregates of the mortar samples.

The analysis procedure is the following:

- a) Fragmentation of samples in order to take indicative unaffected material
- b) Weighing samples on an analytical balance
- c) Separation with little pressure and slight friction of the mortars in porcelain pestle, in order to achieve separation of components<sup>14</sup>
- d) For more detailed separation of the mortar components we performed mechanical removal of the binder material from the surface of the aggregates, with the use of lancet
- e) Then the separated material, was put on a series of sieves in order to continue the parting into fractions
- f) The contents of each sieve are weighed separately

The smaller fraction of sieves (<0.062mm), considered as the binder of the mortars, although sometimes can coexist in this aggregate amount. This is due either to the origin and type of aggregate, either carrying high pressure during the process of separation which resulted in grinding part of them. The particle size analysis shows the ratio of binder/aggregates.

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<sup>14</sup>Particular attention is needed during this process, as the use of excessive pressure can lead to undesirable breakage of aggregates (*Belfiore, et al., 2010*).

### 3.3 Scanning Electron Microscopy (SEM/EDS)

The Scanning Electron Microscopy (SEM) coupled to an Energy-Dispersive X-ray Spectroscopy is an analytical tool that is used for the elemental analysis of the examined sample.

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The obtained signal of the backscattered<sup>15</sup> and secondary<sup>16</sup> electrons is converted to an image. The magnification is ranging from 100 to 100,000 times. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample (Klein, et al., 2012) (Goldstein, et al., 1981)

Energy – dispersive x-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum (Goldstein, 2012).

Samples for SEM/EDS analysis were solid, bulk specimens of different size that was fit within the specimen chamber. For the preparation of the samples was carefully removed the surface layer by each sample from all the sides, in order to approach the inner part of the material which is free of deteriorations. A spot of the samples were coating with a ultrathin tape of electrically conducting material (carbon), which increase signal/noise ratio for samples of low atomic number ( $Z$ )<sup>17</sup>.

The interaction between the source of the X- ray excitation and the sample is translated to a spectrum where the characteristic peaks of the elements are determined.

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<sup>15</sup>Backscattered electrons: A fraction of the incident electrons is retarded by the electro-magnetic field of the nucleus and if the scattering angle is greater than 180°the electron can escape from the surface

<sup>16</sup> Secondary electrons: Generated from the collision between the incoming electrons and the loosely bonded outer electrons

<sup>17</sup>The improvement arises because secondary electron emission for high-Z materials is enhanced.

### 3.4 X-ray Diffraction Imaging (XRD)

By the method of X-ray diffractometer it is possible to directly measure both the angles and intensities of reflection of X-rays impinging onto the grid level of the crystals of different minerals. The method allows the identification of crystalline structure of a sample. Through this technique we conducted qualitative mineralogical analysis of seven mortar samples and six stone samples.

For the analysis of the mortar samples we use the grind material of the finest grain 0.062mm from the previous analysis of grain distribution, to analyze only the binder of the mortars. A fine powder less than 0.062 mm in size is produced by grinding stone samples in porcelain pestle. Subsequently powder (on a few tenths of a gram) placed into a sample holder.

The intensity of diffracted X-rays is continuously recorded as the sample and detector rotate through their respective angles. Results are presented as peak positions at  $2\theta$  and X-ray counts (intensity) in the form of a table or an x-y plot.

Because each mineral has a unique set of d-spacings, matching these d-spacings provides an identification of the unknown sample (Bish & Post, 1989). Files of d-spacings of minerals were available from the American Mineralogist Crystal Structure (AMCSD). This database is an integral portion of the software (X-Powder Ver. 2010.01.12 PRO) that comes with the instrumentation.

Although the XRD is useful for the identification of the crystalline component in the mortar, it is not sufficient for determining the total composition of an ancient mortar (Riccardi, et al., 1998)(Silva, et al., 2011).

#### Limitations of the method:

- a) A mineral in order to be detected, should be at a concentration greater than 5% although this limit depends on the type of compound and the presence of defects in its crystals (Moropoulou, et al., 1995).
- b) Furthermore, whereas exist non-crystalline phases (e.g. aluminum - silicates compounds, volcanic glasses of pozzolanic) in the sample, there are no clear peaks and the detection by diffractometer is not easy, as it is amorphous for the most part and are shown in graphs as noise (Yaseen, et al., 2013)

- c)* The amorphous components (such as soluble silicates formed during the hardening of hydraulic cement), which is usually very important in hydraulic mortars, not recognized or may cause problems in the recognition of the crystalline substances contained.
- d)* As the number of crystalline compounds increased is more difficult the determination of the results (Moropoulou, et al., 1995)

## 4. Results




### 4.1 Microscopic Examination



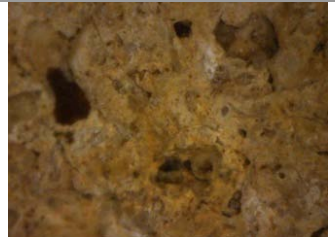







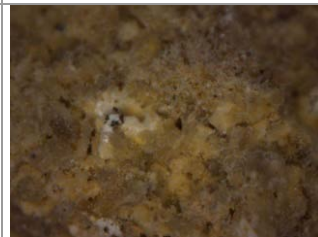







The morphological examination of the samples carried out using an Optical microscopy using a fiber optics system (FOM/i-scope, Moritex) (Moropoulou, et al., 2016). The photographic documentation with LED-OM, initiated from lower x50 to higher magnification x200. Through the optical microscope we can carry out a lot of information concerning the morphological characteristics and the preservation state of the samples.

#### 4.1.1 Stone Samples

Microscopic examination includes the identification of the grain size, their color, their distribution, and their cohesion with the cement, as well as the porosity of the material. Also observed the alterations sustained the structure and the composition of the rock. These parameters affect the physical and mechanical properties of the stones.

Table 18: Sandstone samples under digital microscope (LED)

Sandstone samples under Digital Microscope (LED)			
Sample	Magnification x10	Magnification x50	Magnification x200
1.1.S.In			







<b>2.3.S.Out</b>			
<b>3.4.S.In</b>			
<b>5.3.S.In</b>			
<b>6.4.S.In</b>			
<b>7.6.S.Out</b>			
<b>8.1.S.Out</b>			





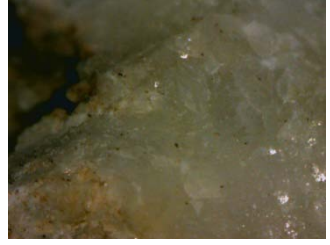



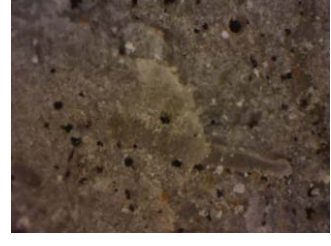

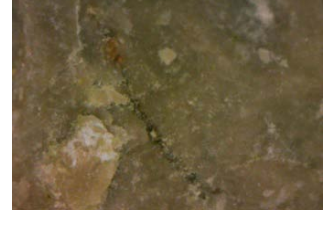
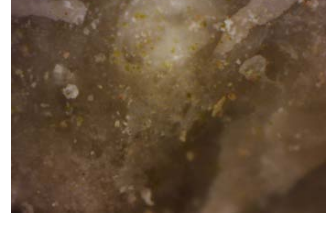
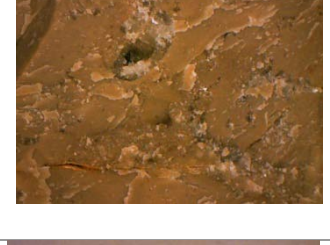





Sandstone's scale is simply too large to be studied microscopically. Individual layers are made visible mostly by the variation in grain size and by the differently colored (Jackson, 1997). Namely, all the sandstone samples are consist of light gray, whitish, beige rounded grains generally of the same size not to fine or coarse (medium). The most significant observation concerns the consistency of the aggregates with the binder. The consistency ranges from quite good to insufficient.

The sandstone binder's color is yellow-gray, and at places detected some orange points, possibly of the presence of iron oxides. Of interest are the various formations of calcite veins, crystals and microstructure which can be found in the same sample, characteristic of the complexity in the rock formation. Furthermore, in the majority of the samples detect their secondary porosity.

The characteristics of the porous structure of materials affect their mechanical properties and their behavior in the respective corrosive environment. We observe both closed (isolated from the surface of the stone) and open pores (linked to the surface of stones and is accessible from moisture) with most spherical and cylindrical shaped.

**Table 19: Limestone under digital microscope (LED)**

<b>Limestone under Digital Microscope (LED)</b>			
<b>Sample</b>	<b>Magnification x10</b>	<b>Magnification x50</b>	<b>Magnification x200</b>
<b>2.2.S.In</b>			
<b>2.2.S.Out</b>			

<b>3.2.S.In</b>			
<b>3.5.S.In</b>			
<b>4.2.S.In</b>			
<b>5.4.S.In</b>			
<b>6.2.S.In</b>			
<b>7.3.S.Out</b>			









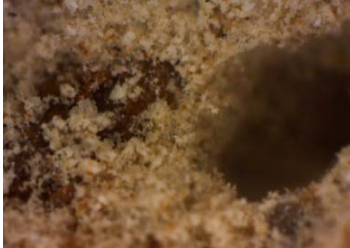
Limestone samples exhibit greater uniformity in the structure and profile, specifically identified veins to a limited extent, presents dense crystalline structure, consistency and homogeneity in the material, small porous, poor appearance of

yellowish - brown impurities (iron impurities) in the binder, and they have gray browning color.

#### 4.1.2 Mortar Samples

On microscopically examination we determined the color and nuances of binder and aggregates. The structure of the sample, i.e. the shape, size, color and the mode of engagement aggregates with binder material, the porosity, discontinuities and cracks, the presence of organic material.

Table 20: Structural mortars under digital microscope (LED)

Structural Mortars under Digital Microscope (LED)			
Sample	Magnification x10	Magnification x50	Magnification x200
1.2.M.In S(s)			
2.4.M.Out (S)			
4.1.M.In (S)			


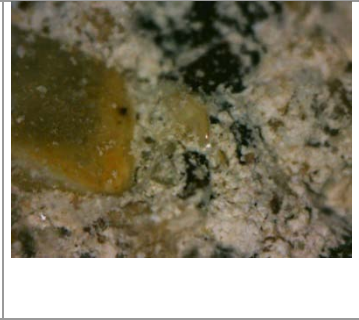





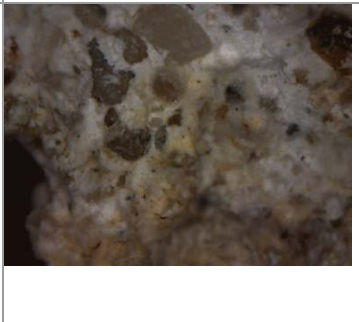


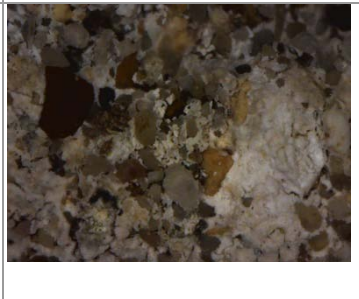


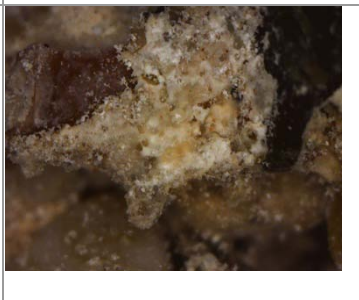

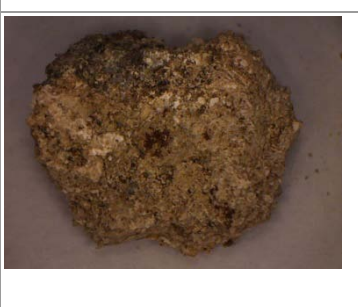

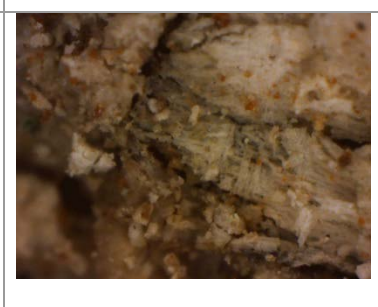




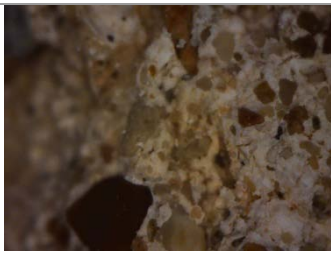

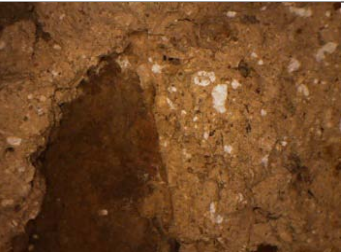

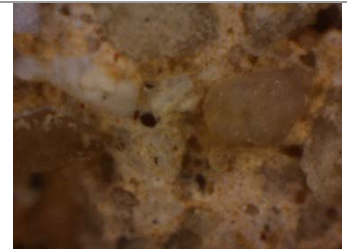



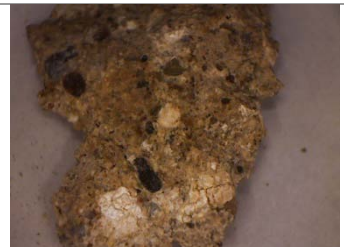

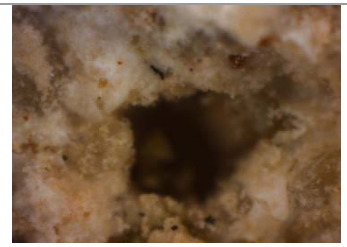
<p><b>5.2.M.In S(r)</b></p>			
<p><b>7.1.M.In (S)</b></p>			
<p><b>7.2.M.Out (S)</b></p>			
<p><b>8.2.M.Out S(r)</b></p>			
<p><b>8.3.M.Out S(s)</b></p>			
<p><b>8.4.M.Out S(s)</b></p>			

Table 20: Forehead - Structural mortars under digital microscope (LED)

Forehead - Structural Mortars under Digital Microscope (LED)			
Sample	Magnificationx10	Magnificationx50	Magnificationx200
2.1.M.Out			
3.1.M.In			
3.3.M.In			
4.3.M.In			
6.1.M.In			

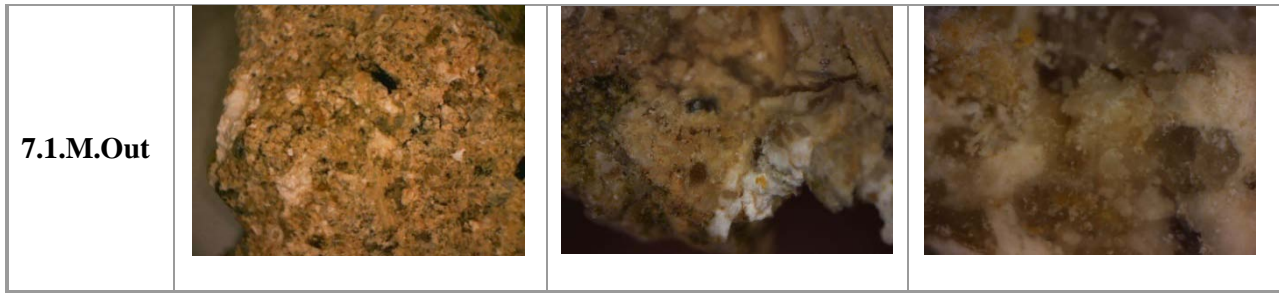

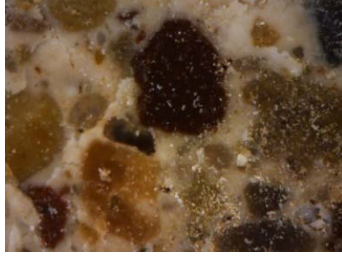






Table 21: Rendering mortars under Digital Microscope (LED)

Rendering Mortar under Digital Microscope (LED)			
Sample	Magnification x10	Magnification x50	Magnification x200
<b>5.1.M.In</b>			
<b>6.3.M.In</b>			

Mortar samples generally show medium adhesion with binder and they are not homogenous. Aggregates vary in particle size from sand for the most part, to few, small pebbles. Also, many samples are detected using crushed ceramic of various sizes which most of them have irregular shape with cracks. Mainly is observed good cohesion of the powder with small aggregates and the ceramic.

In some instances we can distinguish the surface separation of agglomerates from the binder network and other penetration in it. Instead the small pellets are rounded but they have a clear outline, although sometimes seem almost spherical. Their color is whitish and its composition appears to be homogeneous. It is most likely that they are agglomerates of lime.

The agglomerates identified in renderings are limited in size and amount, probably due to better quality of the lime and / or more of careful mixing ingredients. The

opposite occurs in structural mortars. Generally, their presence should be sought in the properties of slaked lime (calcium hydroxide), but also the ratio of water / lime (Lamprou, 2016). Insufficient curing of lime produces material with low plasticity. When this is combined with a small amount of water, the workability of the binder-aggregate mixture is more complicated. These conditions can lead to formation of agglomerates which upon carbonization converted into calcium carbonate pellets.

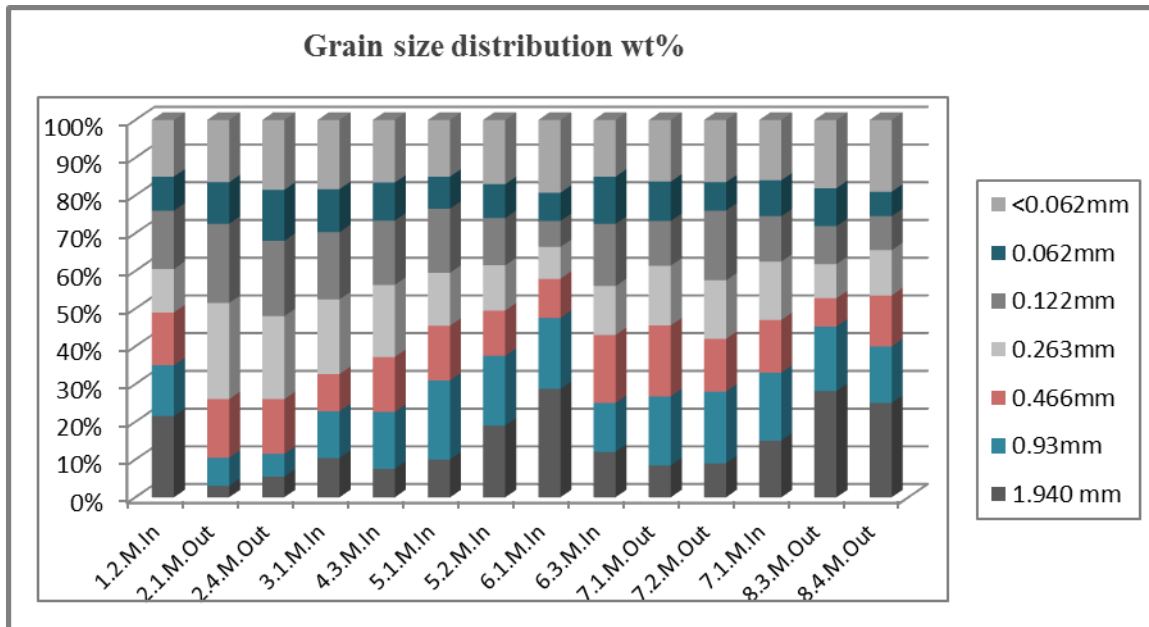
## 4.2 Grain Size Distribution

The physical classification of mortar ingredients gives the first evidence relating to the technical characteristics of the studied materials. From the resulting data create histograms of distribution of aggregates. Also determine the ratio of cement: aggregate (B / A) by weight, and the proportion of the binder. The *table 23* below is regarding the grain size distribution of all the categories of the mortar samples. We comment that there is no clear separation of the mortar categories in relation to the diameter and the participation rates of their aggregates. The coarsest grain mortars are the structural mortar sample from Zematistra (*8.3.M.Out*), and from Southern wall (*6.1.M.In*), this parts of the monument are consider that belong to the same construction phase (1<sup>st</sup> Ottoman Period).

Table 22: Grain size distribution of castle's mortar samples (retained quantities, wt %)

Grain size distribution, percentage (wt%) of the retained quantities							
Sample	1.940mm	0.93mm	0.466mm	0.263mm	0.122mm	0.062mm	<0.062mm
<b>1.2.M.In</b>	21.5	13.5	14	11.5	15.5	9	15
<b>2.1.M.Out</b>	3	7.5	15.5	25.5	21	11	16.5
<b>2.4.M.Out</b>	5.5	6	14.5	22	20	13.5	18.5
<b>3.1.M.In</b>	10.5	12.5	10	20	18	11.5	18.5
<b>4.3.M.In</b>	7.5	15	14.5	19	17	10	16.5
<b>5.1.M.In</b>	10	21	14.5	14	17	8.5	15
<b>5.2.M.In</b>	19	18.5	12	12	12.5	9	17
<b>6.1.M.In</b>	29	19	10.5	8.5	7	7.5	19.5
<b>6.3.M.In</b>	12	13	18	13	16.5	12.5	15
<b>7.1.M.Out</b>	8.5	18.5	19	16	12	10.5	16.5
<b>7.2.M.Out</b>	9	19	14	15.5	18.5	7.5	16.5

<b>7.1.M.In</b>	15	18	14	15.5	12	9.5	16
<b>8.3.M.Out</b>	28	17	7.5	9	10	10	18
<b>8.4.M.Out</b>	25	15	13.5	12	9	6.5	19



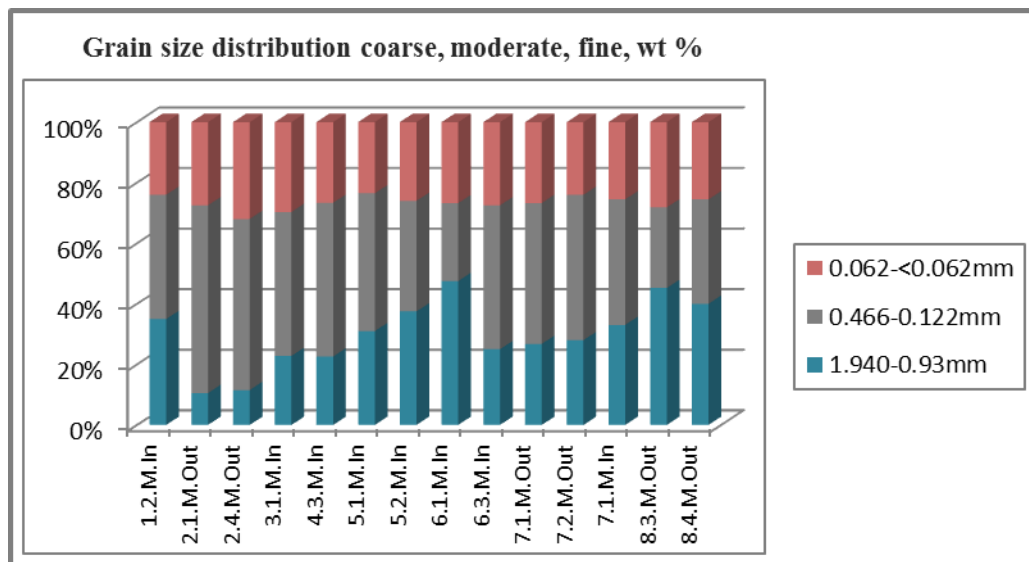
**Graph 1: Grain size distribution of the castle’s mortar samples, percentage (wt %) of the retained quantities.**

For optimum interpretation of the results, we proceeded to classification of the fractions into three groups, coarse (1.940-0.93mm), medium (0.466 - 0.122mm), and fine aggregates (0.062 - 0mm), the last group is considered as the binder material of the mortar. Also we determine the precipitation rate of binder, and the ratio of binder: aggregate (B/A) by weight.

**Table 23: Grain size distribution of mortar samples, classified in coarse, moderate and fine fractions, percentage (wt %) and B/A proportion**

<b>Grain size distribution of mortar samples, percentage (wt %)</b>				
<b>Sample</b>	<b>1.940-0.93mm</b>	<b>0.466 - 0.122mm</b>	<b>0.062 - 0mm</b>	<b>B/A</b>
<b>1.2.M.In</b>	35	41	24	1/3
<b>2.1.M.Out</b>	10.5	62	27.5	1/2.5
<b>2.4.M.Out</b>	11.5	56.5	32	1/2
<b>3.1.M.In</b>	23	48	30	1/2
<b>4.3.M.In</b>	22.5	50.5	26.5	1/3
<b>5.1.M.In</b>	31	45.5	23.5	1/3
<b>5.2.M.In</b>	37.5	36.5	26	1/3
<b>6.1.M.In</b>	48	26	27	1/2.5
<b>6.3.M.In</b>	25	47.5	27.5	1/2.5

<b>7.1.M.Out</b>	27	47	27	1/2.5
<b>7.2.M.Out</b>	28	48	24	1/3
<b>7.1.M.In</b>	33	41.5	25.5	1/3
<b>8.3.M.Out</b>	45	26.5	28	1/2.5
<b>8.4.M.Out</b>	40	34.5	25.5	1/3

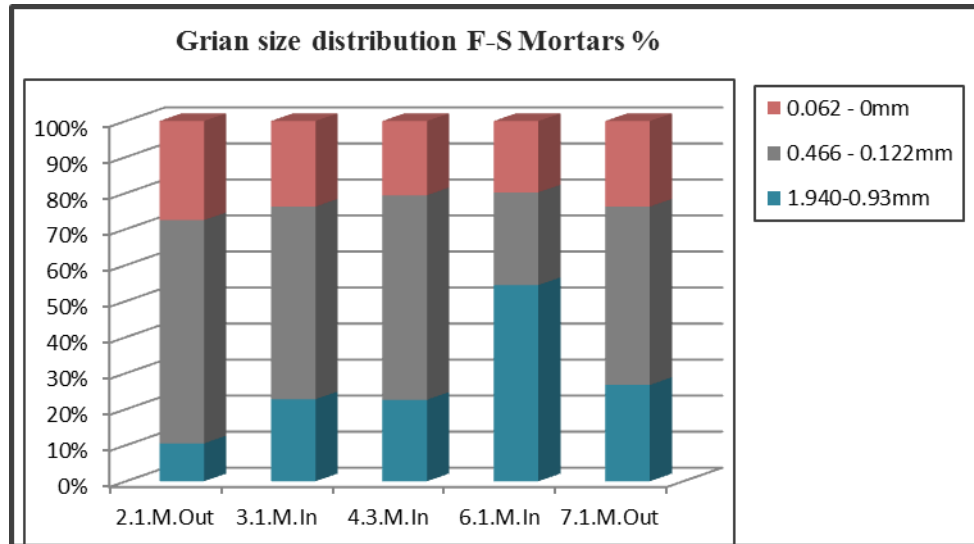


**Graph 2: Grain size distribution of mortar samples, classified in coarse, moderate and fine fractions, (wt %)**

We found that the samples from the northern wall (*2.1.M.Out*, *2.4.M.Out*) are much elevated proportion of medium aggregates, that *1.2.M.In*, *7.1.M.In*, *7.2.M.Out*, and *6.3.M.In* samples have an evenly distributed manner into the mortar, and finally that the *1.2.M.Out*, *7.2.M.Out*, *6.3.M.In*, *2.1.M.Out* samples, showing precisely the same percentage of fine aggregates (*table 24*, *graph 2*). The percentages of the contained binder exhibit variations from 24 – 32% average value of 28%.

From the analysis we identify that the binder / aggregate (B/A) proportions are 1/2 and 1/3 with very small fluctuations, although we study materials of different uses, for instance construction mortars or renderings and of different compositions, for instance those containing coarse or fine crushed ceramic and those not.

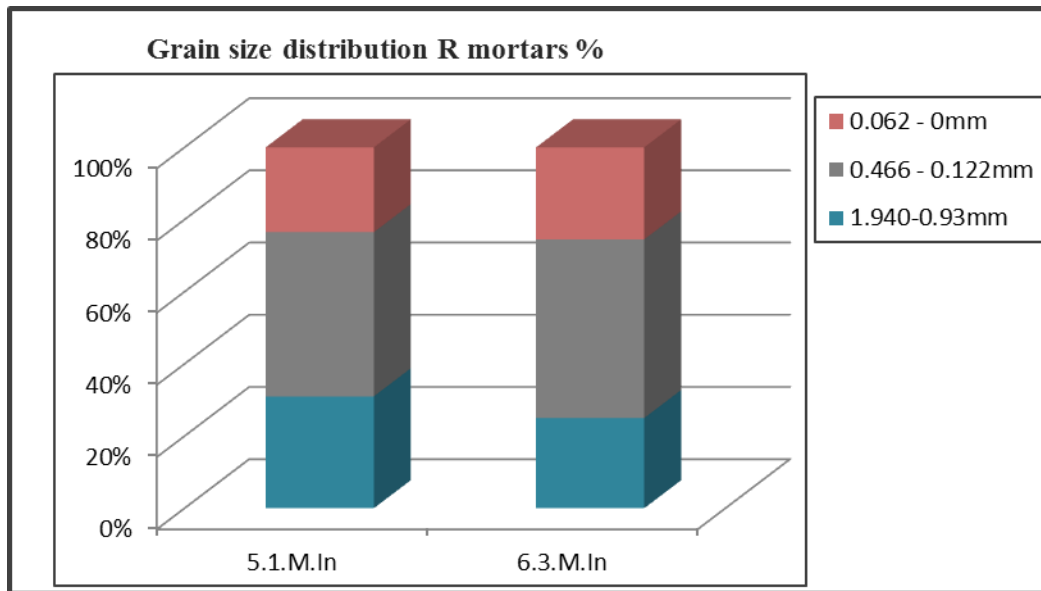
Forehead – Structural mortar samples: Observed similarities between the samples of NW Bastion (3.1.M.In), Bastion I (7.1.M.Out) and Western Wall (4.3.M.In) in relation to grain size distribution. On the other hand, sample from the southern wall (6.1.M.In) differs from the other forehead – structural mortars completely, is much coarser as well as sample 2.1.M.Out from the N wall is much finer (graph 3).



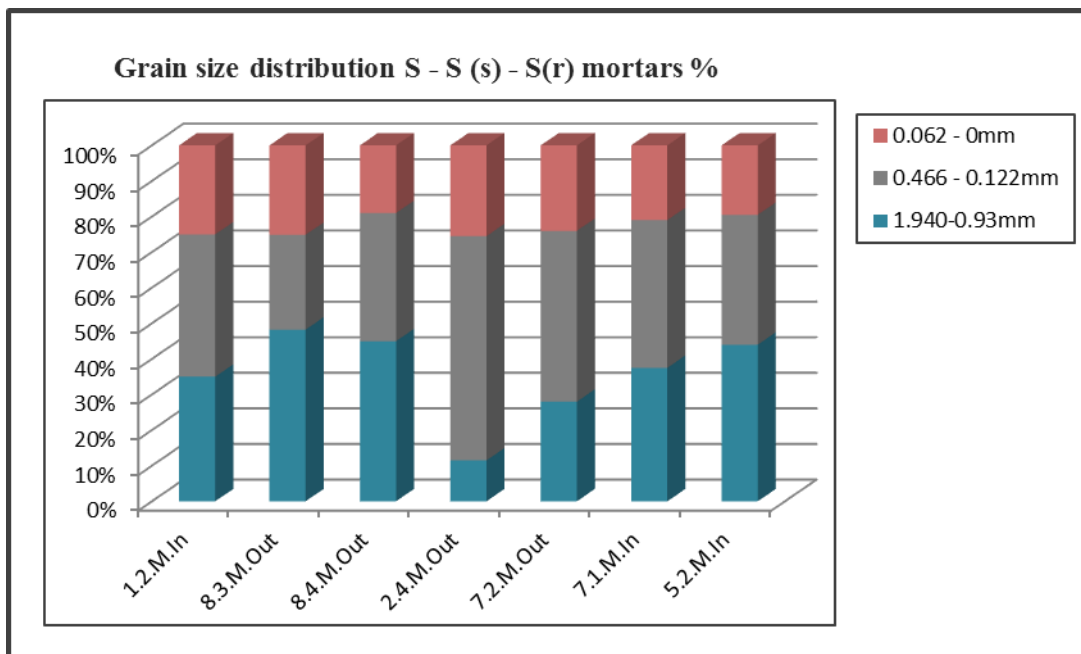
**Graph 3: Grain size distribution Forehead-Structural Mortars, wt %**

Structural mortar samples (graph 5): At samples 1.2.M.In and 7.1.M.In is observed good dispersion of all sizes. Precisely, we can identify that in the case of the reconstruction mortar of 7th Bastion (5.2.M.In) with 8.4.M.Out of “Zematistra” gate, there is similar size distribution of their aggregates which can be either random or denotes a single manufacturing phase. Furthermore, at these two samples is observed extremely low proportion of the fine aggregates, which may be is arising from their bad preservation state. Finally the sample which differs significantly from the others is 2.4.M.Out from the outside of Northern wall, presents greatly increased of the medium fraction.

Rendering mortar samples are from 7<sup>th</sup> Bastion and Southern wall have equal proportions in grain size distribution, and very good dispersion of them. They look like to belong at the same construction period.







**Graph 4: Grain size distribution of rendering mortars, wt %**





**Graph 5: Grain size distribution of Structural, Structural for sandstone blocks and restoration structural mortars, wt%**

Extremely helpful for deeper understanding of the manufacture techniques of our samples and for insightful interpretation of the analysis has been the visual observation of the coarse fractions of aggregates, in relation to the shape, color, and the amount of their participation (*table 26*).


**Table 25: Macroscopic observation of coarse aggregates (1.940 – 0.93mm), of structural mortars**


<b>Coarse aggregates in Structural Mortars</b>		
<b>Sample</b>	<b>Comments</b>	<b>Coarse grains (1.940- 0.93mm)</b>
<b>2.4.M.Out</b>	Aggregates: ceramic (fine grains), gray, green, beige, brown, both rounded and angular (mostly), fine material.	
<b>5.2.M.In</b>	Aggregates: locally coarse or fine grained, brown, yellow, red, beige, dark gray, both angular and rounded. It isn't a good distributed mortar.	
<b>7.1.M.In</b>	Aggregates: pale colors, yellow, beige, red, light and dark gray, green, pink, brown, angular shaped, coarse grained mortar.	
<b>7.2.M.Out</b>	Aggregates: brown, gray, red and green, coarse grains.	

**Table 26: Macroscopic observation of the coarse aggregates (1.940 – 0.93mm), structural mortars for sand stone blocks**




<b>Coarse aggregates in Structural mortars for Sandstone blocks</b>		
<b>Sample</b>	<b>Comments</b>	<b>Coarse grains (1.960, 0.966mm)</b>
<b>1.2.M.In</b>	Aggregates: ceramic granules (more coarse than fine), brown, yellow, red, dark gray, green, beige colors, both angular and rounded shaped, and sandstone pieces (coarse). Medium coarse grained.	
<b>8.3.M.Out</b>	Aggregates: coarse crushed ceramic, fairly coarse grained, the coarse aggregates are rounded pebbles, light and dark brown, green, off-white, yellow, light and dark gray. Smaller fragments are angular, many red, beige, gray, brown yellow. It is a thick mortar (many aggregates).	

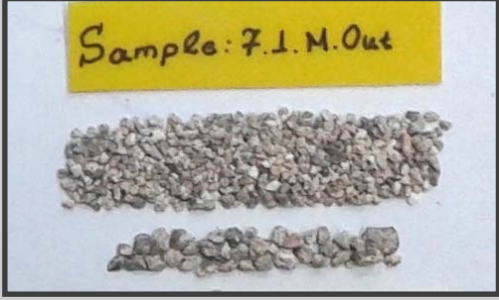
**Table 27: Macroscopic observation of coarse aggregates (1.940 – 0.93mm), in rendering mortars**

<b>Coarse aggregates in Rendering Mortars</b>		
<b>Sample</b>	<b>Comments</b>	<b>Coarse grains (1.940, 0.93mm)</b>
<b>5.1.M.In</b>	Aggregates: crushed stones dark gray, green, and brown. Fine grains of green, red, yellow, light gray, brown colors, a lot of small red grains from ceramic, is a thick mortar (enough inert).	

<p><b>6.3.M.In</b></p>	<p>Aggregates: beige, gray, brown, red, most of angular shaped, from stones crushing, fairly coarse, and crushed ceramics as inert material.</p>	
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**Table 28: Macroscopic observation of coarse aggregates (1.940 – 0.93mm), of forehead - structural mortars**

<p><b>Coarse aggregates in Forehead – Structural Mortars</b></p>		
<p><b>Sample</b></p>	<p><b>Comments</b></p>	<p><b>Coarse grains (1.960, 0.966mm)</b></p>
<p><b>3.1.M.In</b></p>	<p>Aggregates: brown, beige, orange, few gray, yellow, mainly angular shaped, fine and coarse crushed ceramic. Fine grained mortar.</p>	
<p><b>4.3.M.In</b></p>	<p>Aggregates: red, brown, green, gray, angular shaped grains, medium grained mortar.</p>	
<p><b>6.1.M.In</b></p>	<p>Aggregates: orange, beige, gray, brown, red, most of angular shaped, from stones crushing, fairly coarse, likely use crushed sandstone as inert material, coarse grain mortar.</p>	

<p><b>7.1.M.Out</b></p>	<p>Aggregates: not many coarse grains, brown, yellow, red, green, gray, beige, angular shaped, crushed ceramic, thick mortar.</p>	
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### 4.3 Surface Chemical Analysis (SEM – EDS)

At the Laboratory of Archaeometry at University of Peloponnese, Kalamata, Greece we performed the surface chemical analysis through a Scanning Electron Microscopy type JEOL JSM-6510LV coupled with an Oxford Instruments EDSEDS (Oxford Systems) provided the analytical data using the INKA software (Palamara, et al., 2015).

This analytical technique was used for detailed high resolution images of the microstructure and texture of the mortars and stones specimens and for elemental identification and quantitative compositional information. The measurements were carried out using accelerating voltage, of 20 keV, the collection time for the measurements was 120 sec and the magnification for bulk analysis ranging from x200 to x500 depending on the event that we want to study, and the type of sample (stone or mortar).

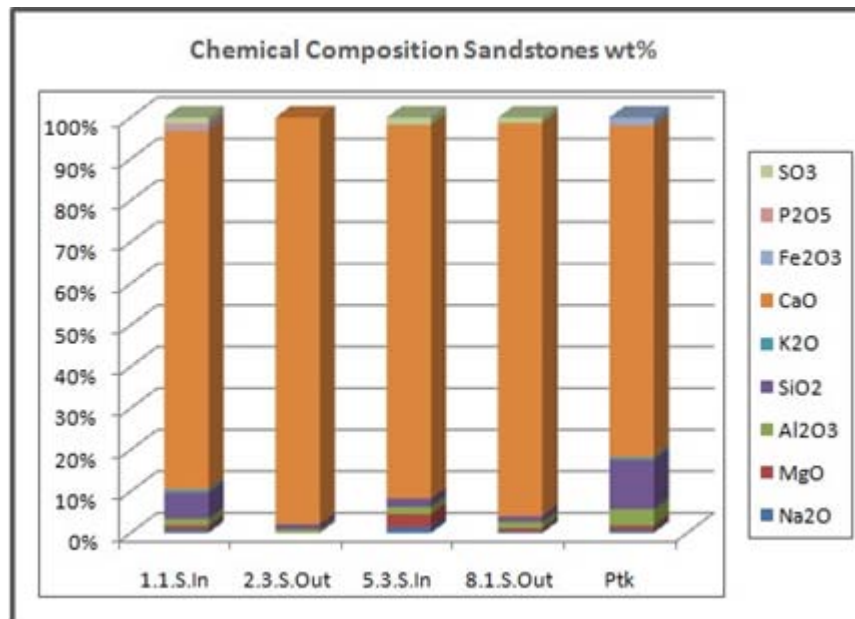
Bulk analysis of oxide concentration (wt%) for 15 mortar samples, 7 stone samples, and 2 referent stone samples from Pylos region was carried out. The chemical characterization was significantly important in this study, for the classification and identification of samples. Also surface modification and microtopography were also studied thoroughly. Generally, at the following micrographs of the studied samples, the lightly colored zones correspond to that of nearly pure Ca-carbonate, the darker zones are rich in silica, and the black zones corresponding to the porosity.

The bulk analysis and the micrographs of mortar and stone samples from the castle and from the region of Pylos are shown in the tables below.

### 4.3.1 Stone Samples

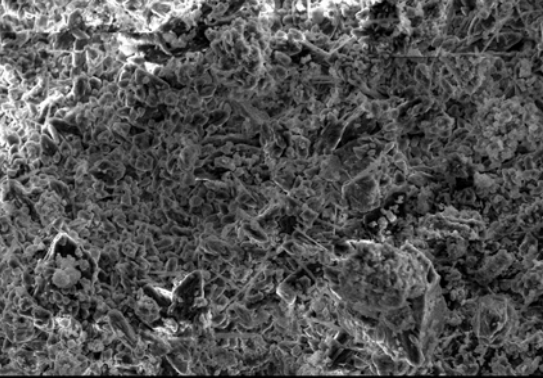
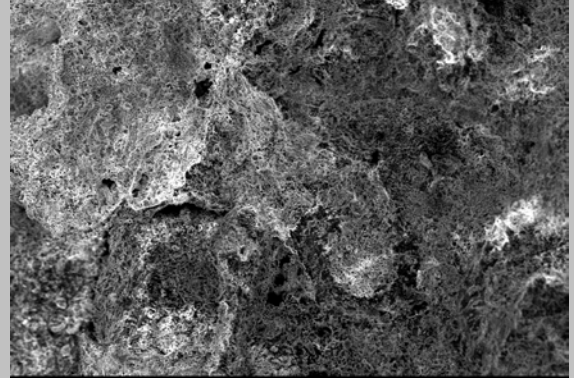
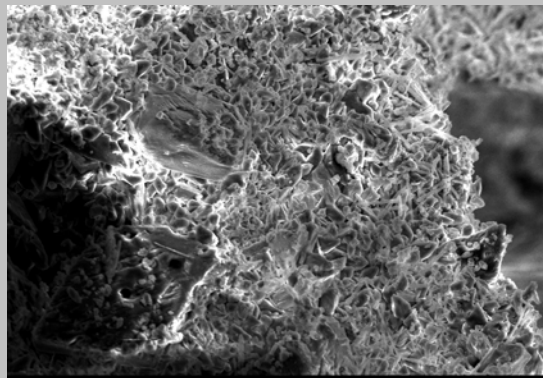
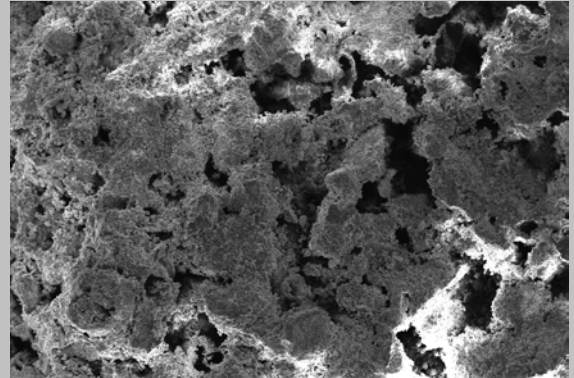
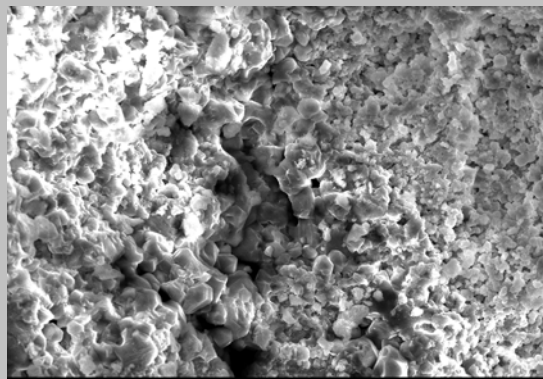
Table 29: Chemical composition, major oxides of sandstone samples (SEM/EDS), wt%

Sample	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K	CaO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Total
1.1.S.In	0.84	0.95	1.68	6.31	0.77	88.57	0.74	1.04	1.44	100
2.3.S.Out	n.d.	n.d.	0.79	1.32	n.d.	97.8	n.d.	n.d.	n.d.	100
5.3.S.In	1.35	3.3	1.85	2.05	n.d.	92.79	n.d.	n.d.	1.8	100
8.1.S.Out	0.44	0.67	1.55	1.50	n.d.	96.86	n.d.	n.d.	1.36	100
Ptk	0.75	1.05	3.84	11.74	0.62	79.28	1.78	n.d.	n.d.	100

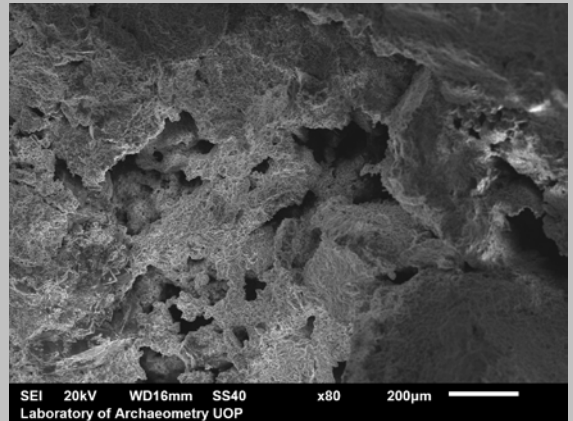
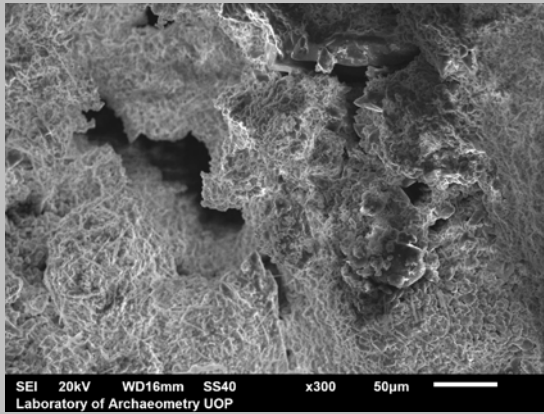
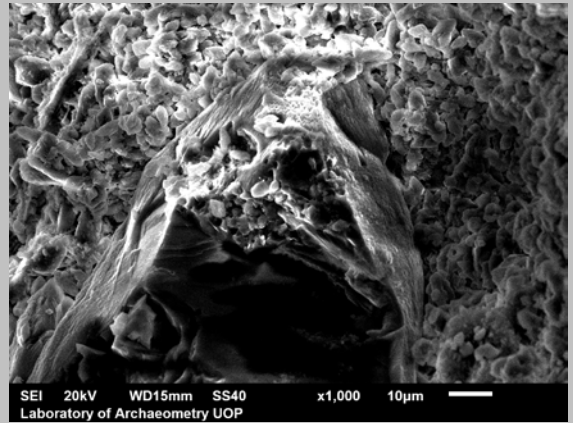
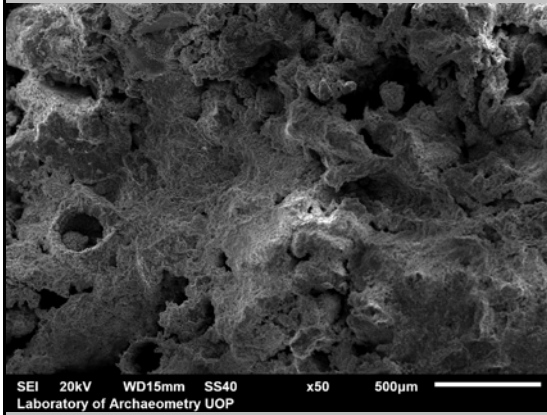


Graph 6: Chemical composition of Sandstone (bulk analysis), wt%.

Table 30: Micrographs of sandstone samples under SEM Microscopy

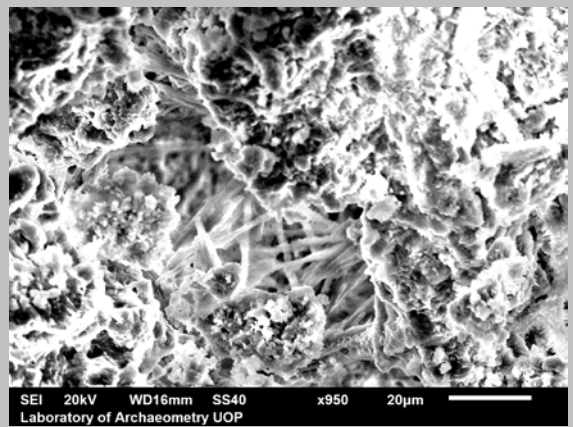
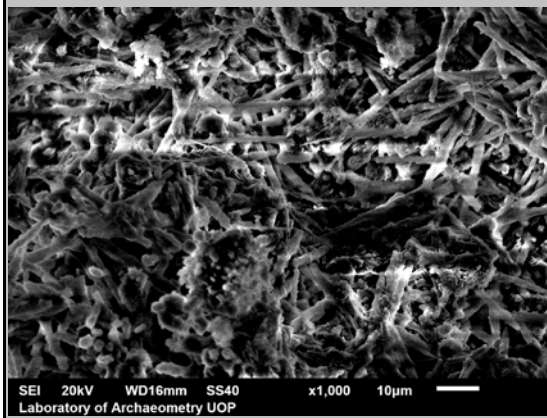
Sample	Sandstone Samples under SEM microscopy	
<p><b>1.1.S.In</b></p>	 <p>SEI 20kV WD16mm SS40 x500 50µm Laboratory of Archaeometry UOP</p>	 <p>SEI 20kV WD16mm SS40 x100 100µm Laboratory of Archaeometry UOP</p>
	 <p>SEI 20kV WD18mm SS40 x500 50µm Laboratory of Archaeometry UOP</p>	 <p>SEI 20kV WD16mm SS40 x30 500µm Laboratory of Archaeometry UOP</p>
	<p>Needle fibers, silicate and calcitic grains, calcitic binder, dendritic crystallites, calcite – rhombohendral crystals, high porosity</p>	
	<p><b>2.3.S.Out</b></p>	 <p>SEI 20kV WD14mm SS40 x1,000 10µm Laboratory of Archaeometry UOP</p>
<p>Calcareous binder, medium porosity, homogenous binder</p>		

**5.3.S.In**



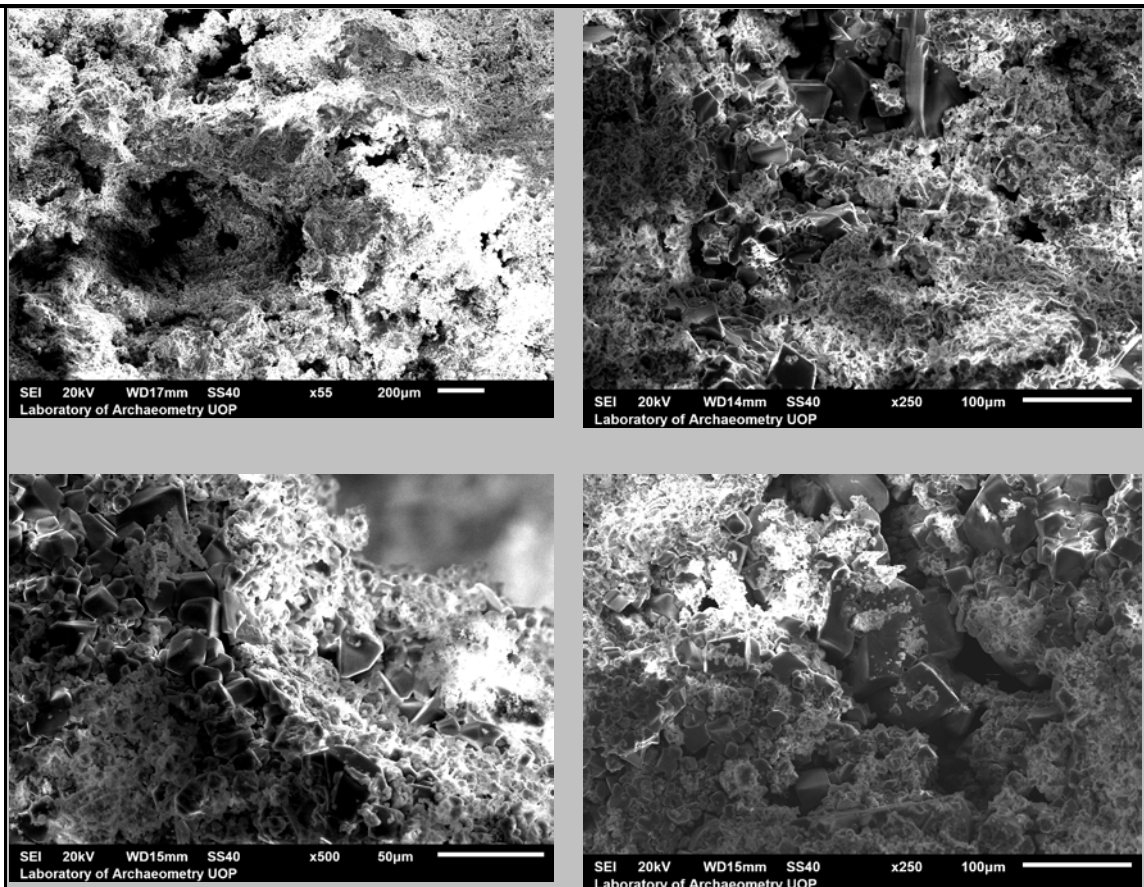
Large porosity, calcareous binder, siliceous and calcareous grains, not distinguished borders of cement and grains.

**8.1.S.Out**



Calcareous binder, needle fiber, hydraulic reactions

Ptk

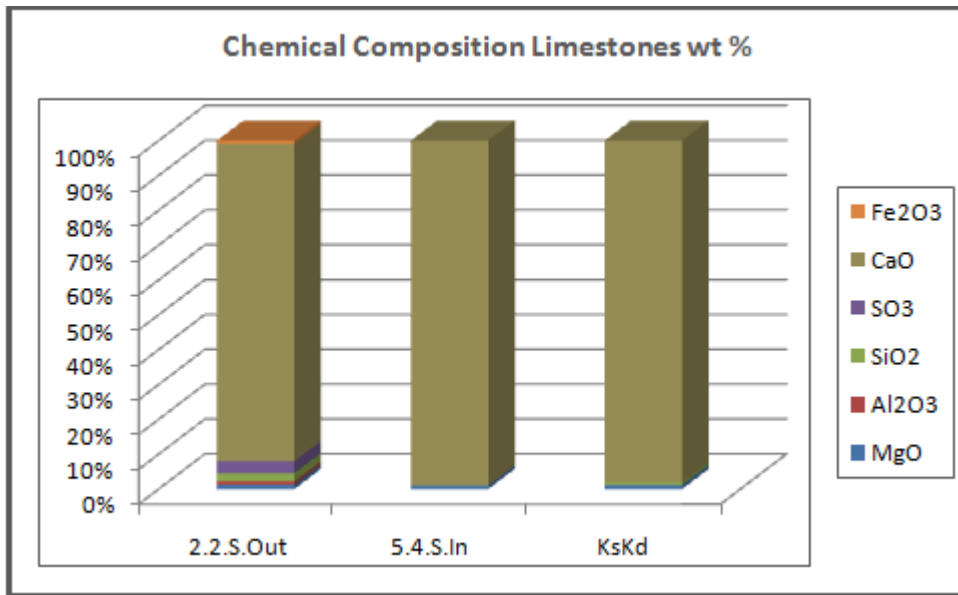


Large porosity, silicate – calcareous grains, hydraulic reactions, good cohesion binder-grains, sparry calcite, clastic texture

Sandstones in general consist of high proportions of Calcite oxides (86-96%), and traces of Si, Al, Mg, and K oxides. Through micrographs we can describe sandstone rocks as clastic coarse grained lime-stones. Sand mainly consisting of limestone fragments, form from the cementation of sand and/or mud by calcite. Each specimen presents variety in the crystalline phases of calcite, in the distribution and the size of the porous in the matrix and in the grain composition and morphology. Furthermore the morphology and the chemical composition of the reference sandstone sample (Ptk) match with the outcomes of the sample *1.1.S.In* from the Main gate.

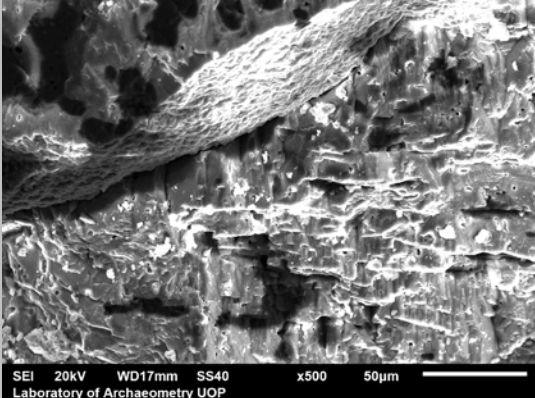
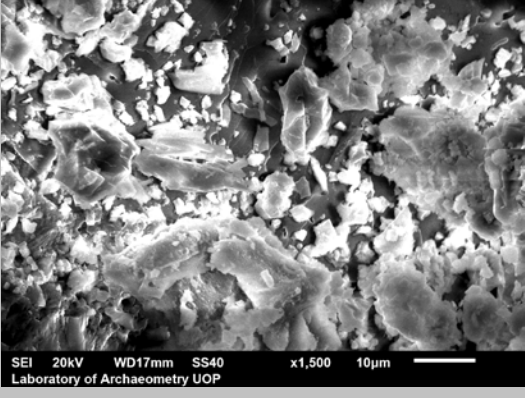
Table 31: Chemical composition, major oxides present on lime-stone samples (SEM/EDS), wt%.

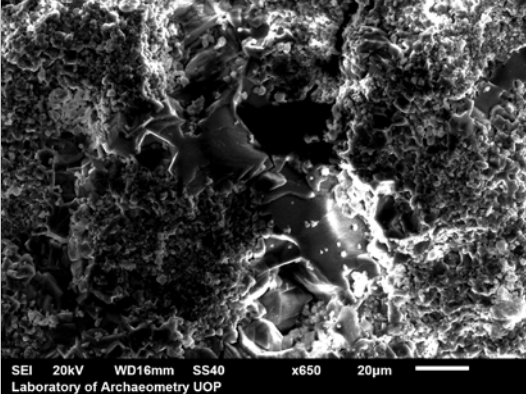
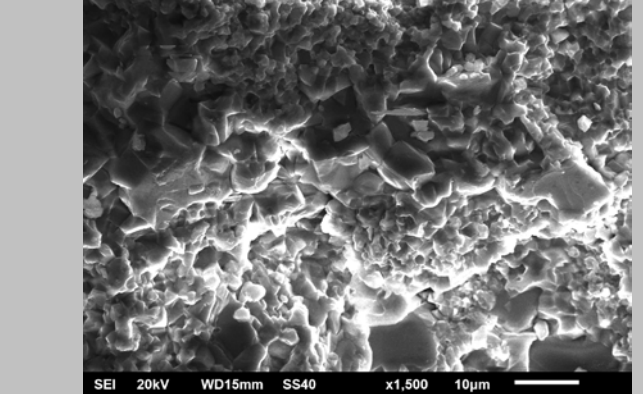
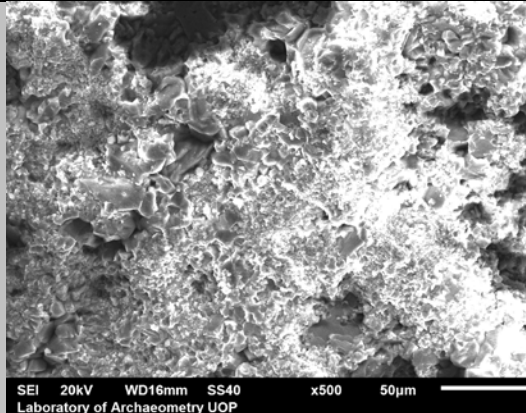
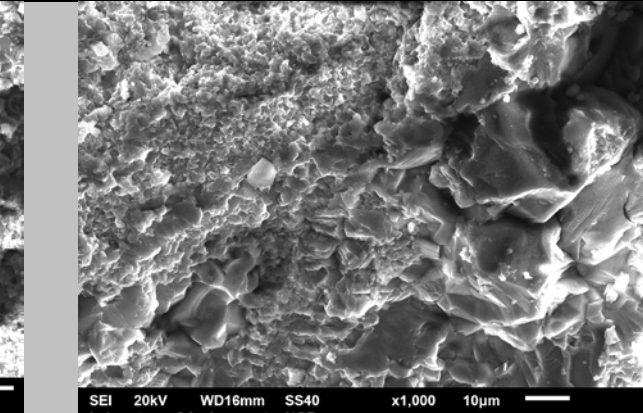
Samples	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Total
2.2.S.Out	1.28	0.98	2.49	3.52	94.8	0.97	100
5.4.S.In	0.94	n.d.	n.d.	n.d.	99.06	n.d.	100
KsKd	1.11	n.d.	0.77	n.d.	98.12	n.d.	100



Graph 7: Chemical composition of limestone samples with reference sample KsKd (bulk analysis), wt%.

Table 32: Micrographs of limestone samples under SEM Microscopy

Lime-stone samples under SEM Microscopy	
2.2.S.Out	  <p>Calcitic binder, small porosity, crystallized material, calcitic microcrystal, different crystalline phases in the specimen.</p>

<p><b>5.4.S.In</b></p>	 <p>SEI 20kV WD16mm SS40 x650 20µm Laboratory of Archaeometry UOP</p>	 <p>SEI 20kV WD15mm SS40 x1,500 10µm Laboratory of Archaeometry UOP</p>
<p>Calcareous binder, crystallized material, calcite microcrystal, low porosity, quartz grains with cracks on their surface, gypsum grains.</p>		
<p><b>KsKd</b></p>	 <p>SEI 20kV WD16mm SS40 x500 50µm Laboratory of Archaeometry UOP</p>	 <p>SEI 20kV WD16mm SS40 x1,000 10µm Laboratory of Archaeometry UOP</p>
<p>Calcite microcrystals, low porosity, non - clastic texture, polycrystalline material, crystals of quartz.</p>		

Lime stones consist of high proportion of calcite oxides (94-99%), and traces of Al, Mg, Si, Fe oxides. Lime stones samples of the Niokastro are characterized as a high purity material. Also the analyzed fracture surfaces of the lime stone specimens present highly crystalline texture.

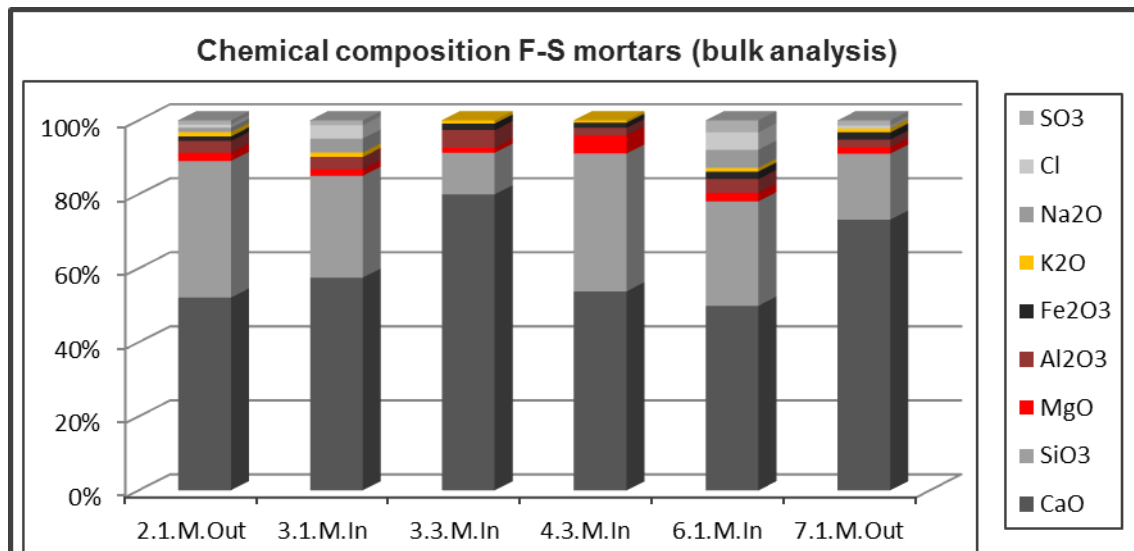
#### *4.3.2 Mortar Samples*

Mortars can be analyzed under SEM/EDS in a lot of different ways, such as through a separation of their components (binder and aggregates) or shuttering samples in resins, we performed bulk analysis to untreated samples, with x200 - x300 magnification. Making a chemical analysis of the binder alone and as a whole is

probably impossible, because it is closely intermixed with the aggregate. The tables below provide the chemical composition of the mortar samples through the bulk analysis, which correspond to the matrix (both binder and aggregates) chemical composition.

**Table 33: Chemical composition of major oxides present on the Forehead – Structural mortars (SEM/EDS, bulk analysis (binder and aggregates), in wt%).**

Sample	CaO	SiO <sub>3</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Cl	SO <sub>3</sub>	Type
2.1.M.Out	52.31	37.09	2.23	3.19	1.26	1.16	1.14	0.9	1.16	F-S
3.1.M.In	57.49	27.49	1.79	3.34		1.22	3.74	3.58	1.36	F-S
3.3.M.In	79.98	11.32	1.28	4.82	1.75	0.9				F-S
4.3.M.In	54.38	37.76	4.88	2.12	1.39	0.66				F-S
6.1.M.In	49.88	28.24	2.29	3.74	2	1.03	4.82	4.8	3.22	F-S
7.1.M.Out	74.86	18.27	1.78	2.09	2.03	1.13		0.81	1.41	F-S

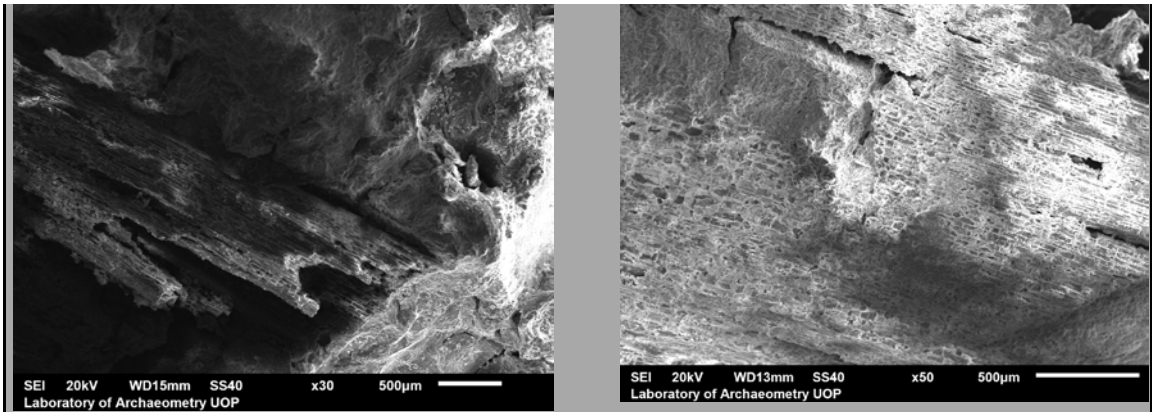


**Graph 8: Chemical composition of forehead – structural mortars (bulk analysis)**

Table 24: Micrographs of the Forehead – Structural mortars (SEM)

Sample	Forehead – Structural mortars under SEM Microscopy	
2.1.M.Out		
<p>Large porosity, silicate – calcareous aggregates, sodium bicarbonate, not good cohesion aggregate-binder.</p>		
3.1.M.In		
<p>Good cohesion, microcrystal of calcite, lime body, silicate - calcareous aggregates, homogenous material, moderate porosity, hydraulic reactions.</p>		
3.3.M.In		
<p>Calcareous material with limited silicate aggregates, irregular micrometric structure.</p>		

<p><b>4.3.M.In</b></p>		
<p>Large porosity, good cohesion binder - aggregates, it is not easy to separate binder from aggregates may be of the same composition.</p>		
<p><b>6.1.M.In</b></p>		
<p>Silicate aggregates, sodium bicarbonate, good cohesion,</p>		
<p><b>7.1.M.Out</b></p>		



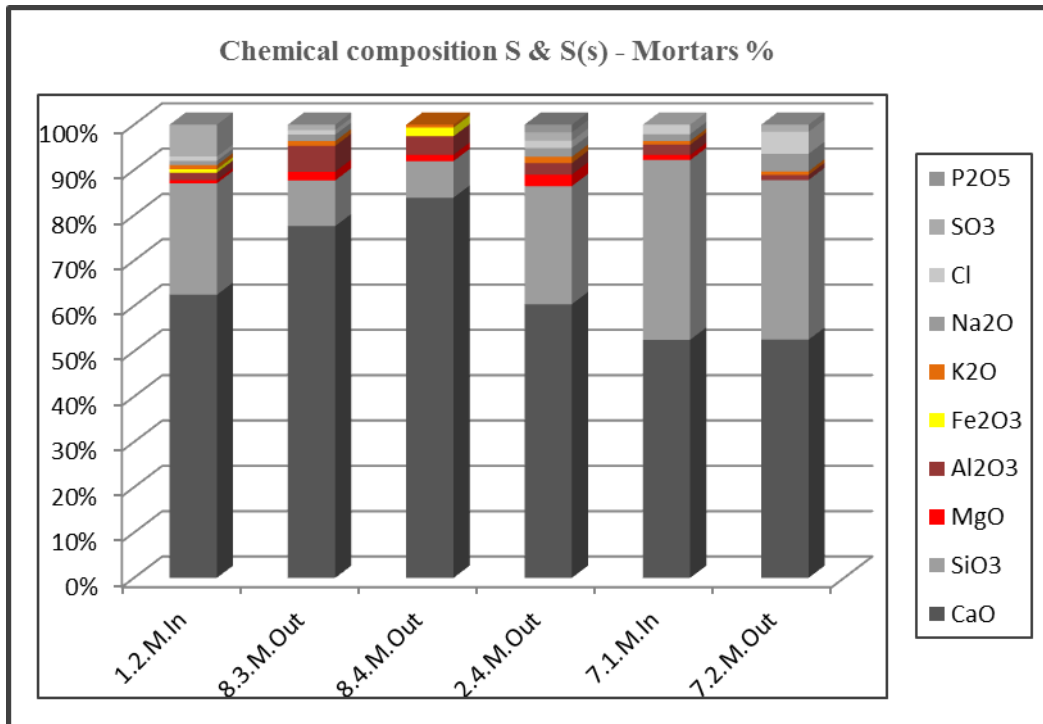
Large porosity, it is not easy to separate binder from aggregates may be of the same composition, good cohesion, crushed aggregate, organic inert.

A first general and important observation in relation to the process of the analysis is that the binder can be very heterogeneous within one mortar sample. If some analysis reveals composition near to that of pure C-S-H, other analysis within the same sample reveals areas that are much poorer in SiO<sub>2</sub>. Also, the presence of chlorides and sulfates with amounts of nitrates in mortar samples suggest an origin of salts caused by contamination/ pollution coming from environmental conditions - pollution.

From the results of the analyzed forehead-structural mortar samples we notice that the mortar samples mainly consist of calcium and silicate oxides with low proportions of aluminum, potassium, magnesium and iron oxides which are an indication of clay materials. The inclusions could be interpreted as silicate and calcite minerals. Specifically, mortar specimens of the north wall (*2.1.M.Out*), of the NW bastion (*3.1.M.In*) of the W wall (*4.3.M.In*) and of the south wall (*6.1.M.In*) are of the same chemical composition, with percentages of lime 50-57% and 28-37% silica, it seems that belong to the same construction period. The rest two samples from Bastion I (*7.1.M.Out*) and from NW bastion (*3.3.M.In*) compared with the other mortars of the same category they have lower proportion of silicate oxides and higher proportion of CaO. Finally, the samples from N wall (*6.1.M.In*) and from NW bastion (*3.1.M.In*) are presented as more corroded as corrosive agents of Na, S, Cl oxides are in increase proportions in contrast with the south wall's sample (*4.3.M.In*) and the second sample of NW bastion(*3.3.M.In*) which presented as unaffected.


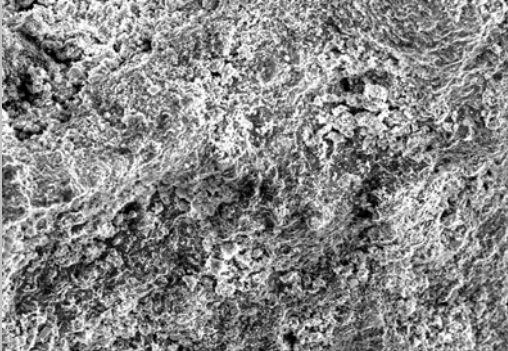
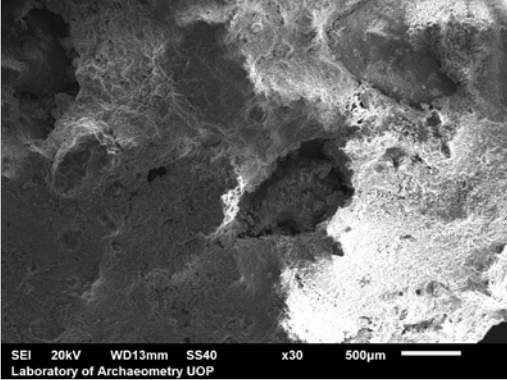
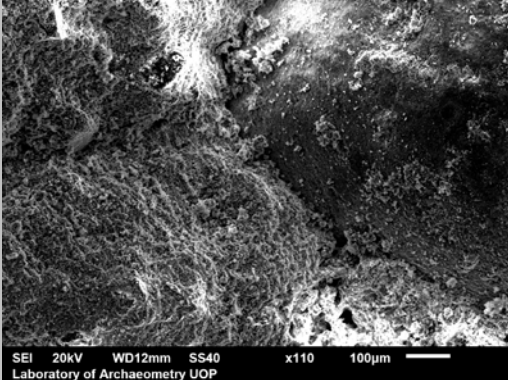
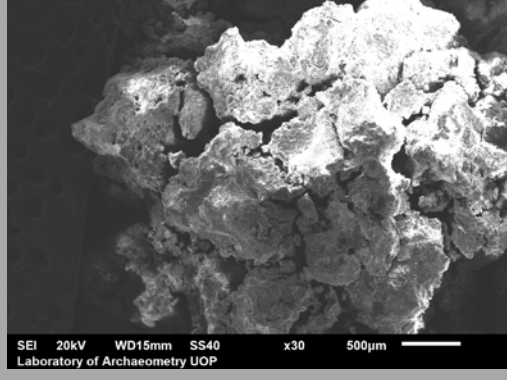
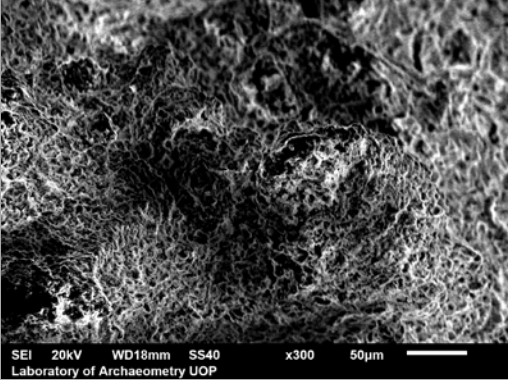
**Table 35: Chemical composition of major oxides present on the Structural mortars (SEM/EDS, bulk analysis (binder and aggregates) in wt%)**

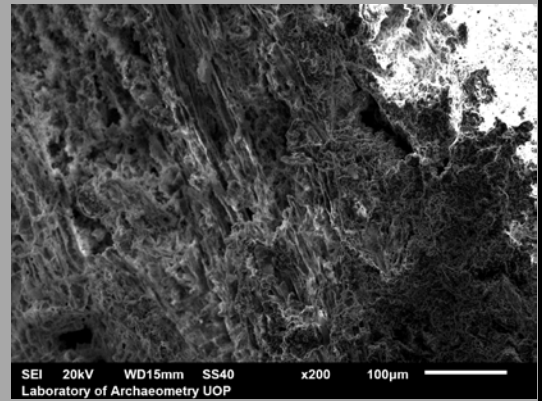
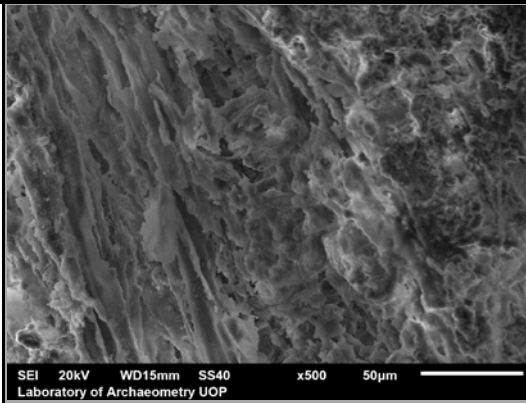
Sample	CaO	SiO <sub>3</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Cl	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Type
1.2.M.In	63.28	24.95	0.65	1.72	0.72	0.94	0.95	0.98	7.12		S (s)
8.3.M.Out	77.02	10.01	1.91	5.66		1.04	1.39	1.05	1.15		S (s)
8.4.M.Out	84.93	8.16	1.42	4.12	1.93	0.66					S (s)
2.4.M.Out	61.25	26.42	2.58	2.57		1.41	1.95	1.66	1.88	1.7	S
7.1.M.In	53.12	40.09	1.13	2.3		0.83	1.52	2.1			S
7.2.M.Out	52.96	35.52		1.12		0.81	3.88	4.93	1.56		S



**Graph 9: Chemical composition of structural and structural mortars for sandstones, wt%**

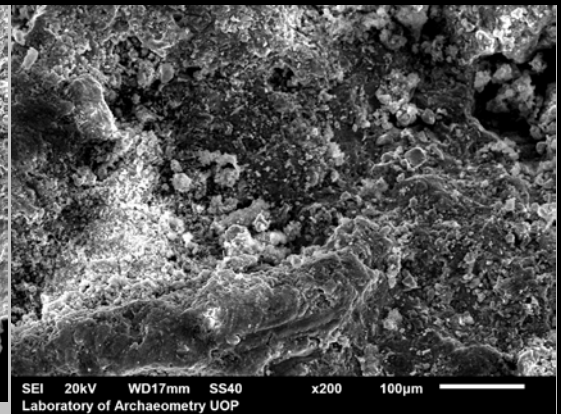
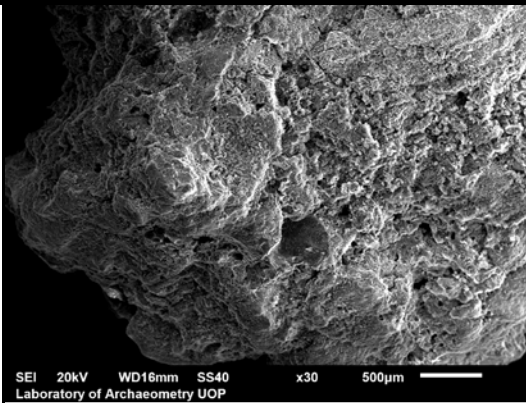
Table 25: Micrographs of the Structural mortars (SEM)

Sample	S – S(s) mortars under SEM Microscopy	
1.2.M.In		
<p>Good cohesion, sodium, coarse silicate aggregate angular shaped, moderate porosity, hydration reactions.</p>		
8.3.M.Out		
<p>Good cohesion, sodium, coarse silicate aggregate angular shaped, moderate porosity, homogenous material.</p>		
8.4.M.Out		



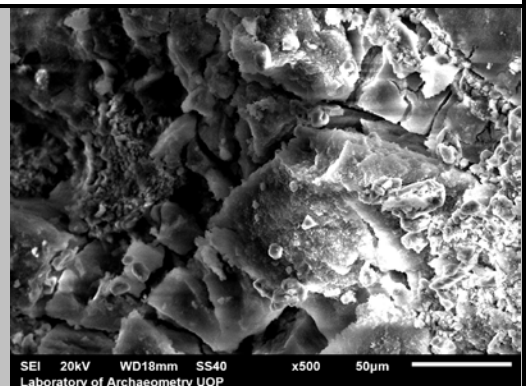
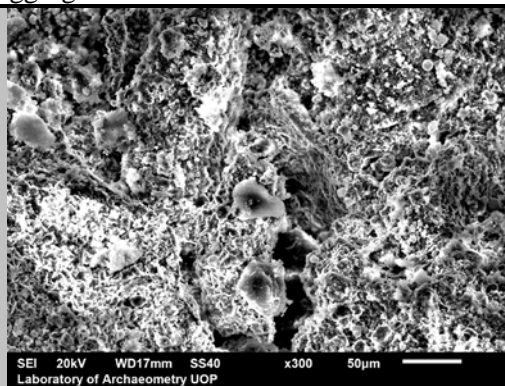
Dentrical fiber resulting from the extensive weathering state of the mortar, it is not easy to separate binder from aggregates may be of the same composition, large porosity, not good cohesion.

**2.4.M.Out**

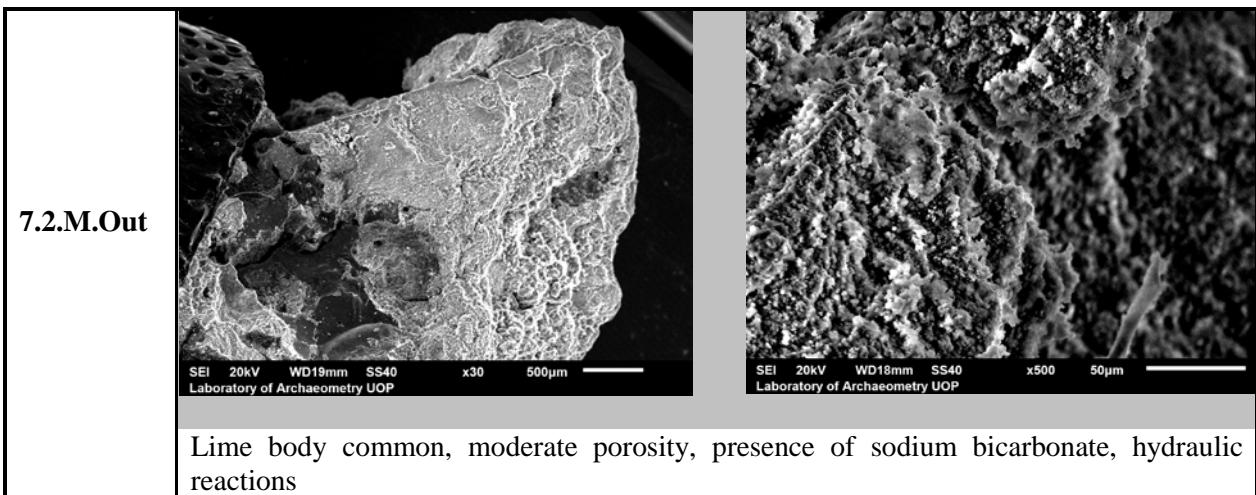


Sodium bicarbonate, good cohesion, not distinguishing the stitching boundaries of aggregates-binder, the binder is homogenized, good mixing, siliceous-calcareous aggregates.

**7.1.M.In**



Hydraulic reactions, lime body common, not distinguishing the stitching boundaries of aggregates-binder, calcite-rhombohedral, not homogenous material, corrosion products

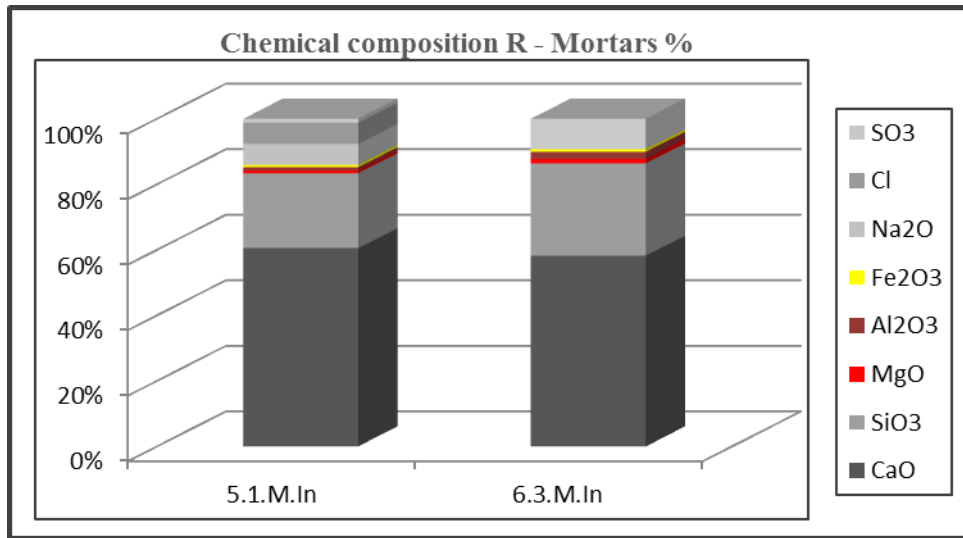


The observations of the structural mortar samples according to their chemical composition are that the main constitute oxides are the calcium and silicon oxides and traces of aluminum, potassium, iron, and magnesium oxides. Furthermore, the extracting observations are that specimens from Bastion I, inside and outside (*7.1.M.In and 7.2.M.Out*), have the same proportioning rates of oxides, and similar to the prevailing percentages of the upper analyzed F-S mortar samples (53% CaO and 35-40% Si<sub>2</sub>O). Noticeable is the difference between these two specimens according their preservation state, specifically the mortar of the external face of the Bastion I shows higher rates in corrosive agents (Na, S, Cl oxides) than the inside sample.

Concerning the mortar samples for jointing the sandstone blocks which are from the two gates (Main gate and Zematistra) we observe differences at their quantitative chemical composition this recognition can be randomly due to the diversity of mortars composition or we can assume that the two gates belong to a different construction phases. “Zematistra” gate’s sample (*8.4.M.Out*) presents the lowest rate of Si<sub>2</sub>O (16%) and the highest rate of CaO (85%) in relation to all the other studied mortar samples.

**Table 26: Chemical composition of major oxides present in rendering mortars (determined by SEM/EDS, bulk analysis (binder and aggregates) in wt%**

Sample	CaO	SiO <sub>3</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Cl	SO <sub>3</sub>	Type
<b>5.1.M.In</b>	60.51	22.84	0.78	1.06	0.65	6.43	6.46	1.23	R
<b>6.3.M.In</b>	58.07	28.11	1.25	2.24	0.8			9.3	R



Graph 10: Chemical composition of rendering mortars

Table 38: Micro-topography of rendering mortars (determined by SEM bulk analysis)

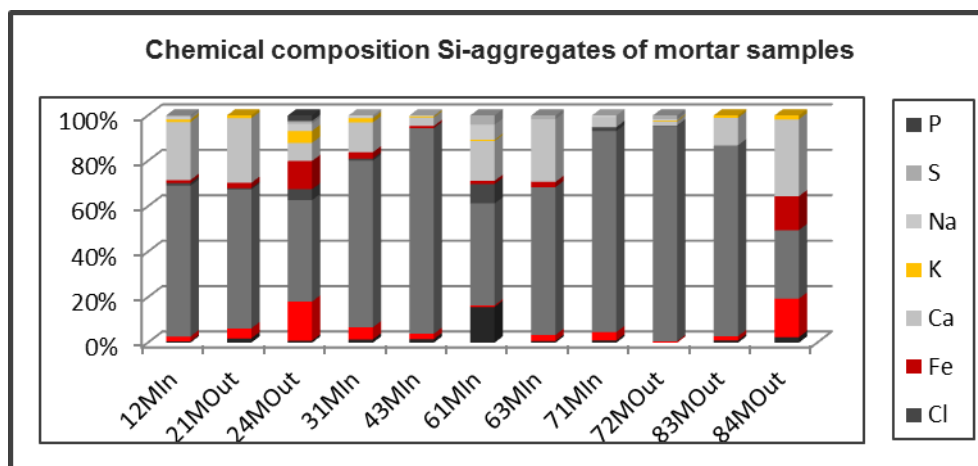
Sample	Micro-topography of the Rendering mortars	
5.1.M.In		
	Needle fiber from hydration processes, good cohesion, not distinguishing the stitching boundaries of aggregates-binder, presence of sodium bicarbonate.	
6.3.M.In		
	Angular aggregates, sodium bicarbonate, large porosity, needle fibers	

The two rendering samples from the south wall (6.3.M.In) and the 7<sup>th</sup> Bastion (5.1.M.In) exhibit similar properties both in relation to their microstructure by microscopic observation (SEM) and by the results of their chemical composition which is nearly identical. Also in contrast with the two other categories of mortar samples (S and F-S) they present lower proportion in Si<sub>2</sub>O which probably means less precipitation of silicate aggregates in their matrix.

In the areas wherein located coarse aggregates, by increasing the magnification we can extract information about their chemical composition. Inclusions show a core with high silicon and aluminum contents could be interpreted as silicate minerals (table 39).

Table 27: Chemical composition of coarse aggregates in the matrix of mortar samples

Sample	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>3</sub>	Cl	Fe <sub>2</sub> O <sub>3</sub>	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
1.2.M.In	0.57	2.14	66.37	1.12	1.34	25.53	1.13	1.32	0.47	
2.1.M.Out	1.84	4.43	61.15	0.56	2.36	28.42	1.26			
2.4.M.Out	0.85	17	44.02	4.72	12.26	7.88	5.19	3.19	1.13	2.39
3.1.M.In	1.43	5.33	73.39	0.84	2.82	13.15	1.89	1.15		
4.3.M.In	1.54	2.36	90.55		0.92	3.73	0.52	0.4		
6.1.M.In	15.74	0.68	44.85	8.54	1.42	17.48	0.6	6.66	4.02	
6.3.M.In	0.73	2.67	65.06		2.29	27.65			1.6	
7.1.M.In	0.92	3.69	88.52	1.7		4.19		0.95		
7.2.M.Out		0.62	94.77	0.22		1.74	0.43	0.54	1.68	
8.3.M.Out	0.93	1.91	84.01			12.09	1.06			
8.4.M.Out	2.42	16.9	30.19		14.92	33.83	1.74			



Graph 11: Chemical composition of Si-aggregates of mortar samples

## 4.4 X-ray Diffraction (XRD)

For the mineralogical analysis was used in-Xitu BTX benchtop XRD/XRF instrument connected to a computer unit, on which becomes the process of the registration and identification of the results through the X-Powder Ver. 2010.01.12 PRO software. The diffractometer worked with a  $\text{CoK}\alpha$  radiation, instead of the most common used  $\text{CuK}\alpha$  and so there is a slight variation in the grades of the  $2\theta$  peaks used to identify minerals. The analysis took place at the laboratory of Metal objects, of the department of Conservation of Antiquities and Works of Art, at Technological Educational Institute of Athens (TEI Athens).

The analysis conducted at the binder ( $<0.062\text{mm}$ ) of seven mortar specimens, at the aggregates of 3 of the upper mortar samples, at 5 stone samples and finally at 3 reference stone samples of the region of Pylos. Mineralogical composition of its sample presented in the followings tables and charts.

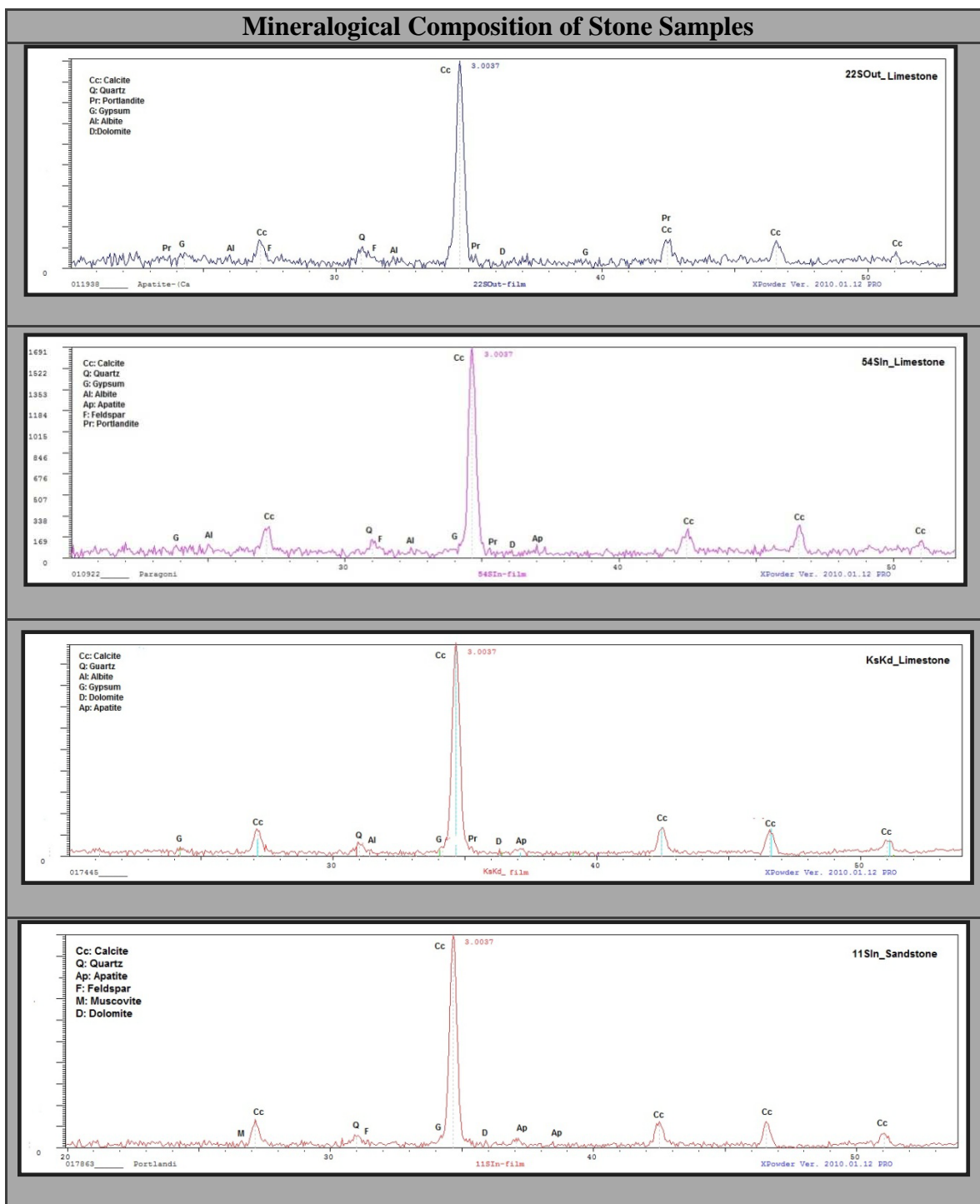
### 4.4.1 Stone Samples

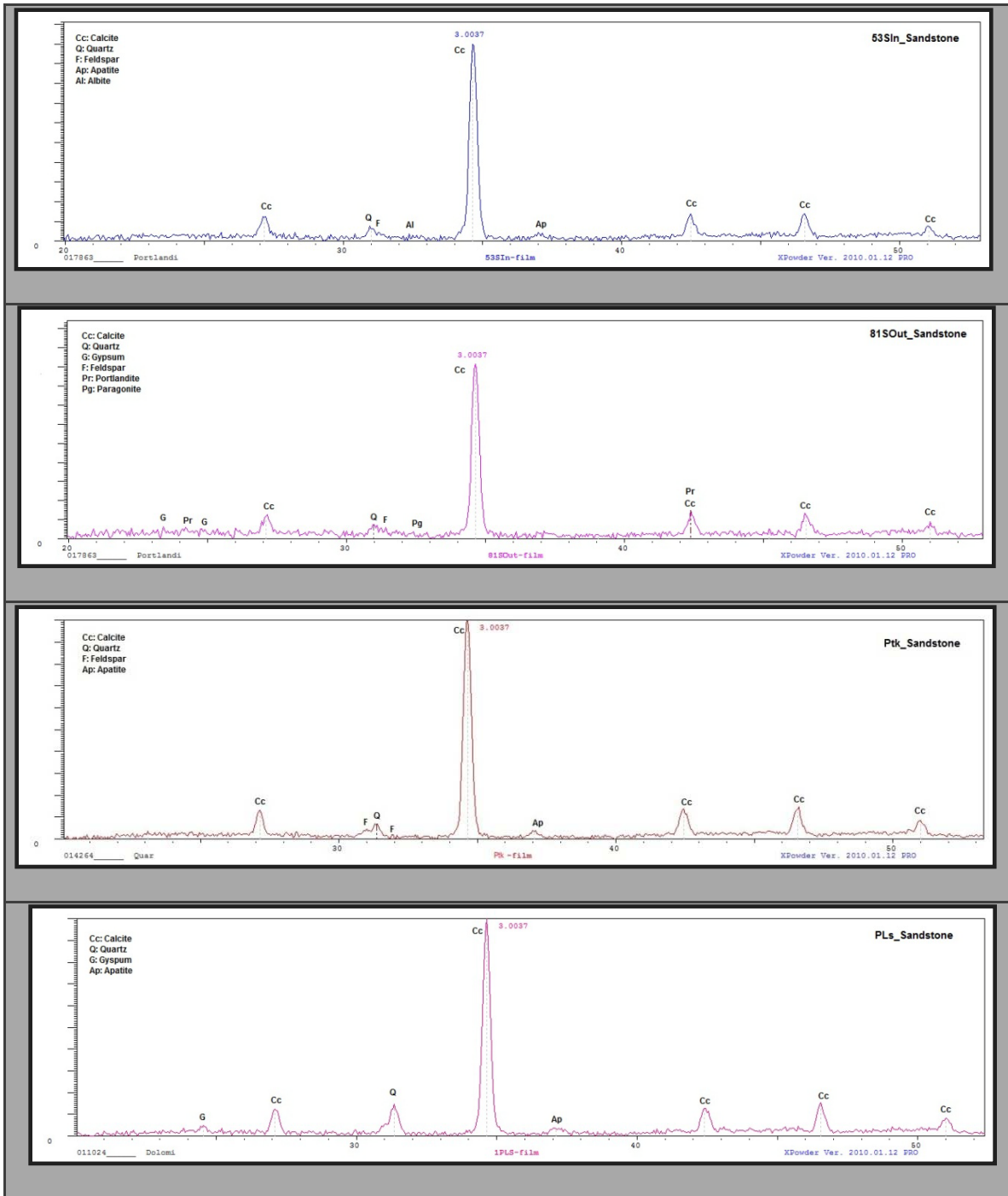
Table 28: Mineralogical composition, structural stone samples and reference stone samples

Sample	Main Peaks	Secondary Peaks
<b>2.2.S.Out(L)</b>	Calcite	Quartz, Portlandite, Gypsum, Albite, Dolomite
<b>5.4.S.In(L)</b>	Calcite	Quartz, Gypsum, Albite, Apatite, Feldspar, Portlandite
<b>KsKd (L)</b>	Calcite	Quartz, Albite, Gypsum, Apatite, Dolomite
<b>1.1.S.In(S)</b>	Calcite	Quartz, Apatite, Feldspar, Muscovite, Dolomite
<b>5.3.S.In(S)</b>	Calcite	Quartz, Feldspar, Albite, Apatite
<b>8.1.S.Out(S)</b>	Calcite	Quartz, Paragonite, Portlandite, Gypsum, Feldspar
<b>Ptk (S)</b>	Calcite	Quartz, Feldspar, Apatite
<b>PLs (S)</b>	Calcite, Quartz	Gypsum, Apatite

Limestone(L), Sandstone (S), Calcite ( $\text{CaCO}_3$ ), Quartz ( $\text{SiO}_2$ ), Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), Feldspar ( $\text{KAlSi}_3\text{O}_8$ ), Albite ( $\text{NaAlSi}_3\text{O}_8$ ), Apatite ( $\text{CaOH}$ ,  $\text{CaF}$ ,  $\text{CaCl}$ ), Paragonite ( $\text{Al}_3\text{NaH}_2\text{Si}_3\text{O}_{12}$ ), Portlandite ( $\text{Ca}(\text{OH})_2$ ), Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ).

**Table 29: Graphs illustrate mineralogical composition of castle's stone samples and of referenced stone samples from Pylos region.**





By the results of mineralogical study of the castle's construction stones, we observe that regardless of the type of stones (lime-stone and sandstone) consist mainly of calcite ( $\text{CaCO}_3$ ) with small amounts of quartz impurities. Calcium carbonate react with water that is saturated calcium bicarbonate ( $\text{Ca}(\text{HCO}_3)_2$ ). This reaction is important in the erosion of carbonate rock, forming caverns. Dolomite is common in hydrothermal vein deposits and in sedimentary rocks.

Sandstones formed from cemented sand-sized clast, the cement that binds clasts is mainly from calcite. Calcite cemented sandstones are subject to acidic dissolution and are more easily eroded than the silica cemented sandstones.

Significant finding of the analysis is that the mineralogical composition of the reference stone samples (PLs, Ptk, KsKd) with the construction stones of the castle have same mineralogical composition. This finding is consistent with the primary assessment of the origin of the castle building materials from locally available materials.

#### 4.4.2 Mortar Samples

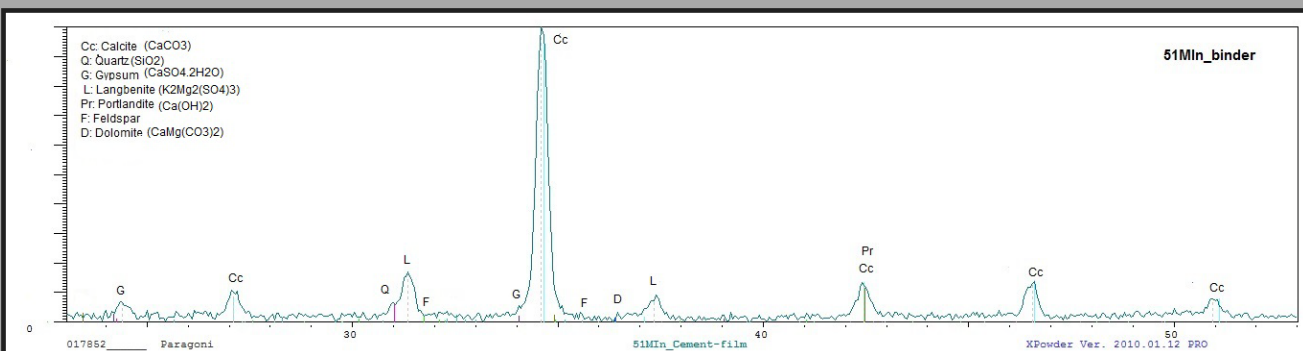
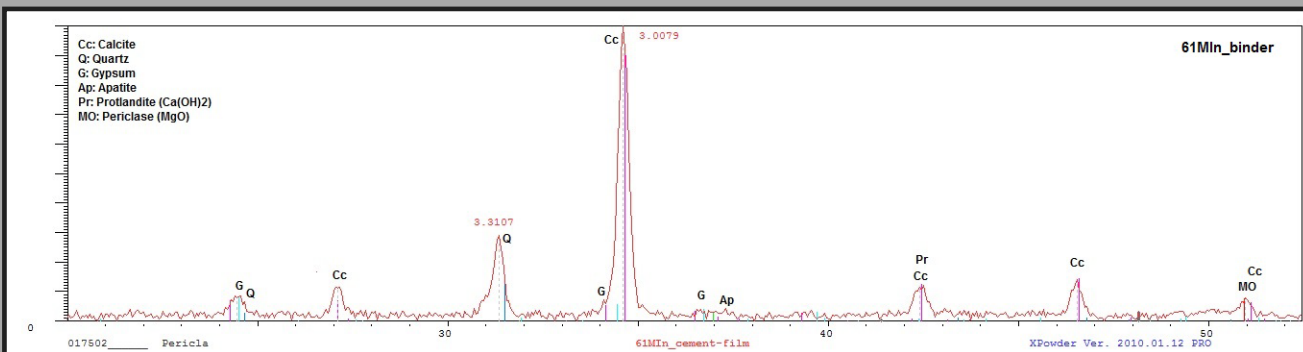
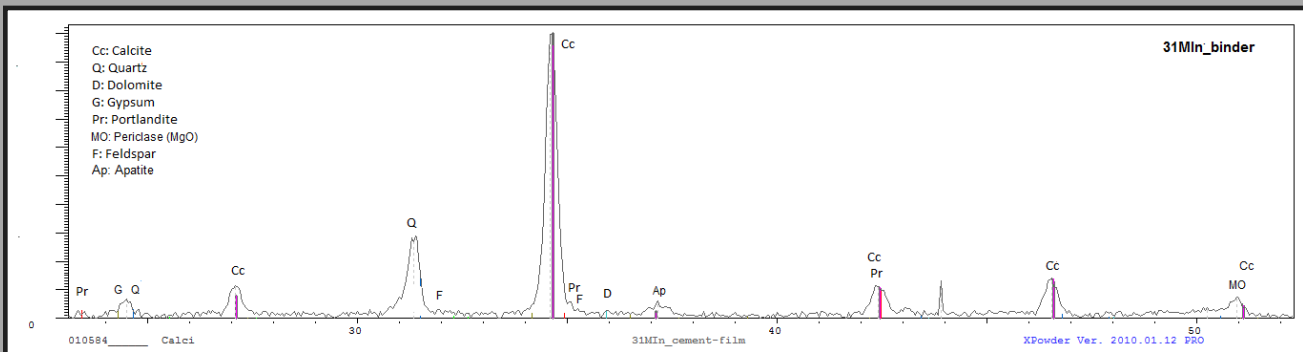
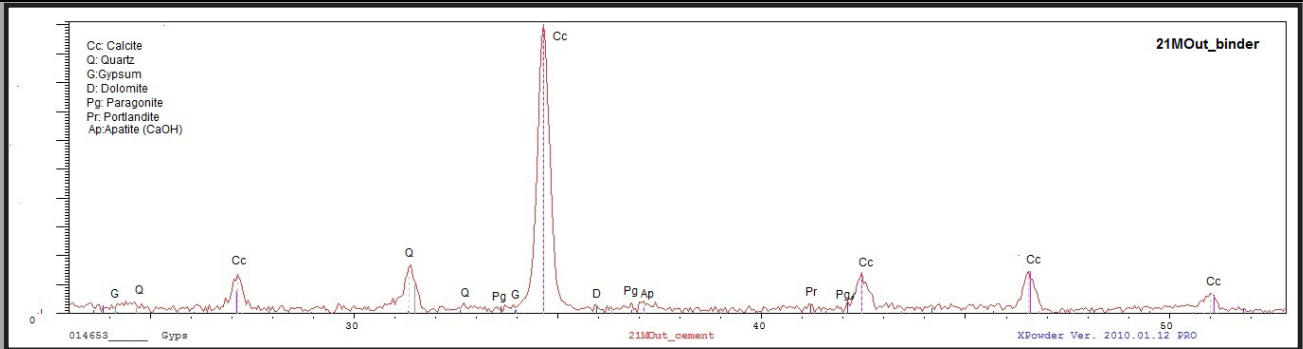
**Table 30: Mineralogical composition of binding material of historic mortar samples**

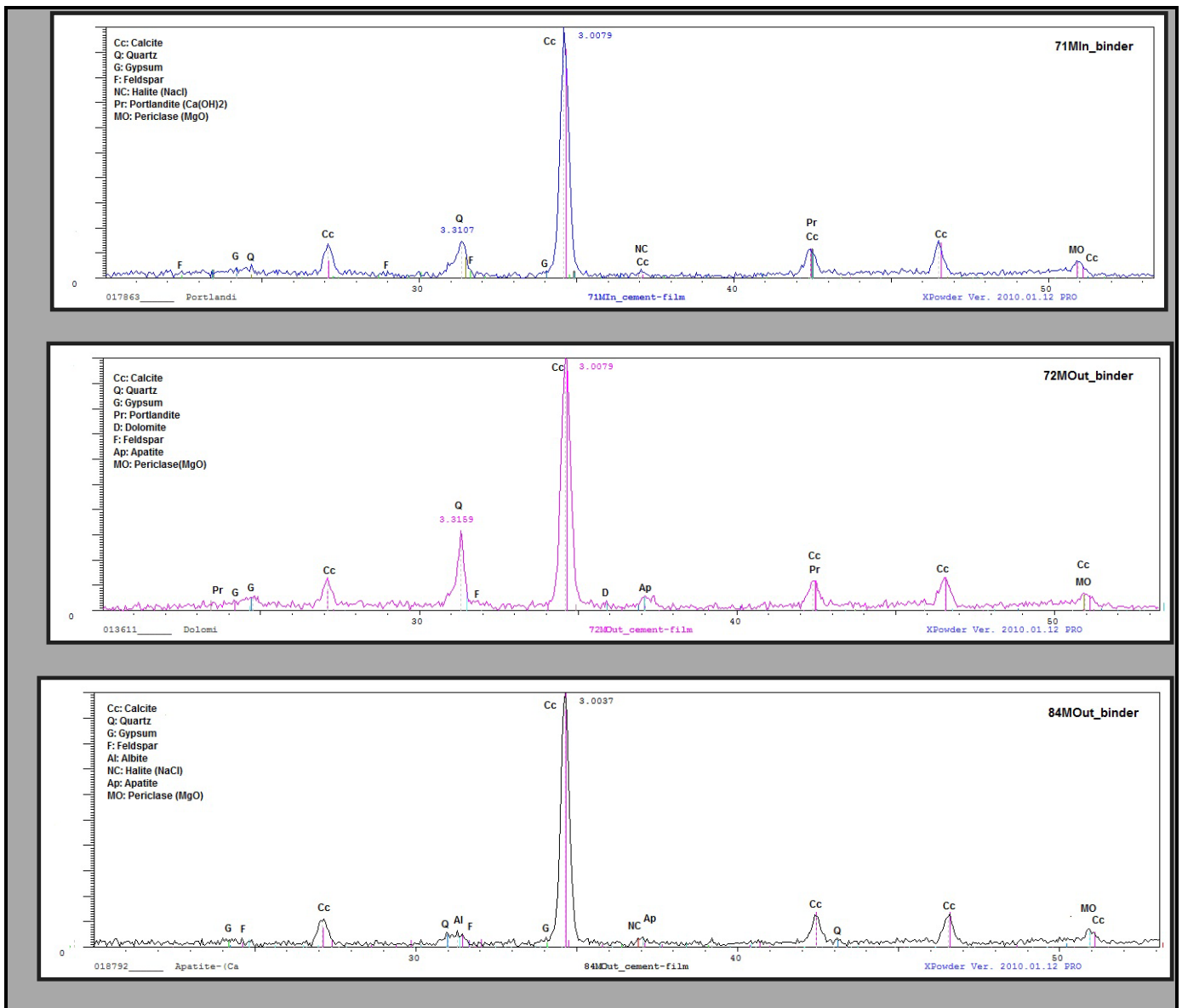
<b>Mortar Sample</b>	<b>Main Peaks</b>	<b>Secondary Peaks</b>
<b>2.1.M.Out_binder</b> (F-S)	Calcite, Quartz	Gypsum, Dolomite, Paragonite, Portlandite, Apatite
<b>3.1.M.In_binder</b> (F-S)	Calcite, Quartz	Gypsum, Dolomite, Portlandite, Periclase, Feldspar, Apatite
<b>6.1.M.In_binder</b> (F-S)	Calcite, Quartz	Gypsum, Portlandite, Apatite, Periclase
<b>7.1.M.In_binder</b> (S)	Calcite, Quartz	Gypsum, Feldspar, Halite, Portlandite, Periclase
<b>7.2.M.Out_binder</b> (S)	Calcite, Quartz	Gypsum, Portlandite, Dolomite, Apatite, Feldspar, Periclase
<b>8.4.M.Out_binder</b> (S(s))	Calcite, Quartz	Gypsum, Feldspar, Albite, Halite, Apatite, Periclase
<b>5.1.M.In_binder</b> (R)	Calcite, Quartz	Gypsum, Langbenite, Feldspar, Dolomite, Portlandite

Calcite ( $\text{CaCO}_3$ ), Quartz ( $\text{SiO}_2$ ), Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), Feldspar ( $\text{KAlSi}_3\text{O}_8$ ), Halite ( $\text{NaCl}$ ), Periclase ( $\text{MgO}$ ), Langbenite ( $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ ), Albite ( $\text{NaAlSi}_3\text{O}_8$ ), Magnesium ( $\text{Mg}$ ), Apatite ( $\text{CaOH}$ ,  $\text{CaF}$ ,  $\text{CaCl}$ ), Paragonite ( $\text{Al}_3\text{NaH}_2\text{Si}_3\text{O}_{12}$ ), Portlandite ( $\text{Ca}(\text{OH})_2$ ), Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ).

Table 31: Graphs of mineralogical composition of bind material of seven mortar specimens.

### Mineralogical Composition of Mortar's Binder Material





Spectra show that in all the samples calcite and quartz are the main mineralogical components. One of the Ca-carbonate polymorphs, calcite ( $\text{CaCO}_3$ ) is observed in each x-ray diffraction pattern of the binder-enriched fraction (<0.063mm fraction of the gently disaggregated mortar samples). The strong presence of calcite is due to the carbonization of the lime used as binder powder. Also the presence of portlandite mineral justified from the carbonation of pure lime.

The presence of a small amount of dolomite in the binder specimens indicates that the raw material was used for the manufacture of hydrated lime were of high purity limestone with small dolomites participation rates in its recommendation(Siedel, et al., 2012). In addition, the presence of apatite (phosphate mineral) is also could be

originated to the content of the raw material produced the binder or in organic inert material.

The increased amount of quartz (silicon dioxide) estimated that comes from the very first production of the binder material calcareous composition and more specifically from flint appearances that existed within the limestone formation in combination with a small proportion originated in the silicate aggregates and to the addition of the ceramic in the mortars matrix.

Furthermore, the restricted presences of albite (plagioclase), paragonite (phyllosilicate, mica) and of periclase (MgO) are originated from the fine fractions of aggregates that passed in the fraction of the binder.

Contents of gypsum were found in most of studied binders associated with exposure of materials to external conditions. This pattern is well- known from many other case studies on historic buildings with dolomitic lime mortars and must be attributed to intensive chemical weathering due to environmental influences.

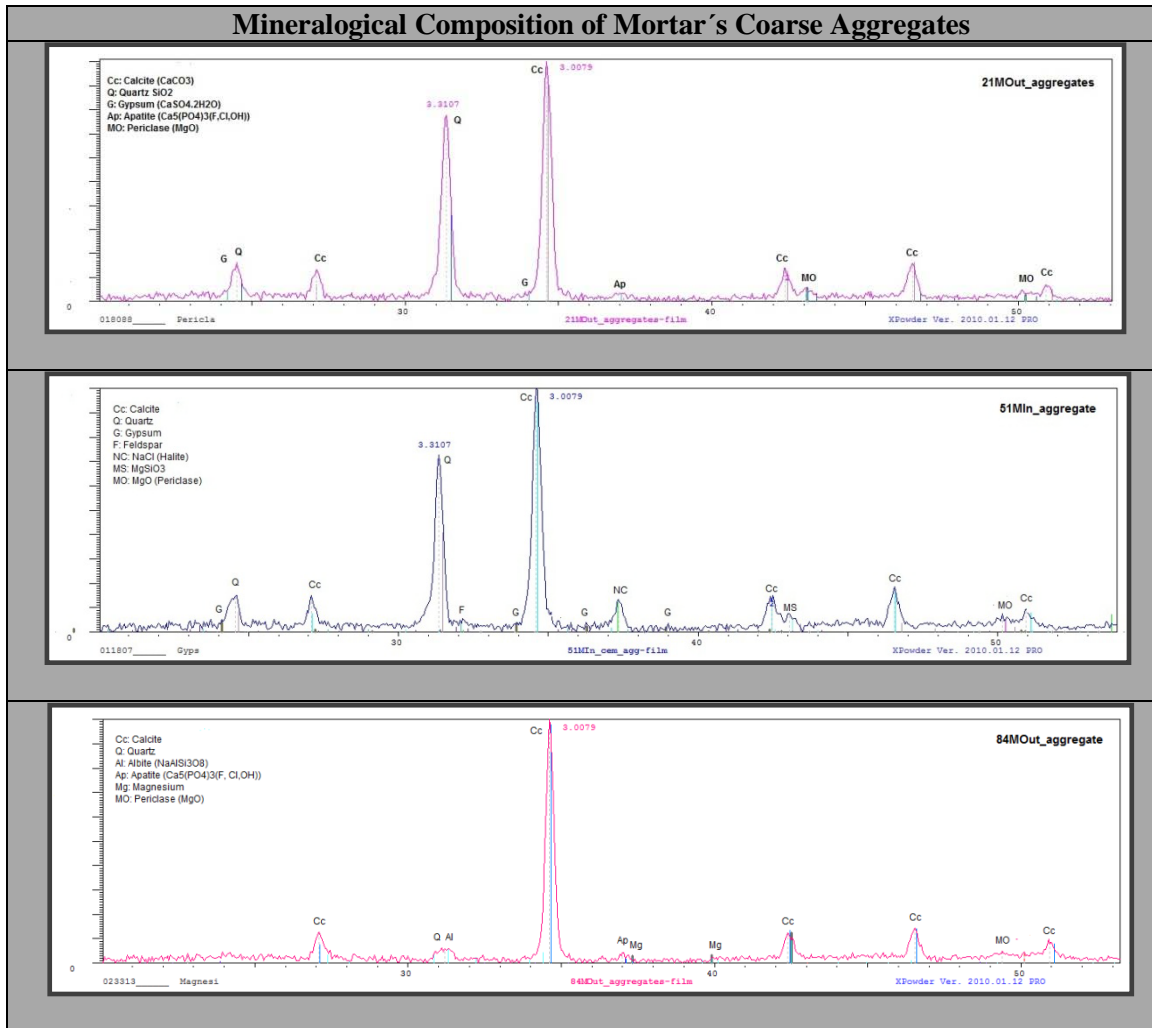
The mineralogical content of the main elements in all binder sample are relatively similar regardless of the category to which they belong (F-S, S, R, S(s)). With small exceptions the binder of sample *8.4.M.Out (S(s))* from the initial gate (“Zematistra” gate) which has a very limited content of quartz, which corresponds with the results of previous analyzes, namely that this mortar does not contain in its matrix silica sand but the aggregates are mainly crushed stones from the construction porous stone of this part of the monument (calcareous composition).

The most important conclusion from the mineralogical investigation into the binders, in relation to the lime used in the production of the historic mortars is that demonstrated the permanent use of local limestone over the centuries.

**Table 32: Mineralogical composition of coarse aggregates included in the matrix of historical mortars (XRD analysis)**

Sample	Main peaks	Secondary peaks
<b>21MOut_ aggregates</b>	Calcite, Quartz	Gypsum, Apatite, Periclase
<b>51MIn_ aggregates</b>	Calcite, Quartz	Gypsum, Feldspar, NaCl, MgSiO <sub>3</sub> , Periclase
<b>84MOut_ aggregates</b>	Calcite, Quartz	Albite, Apatite, Magnesium, Periclase

**Table 45: Graphs of mineralogical composition of the coarse aggregates included in the matrix of the historical mortars (XRD spectra)**



Aggregates present mineralogical characteristics referred to siliceous and calcareous composition. The silicate phases identified (quartz, feldspar, mica, phyllosilicates) are the main minerals of aggregates, suggesting a possible origin of the sedimentary sources (clastic sediments) such as river sand and/or in the ceramic inert. The raw materials of ceramic are natural clays contain quartz, feldspar and other mineral additives. The clay minerals provide plasticity and the quartz (sand) is added as filler space to reduce the plasticity of the final product.

In the sample from northern wall (*2.1.M.Out*) and in the sample from 7<sup>th</sup> bastion (*5.1.M.In*) we identify the use of the same inert material, although we have different manufacturing phases, which indicating that are derived from materials available in the area. In contrast, in the sample from the “Zematistra” gate (*8.4.M.Out*) we observe different type of inclusions, they are mainly calcareous.

## Conclusions

The condition survey through the analysis of construction materials of the castle is not considered as integrated, but we have brought forward significant bases for further development of the research. In the framework of this study a number of analytical techniques were selected to yield basic results regarding the characterization, classification and the preservation state of the construction materials of the Niokastro (castle of Pylos).

A) *Identification of the preservation state of the construction materials in relation to their physic - chemical properties:*

Niokastro even if it is a coastal monument showed relatively limited decay forms like: a) surface alteration of stones and mortars due to salt depositions, b) biological colonization is evident but not extensively, and c) at the base of the walls few missing masonry units. The present good preservation state of the monument is resulted by: the systematically restoration works, the unpolluted coastal area that may not exhibit high levels of salt-related weathering, and finally because it's constructive location (on rocky bedrock, a substrate normally considered stable by coastal erosion studies). Salts may not always be the original cause of deterioration but their presence in conjunction with water and/or moisture may significantly increase the deterioration rate of stone and mortars (Bolton, 2007). Additional sources of marine salts in a coastal monument may include the use of unwashed beach sands as a mortar aggregate and even the use of sea water to mix the mortar. The amount and depth of penetration of salts is depended on the type and nature of the materials.

### Stone samples:

For the construction of the castle two basic types of stones have been used, gray limestone in masonries (walls) without any specific shape or size, and yellowish porous stones (sandstone rocks) in plucked and large blocks. The second one was used for the construction of the gates, and of various structural elements such as frames for the cannons or as the corners of the buildings.

✓ Limestone samples exhibit great uniformity in the structure and profile, are non-clastic, dense crystalline structured materials with low porosity, of high consistency and homogeneity in the matrix, present limited veins and poor appearance of yellowish - brown impurities (iron impurities) in the binder,. Lime-stones consist of high proportion of calcium oxides (94-98%), and traces of Al, Mg, Si, Fe oxides. Lime-stone samples of the Niokastro are characterized as a high purity material. By the results of mineralogical study we observe that lime-stones consist mainly of calcite ( $\text{CaCO}_3$ ) with small amounts of quartz impurities and traces of dolomite. Their preservation state is considered satisfying as they retain their integrity, while biological and salt deposits have altered their original image.

✓ The sandstones are clastic coarse grained lime-stones consist of binders of yellow-gray color and of light gray, whitish, beige rounded grains generally of the same size not to fine or coarse (moderate). Sandstone samples present differences between them in roughness, in porosity, and in cohesion between their components. This is due to formation processes of the sedimentary rocks, which take place in many deposits that are episodic in nature and the resulting layer can be very different from previous layers (Folk, 1954). It is consequently very difficult to define the essential properties of a given specimen.

Sandstones consist of high proportions of calcium oxides (86-96%), and traces of Si, Al, Mg, K, P, Mn oxides. Sand mainly consisting of limestone fragments, form from the cementation of sand and/or mud by calcite. Calcareous cemented sandstones are subject to acidic dissolution and are more easily eroded than the silica cemented sandstones. Also the characteristics of the porous structure of sandstones affect their mechanical properties and their behavior in the respective corrosive environment. Their preservation state is considered moderate as extensive losses of the stone material are observed, combined with fractures, crushing and distortions.

#### Mortar samples:

The categories of mortars detected on the monument divided into five groups, Structural for the sandstone blocks, Forehead – Structural (structural mortars that covers the outer surface of gray lime-stones), Structural, Renderings and finally Structural reconstruction or restoration mortars.

- ✓ All the mortar samples consist of light colored binder materials with an exception the F-S mortar sample from NW bastion (*3.3.M.In*), which has red terracotta color of binder, due to the pozzolanic inert material.
- ✓ The aggregates of the mortar samples are particles of rock, naturally occurring or artificially crushed distinctly different shaped, mostly angular, vary in particle size and are of light-pale colors. Fragments of ceramic in the matrix of most of the samples are identified (mainly at S(s) and R mortar samples), both coarse and fine sized. Also, inside the binder in most of mortar samples are found a lot of calcite lumps, which are limited in size and amount in rendering mortars probably due to better quality of the lime and / or more of careful mixing ingredients, the opposite occurs in structural mortars.
- ✓ Furthermore, in a limited number of mortar samples we tracked down organic materials (*7.1.M.In*, *7.1.M.Out*, *8.4.M.Out*) and charcoal (*1.2.M.In*, *3.1.M.In*, *4.3.M.In*), which their presence is difficult to distinguish between the deliberate use of these admixtures and their accidental addition.
- ✓ An interesting outcome in relation to the inert materials used in the matrix of historical mortars is the use of crushed sandstones only in the structural mortars for joining the sandstone blocks. This remark revealed through the macroscopic observation after the grinding process and from the presence of P, Ti, Mn oxides from the chemical analysis in the matrix of these mortars. The presence of these oxides is referred to the chemical analysis of the sandstone specimens.
- ✓ Characteristically we should mention that the coarser aggregates (*1.960 and 0.966mm*) of the monument mortars, encountered angular grains siliceous composition of different shades, and crushed ceramic fragments. On the other hand, at the moderate and fine fractions prevail mainly-white granules of angular shape, calcareous composition, and/or crushed sandstone and limestone fragments. Mainly is observed good cohesion of the powder with small aggregates and crushed ceramics.
- ✓ From the results of the analyzed mortar samples we notice that the mortar samples mainly consist of calcium and silicate oxides with low proportions of aluminum, potassium, magnesium and iron oxides. The binding material is finely crystallized calcite, totally carbonated. A lot of different kinds of crystalline fibers are observed in the matrix of the specimens, such as needle fiber, microcrystal of lime or of silicate minerals. Hydration processes are also observed in most of the samples as the influence of the crushed ceramics components.

✓ Although we study materials of different uses and construction phases, the mineralogical content of the main elements in all binder samples are relatively similar regardless of the category to which they belong (F-S, S, R, and S(s)). Mortars have calcareous origin, with a low proportion of quartz. With an exception, the binder of sample *8.4.M.Out (S(s))* from the initial gate (Zematistra gate), has a very limited content of quartz. Its aggregates are mainly crushed stones from the construction porous stone (calcareous composition).

✓ According to the results of grain size distribution analysis, of historical mortars, we identify that the binder / aggregate (B/A) proportions are from 1/2 to 1/3 with very small fluctuations. The percentages of the contained binder exhibit variations from 24 – 32% have an average value of 28%. We comment that there is no clear separation of the mortar categories in relation to the diameter and the participation rates of their aggregates. The coarsest grain mortars are the structural mortar sample from Zematistra (*8.3.M.Out*), and from Southern wall (*6.1.M.In*).

✓ Gypsum contents, and the presence of chlorides, sulfates and nitrates in mortar samples, suggest an origin of salts. This is associated with the exposure of materials to external conditions (environmental influences) resulting by the absorption of sulphur dioxides or the migration of salt-containing solutions (Groot, et al., 2004). In addition to, the moderate preservation state of the historical mortars is supported by the presence of biological deposits, rootlets and dirt in their matrix. The samples of mortars that appear more contaminated are: a) from the areas of “Zematistra” gate and the Western Wall, b) the intervention mortars and c) the mortars found to the external sides of the monument. The reactivity of SO<sub>2</sub> is higher to mortars than in stones.

#### *B) Investigation of the provenance of the materials*

Extremely helpful in confirming historical sources and early scientific studies concerning the construction of historical monuments from local available materials was the mineralogical and chemical analysis of reference stone samples from the region of Pylia. We analyzed the nearby geographically (maxim distance 3 km from the castle) geological formations. First approach was made by macroscopic examination where the closest in the area of the castle reference stone (E.Pc.k, limestone) was discarded from the process of insight investigation because of its different morphological characteristics. The other three reference stones were

analyzed by SEM/EDS and XRD analysis (PLs: sandstone, 1 km distance from the castle, Ptk: sandstone, 3Km from the castle, and KsKd: limestone, 1km distance from the castle).

✓ Significant finding of the mineralogical analysis (XRD) is that the compositions of the reference samples, in comparison with the results of the construction stones of the castle have the same mineralogical composition. In particular the outcomes of castle's limestone samples are totally identical with the results of the reference limestone, while between the two reference sandstones the Ptk sample is more compatible with the results of the monument's sandstone samples. This finding is consistent with the primary assessment of the provenance of the castle's building materials from locally materials.

✓ Consequently, we tried to extract outcomes in relation to the binder materials of the historical mortars by comparing the mineralogical and chemical results of the binder specimens with the analog results of the reference stone samples. We observed that their results are equivalent the chemistry of the binder material is identical to that of the limestone used to prepare the lime. According the results of the binders of the historical mortars is demonstrated the permanent use of local limestone for the lime production over the centuries.

✓ Finally, the calcareous and siliceous aggregates in the matrix of historical mortars, suggesting a possible origin of the sedimentary sources (clastic sediments) such as river source materials which consist of rock fragments that exist in the area (limestone, sandstone and other rocks of the unity of flysch).

### *C) Assist in documentation of the construction phases of the monument*

For the identification of the construction phases of the castle's sections through the analysis of the structural mortars we encountered obstacles, both due to restricted historical documentation of the monument, and the permanent use from the same origin construction materials (lime-stone from the region of Pylos) over the centuries, this awareness emerged after the application of series of analytical techniques. Nevertheless we tried to supplement the so far known data with some conclusions reached through the analysis process of mortar samples.

✓ We identify that the initial building mortars (1<sup>st</sup> Ottoman period) of Niokastro castle may be the historical mortars from the “Zematistra” gate (8.3.M.In and 8.4.M.In), from 7<sup>th</sup> bastion (5.1.M.In), and from the South Wall (6.1.M.In and 6.3.M.In).

In light of the analysis in initial historical mortars demonstrated the following conclusions:

- Their binder material is lime from a very pure quality limestone with low content of magnesium, less than 5% (calcitic lime).
- Their aggregates are mainly of calcareous composition from sandstone fragments, with the coarser fractions of siliceous composition materials and of fired ceramic fragments.
- They are not good stirring materials; they are coarse mortars with several agglomerates of lime while the construction mortars are coarser than the renderings.
- The binder / aggregate (B/A) proportions are identified to be from 1/2.5 to 1/3.

✓ Concerning the mortar samples from the two gates of the castle (Zematistra and Main gate) 1.2.M.In, 8.3.M.In, 8.4.M.Out we observe differences both at their quantitative chemical composition and at their grain size distribution, this recognition can be randomly due to the diversity of mortars composition or we can assume that the two gates belong to a different construction phases.

✓ In respect to the other mortar samples of the forehead – structural category we detect that 3.1.M.In sample from NW bastion is identical with the mortars from Western wall 4.3.M.In and with 2.1.M.Out from the Northern wall. These three mortar samples have similar chemical and mineralogical composition while 2.1.M.Out presents small discrepancy in its grain size distribution in relation with the other two foreheads – structural mortars. We assume that these three specimens belong to the same construction phase.

✓ Furthermore, similarities according to their physicochemical properties we encountered between samples 5.2.M.In structural reconstruction mortar from the 7<sup>th</sup> bastion which dates at the French occupation period, with the mortars from the

main gate (*1.2.M.In*), and from the Bastion I of the citadel (*7.1.M.In and 7.2.M.Out*). It is quite likely to belong to the same construction phase.

✓ Finally, the sample *3.3.M.In* from NW Bastion which contained pozzolanic material in its binder belongs to another construction period in relation with the other specimens as we didn't encounter other equivalent material between the examined mortar samples.

*D) Highlight the usefulness and importance of the ArcGIS mapping program in the study area of archaeological research.*

Via ArcGIS map computer program we enabled to:

- Compiling, explore, and analyze the historical and the experimental data, through two distinct sections of the program, the table of contents and the data frame.
- Symbolize features, into an interactive map project.
- Create high resolution maps to emphasize different views of our project, were we can display photos, and different databases.
- Managing and sharing scientific information in a database available openly on the Web

## Discussion

In particular, stone monuments present a particularly interesting field of study as they tend to be good survivors. However, we came across with many obstacles - difficulties during our research. Specifically, historical mortars are complex systems with a very heterogeneous binder material within one mortar sample, the identification of the binding and the inert materials that constitute the matrix of a mortar is a demanding process. Also, the analysis of historical lime binders is not a straightforward process both due to the difficulties in physical separation into binder and aggregates, and the commonly limited quantities of the samples.

In addition, there are a lot of limitations in the wet chemical analysis which alone is probably insufficient to give a clear indication about the hydraulicity of the binders. The complicity of the method is due to mortars physic-chemical evolution through time. For instance the hardening due to carbonation, hydration, the addition of substances due to environmental actions (penetration of salt, washing out, etc.) and the normal hydration and carbonation processes. In these cases, special knowledge of regional construction materials and practices is required, in order to make estimations/ approximations.

Also, the microprobe analysis in stone and mortar samples can only reflect the chemical composition of a specific location in the matrix, but not necessarily reveal the exact mineralogy of the different components. Furthermore, the XRD mineralogical analysis alone cannot be used to determine mortars, but act as supplementary data. Multidisciplinary study with a lot of different analytical techniques is the most representative way to approach more accurate outcomes.

Finally, a repair mortar is suitable for a restoration purpose when it has an aesthetic, chemical, mineralogical, mechanical and physical compatibility with the substrate on its application. As the original mortars have been analyzed, it is proposed to take in consideration research's outcomes, for the future restoration works, with respect to the history of the monument.

Critical evaluation of the available information and innovative solutions drawing on a mixture of disciplines are likely to become the accepted norm for the conservation of monuments and repairs, on a minimum intervention basis to stabilize vulnerable sections of masonries.

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## Appendix 1 (Figures of Niokastro)

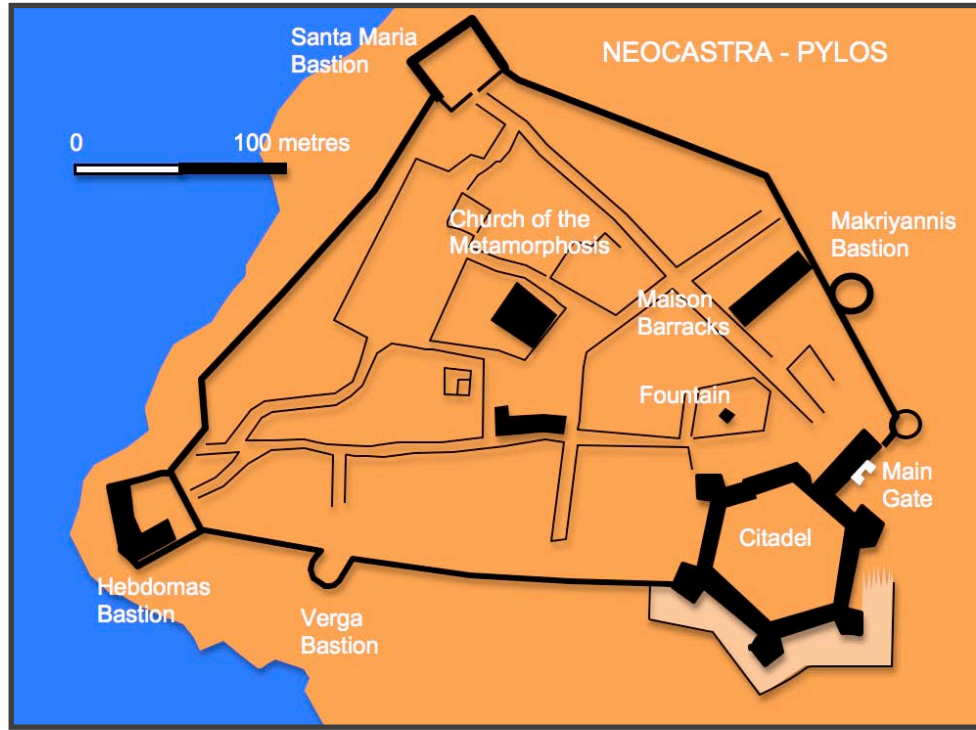


Figure 5: Ground plan of Niokastro. It is depicted the areas of the Castle and the building that host

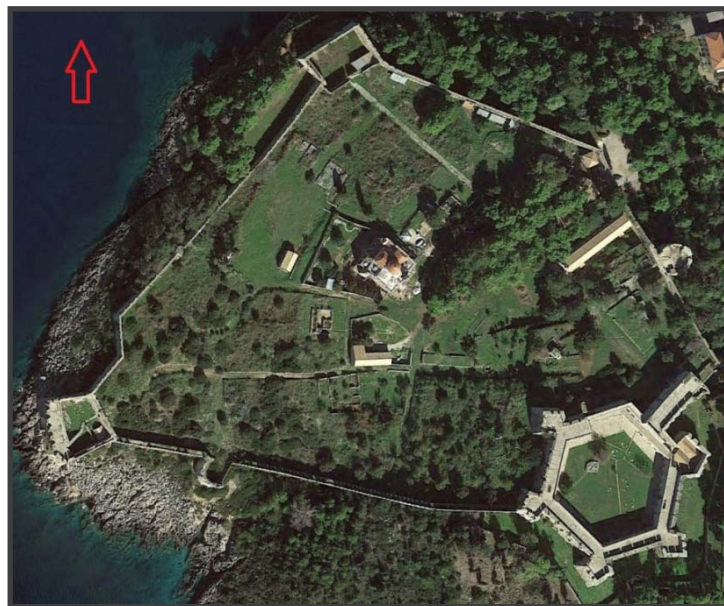
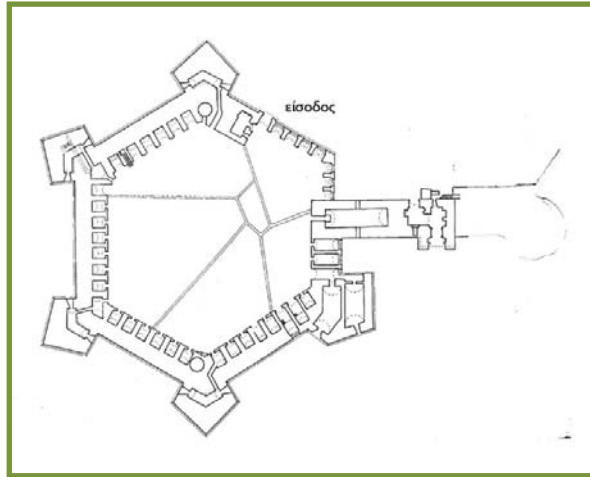
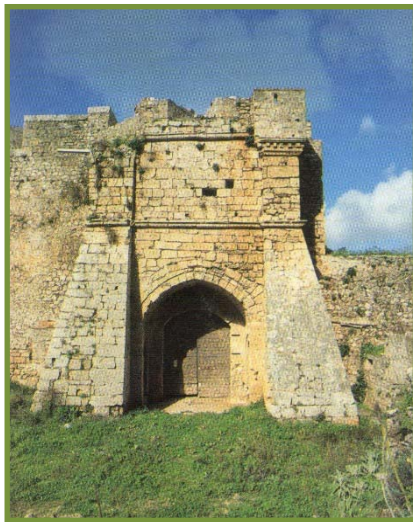


Figure 6: Air-photograph of the Niokastro, (Google earth)



**Figure 7: Citadel plan under the passageway, and Zematistra the initial gate**



**Figure 8: "Zematistra" gate**



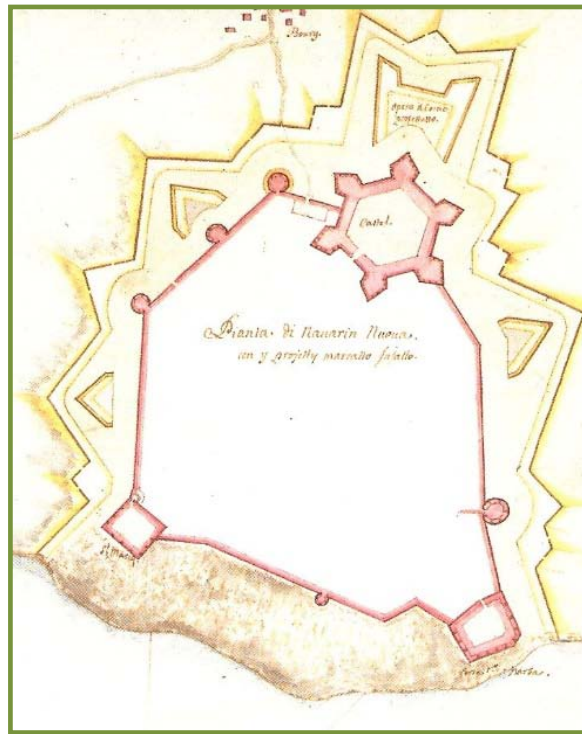
**Figure 9: Hebdomos bastion entrance**



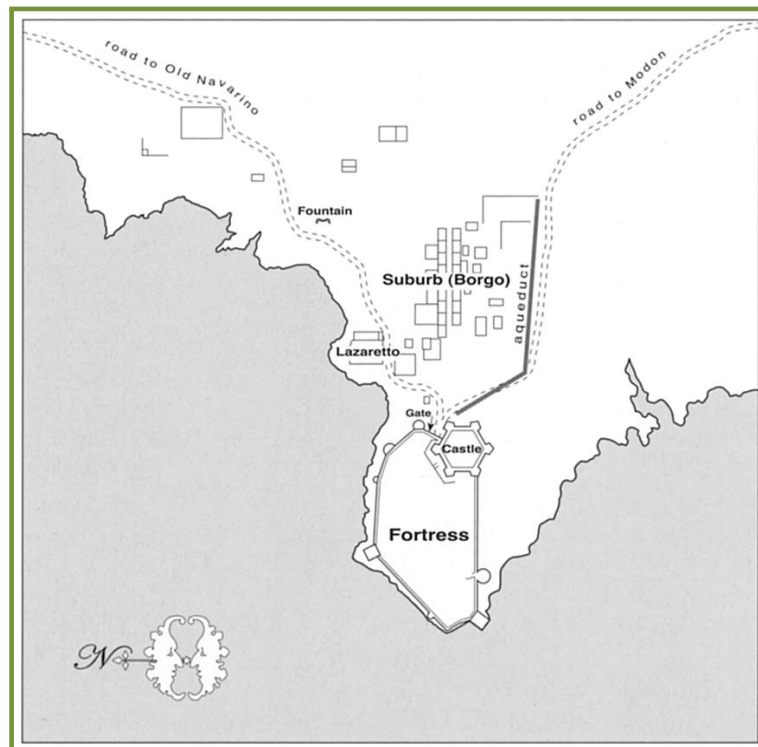
**Figure 11: Main gate of the castle**



**Figure10: Citadel gate**



**Figure 12: Drawing of Venetian proposal to strengthen the castle by extending the outer moat and earthworks. Grimani Plan**



**Figure 13: Plan of New Navarino ca. 1700. After Andrews 1953 pl.XI**

## Appendix 2 (ARC-GIS Mapping Process)

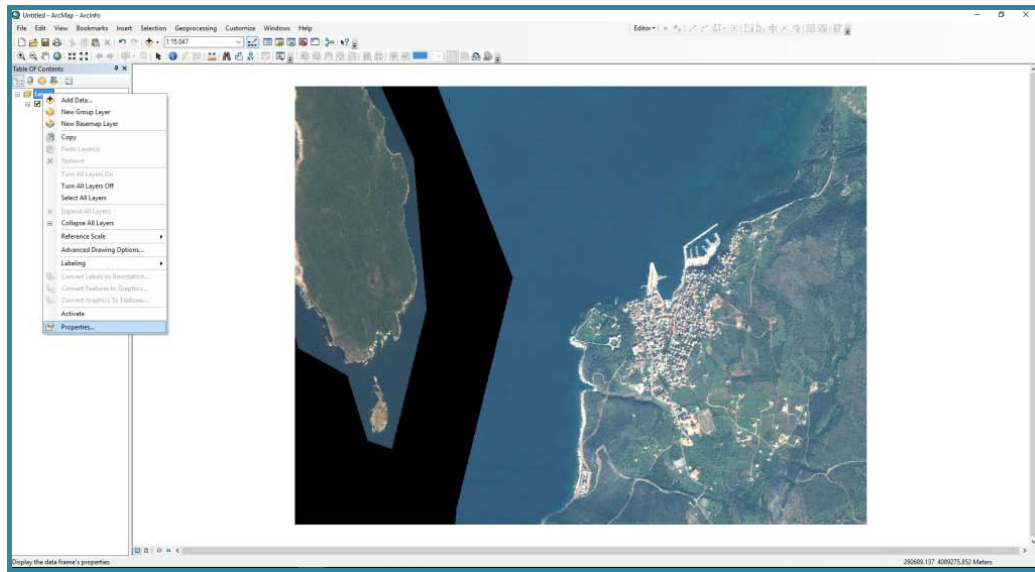


Figure 14: Adding and geo-referencing satellite image, from SAS planet software

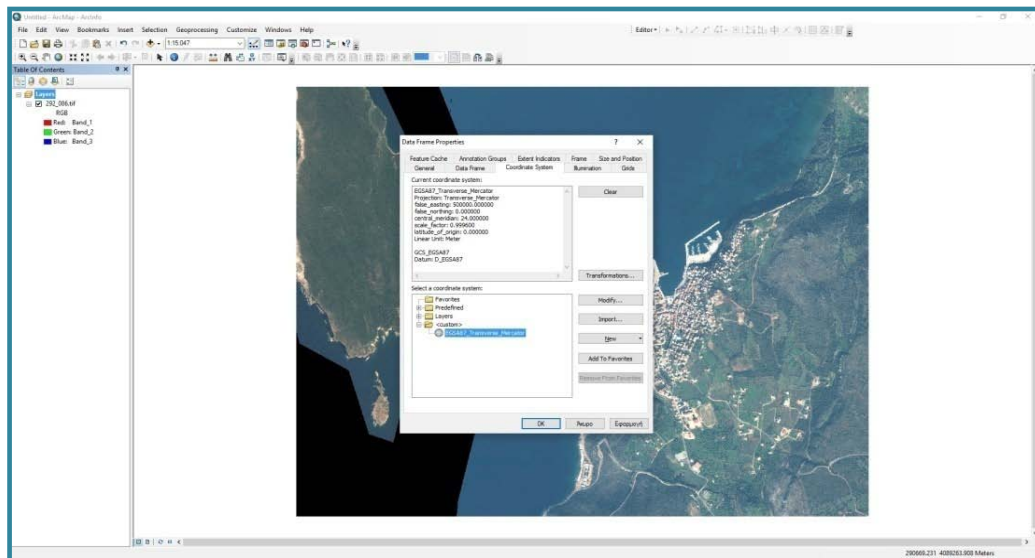


Figure 15: Geo-referencing via Greek geodetic reference system 1987 (GGRS-87)

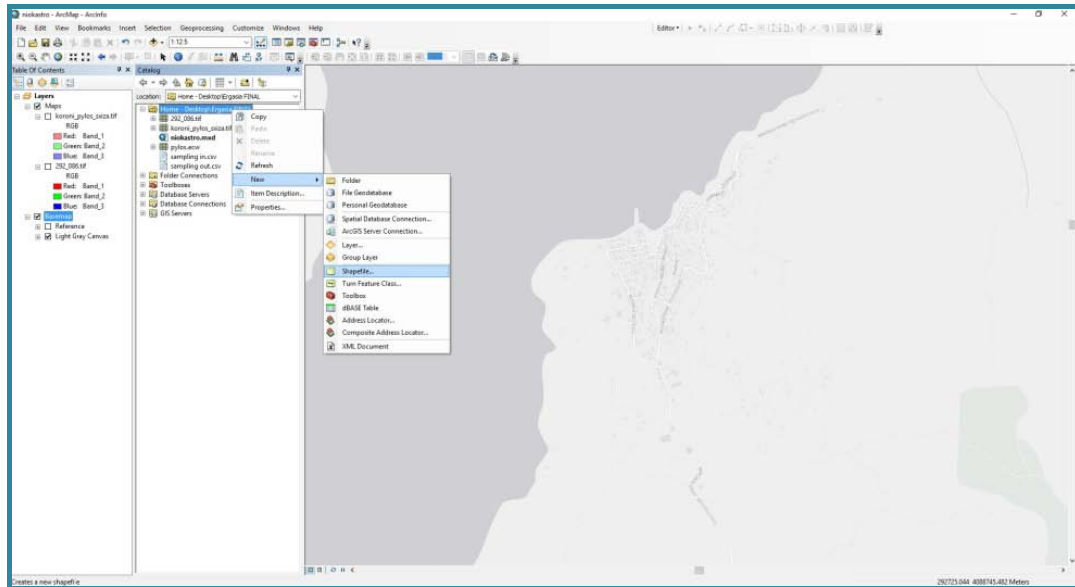


Figure 16: Creation of shape-files.

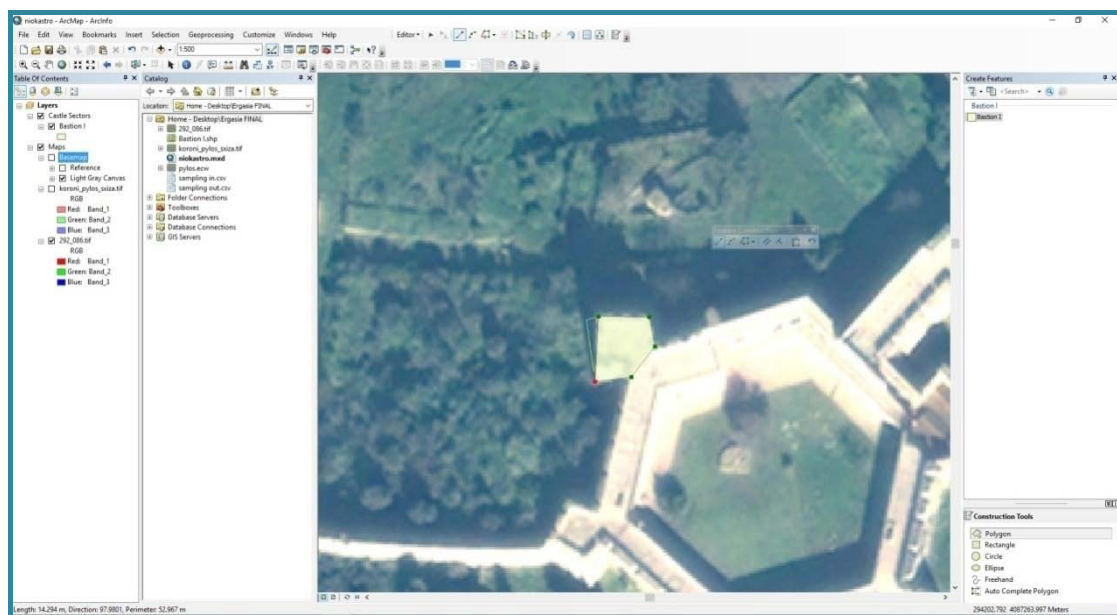


Figure 17: Creation of the ground plan of castle by using polygons.

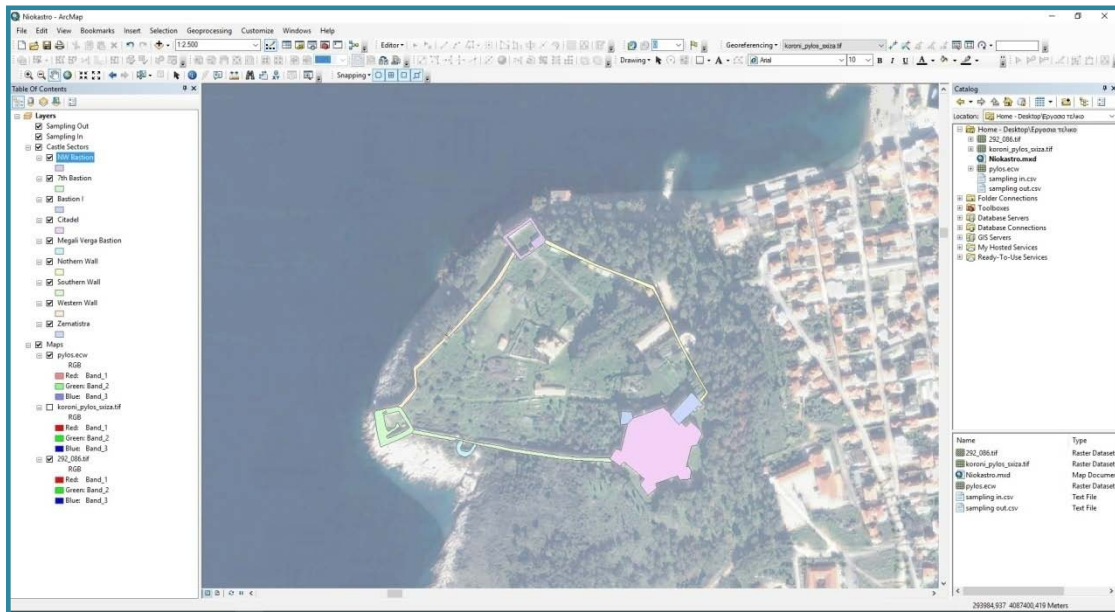


Figure 18: Ground plan of Niokastro with shape-files (Polygons, Polylines)

sampling in - Excel

1	2	3	4	5	6	7	8	9	10	11	12
Id	Region	Info:	Stone sample:	Stone sample info:	Mortar samples:	Mortar info:	Analysis:	Reconstruction Phases:			
1	1 Main Gate	(1.1.S.In),(1.2.M.In)	(1.1.S.In)	(1.1.S.In:Structural sai	(1.2.M.In)	(1.2.M.In: Structur	(1.2.M.In: SEM, C	(1988-2011:Restoration works)			
2	2 Nothern Wall insid	(2.2.S.In),(2.1.M.In)	(2.2.S.In)	(2.2.S.In:Structural stc	(2.1.M.In)	(2.1.M.In: Forehead - Structural mor	(1982-1986:Extensive restoration works)				
3	3 Nothern Wall outs	(2.2.S.Out),(2.3.S.O)	(2.2.S.Out),(2.3.S.O)	(2.2.S.Out: Structural	(2.1.M.Out),(2.4.M.Out)	(2.1.M.Out: Forehe	(2.1.M.Out: SEM, C	(1982-1986:Extensive restoration works)			
4	4 NW Bastion	(3.2.S.In),(3.4.S.In)	(3.2.S.In),(3.4.S.In)	(3.2.S.In: Structural, ci	(3.1.M.In),(3.3.M.In)	(3.1.M.In: Forehe	(3.1.M.In: SEM, C	(1988-2011:Restoration works)			
5	5 Western Wall	(4.2.S.In),(4.1.M.In)	(4.2.S.In)	(4.2.S.In: Structural, ci	(4.1.M.In),(4.3.M.In)	(4.1.M.In: Structur	(4.1.M.In: OM),C	(1982-1986: Extensive restoration works)			
6	6 7th Bastion	(5.3.S.In),(5.4.S.In)	(5.3.S.In),(5.4.S.In)	(5.3.S.In: Structural dt	(5.1.M.In),(5.2.M.In)	(5.1.M.In: Renderir	(5.1.M.In: SEM, C	(1825: Blown up),(1828-1829: Series of repairs and additions to			
7	7 Southern Wall	(6.2.S.In),(6.4.S.In)	(6.2.S.In),(6.4.S.In)	(6.2.S.In: Structural, ci	(6.1.M.In),(6.3.M.In)	(6.1.M.In: Forehe	(6.1.M.In: SEM, C	(1941-1944: The wall on the south side, exploded),(1982-1986:			
8	8 Bastion I	(7.3.S.Out),(7.5.S.O)	(7.3.S.Out),(7.5.S.O)	(7.3.S.Out: Structural,	(7.1.M.In),(7.1.M.Out),(	(7.1.M.In: Structur	(7.1.M.In: SEM, C	(1686 - 1715: Construction of the gate of the citadel),(1715-1982:			
9	9 Zematistra	(8.1.S.Out),(8.2.M.C	(8.1.S.Out)	(8.1.S.Out: Structural,	(8.2.M.Out),(8.3.M.Out)	(8.2.M.Out: Structu	(8.2.M.Out: OM),	(1715-1821: Walls right and left of the gate are ruin),(1988-201:			

Figure 19: Join layer with CSV excel table



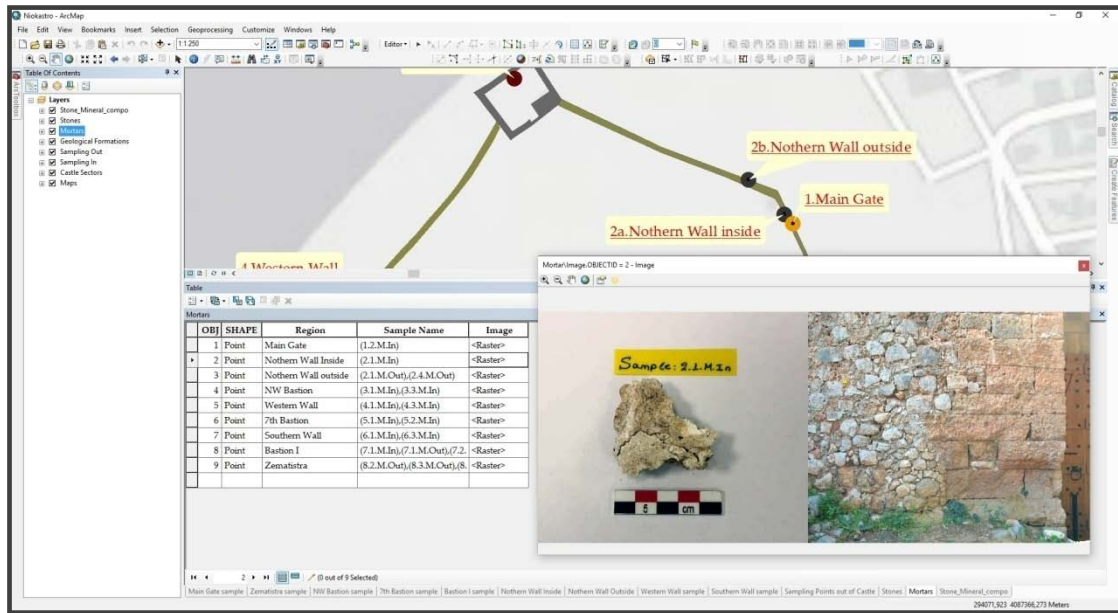


Figure 22: Create geo-database, region, sample code, images of the mortar samples and the sampling area

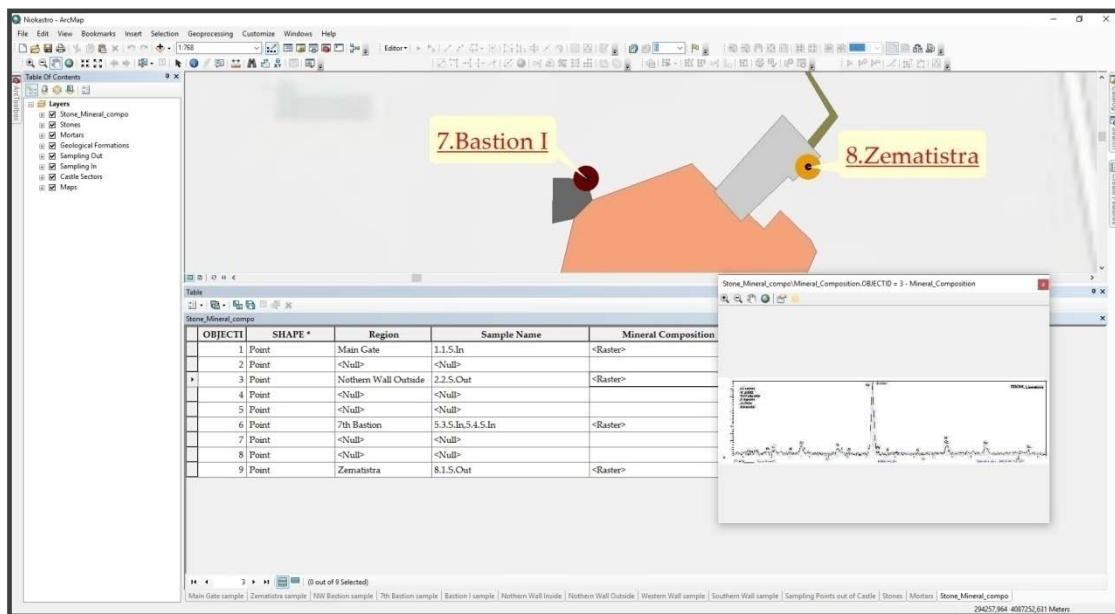


Figure 23: Geo-data base, region, sample, code, mineralogical composition (XRD graph)

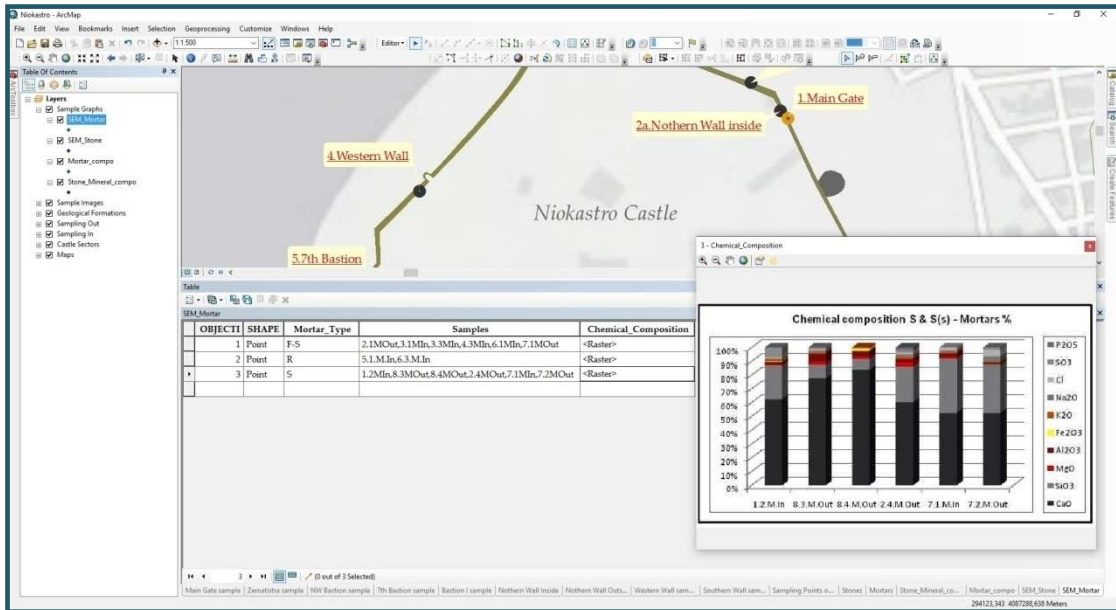


Figure 25 : Geo-data base with chemical composition of structural mortar samples

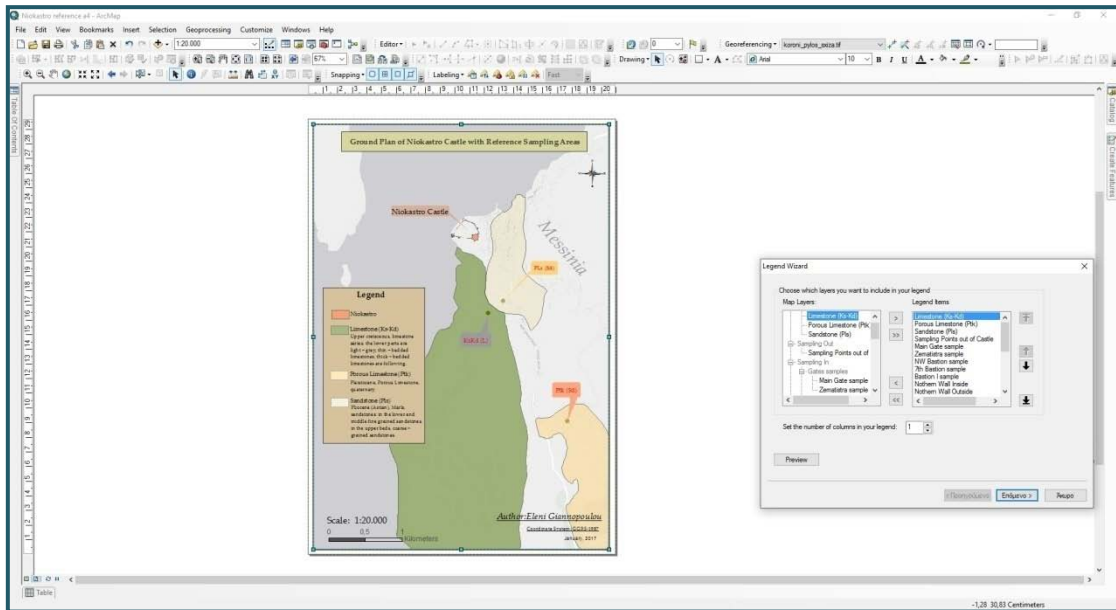


Figure 24: Insert legend on the map

## Appendix 3 (Niokastro Sampling Maps)

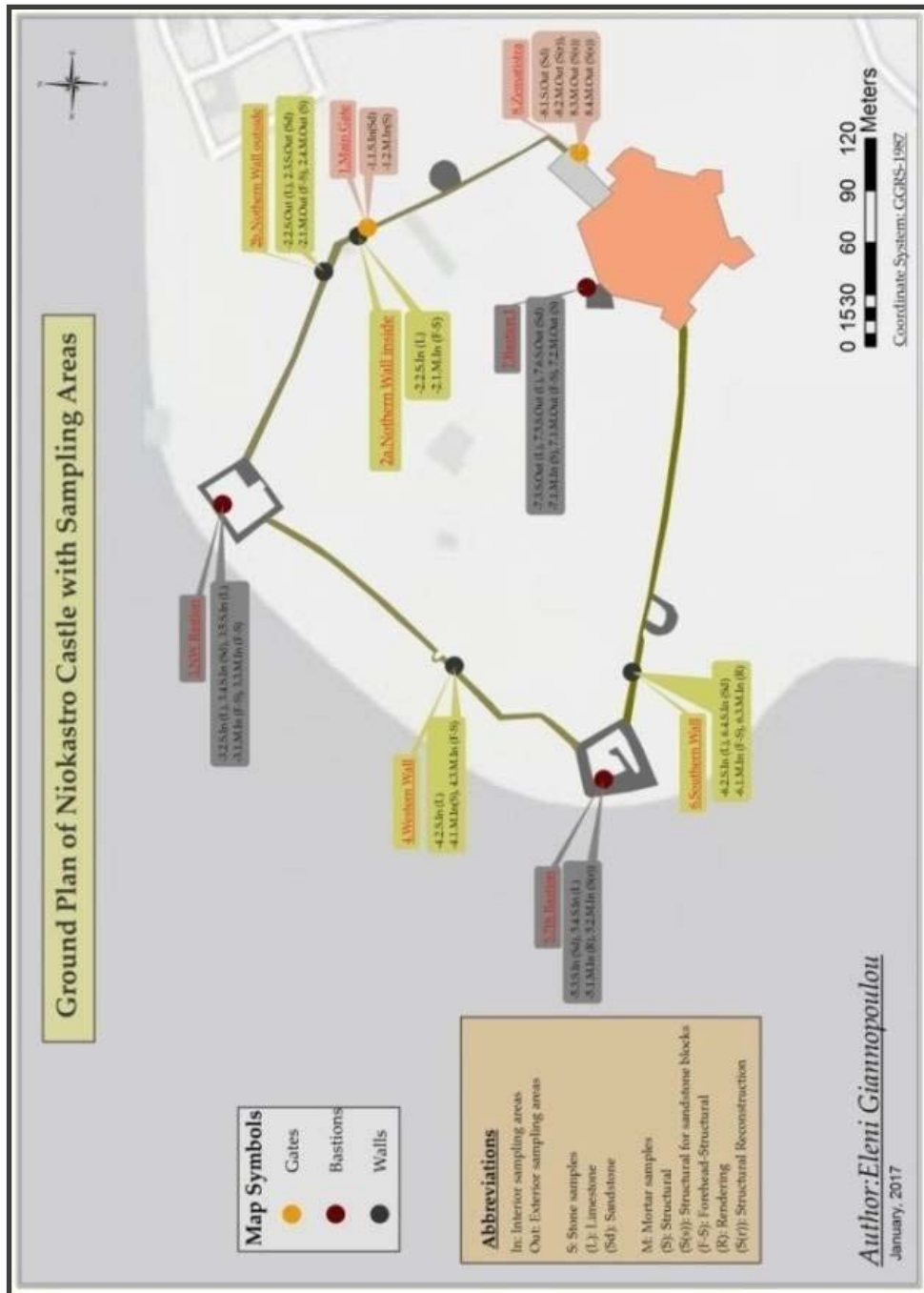


Figure 26: Map illustrating the ground plan of Niokastro, the castle of Pylos, Messinia, Greece, with the stone and mortar sampling areas

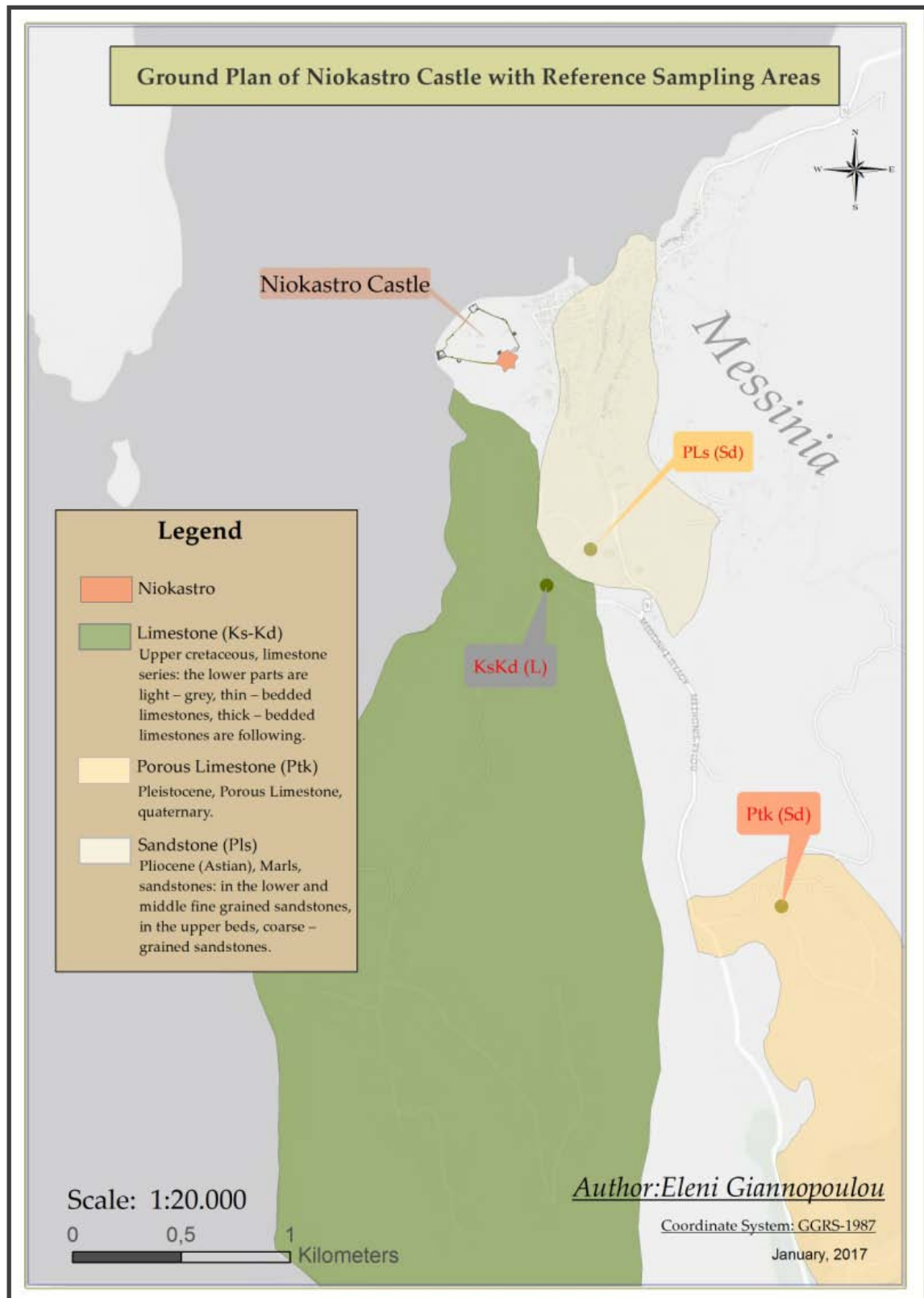
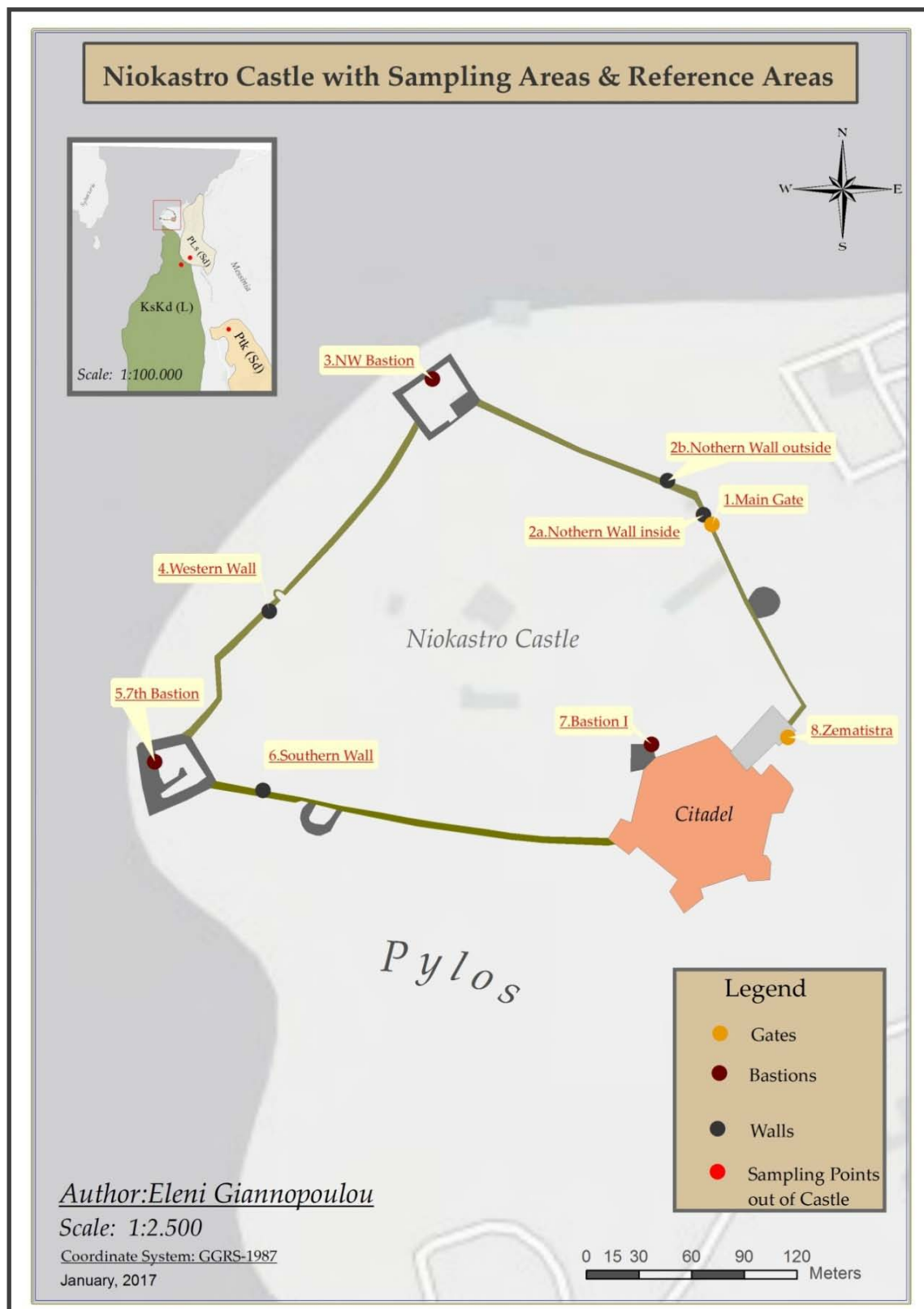


Figure 27: Map illustrate the Castle of Pylos (Niokastro) with the stone reference sampling areas of the region of Pylos, Messinia, Greece



**Figure 28: Map illustrate the ground plan of Niokastro, the castle of Pylos, Messinia, Greece with the stone and mortars sampling areas and the reference stone sampling areas**