



**UNIVERSITY OF THE PELOPONNESE**

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**DIPLOMA THESIS:**

**SEM-EDS Analysis of Late Helladic Pottery  
From Koukonisi – LEMNOS**

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## Abstract:

Twenty Late Helladic pottery samples from the site of Koukonisi which is situated on the northeastern of the Aegean Sea is analyzed through SEM-EDS to identify the technological characteristics. These samples were specifically chosen from a larger assemblage comprised of 77 samples which is chemically grouped by NAA analysis by Hein and Kilikoglou (2016). SEM-EDS analysis on the smaller set of samples (twenty) from the larger assemblage (77) is conducted at the National Center of Scientific Research at Demokritos in Athens. Microstructure and surface treatments are identified through backscattered and secondary electron modes while elemental compositions of the ceramic bodies and the surface slips are identified by EDS. At least three measurements were taken from the bodies and surfaces for each samples. These measurements were compared and four technological patterns identified according to red slipped surface decorations. Thanks to SEM-EDS analysis, different microstructures and surface treatments were observed. According CaO content in the ceramic bodies, microstructural characteristics and the color of the ceramic bodies and surfaces, firing structures and atmospheres are assigned to the samples. According to these general results and the vitrification levels of the samples, possible maximum firing temperatures are proposed. Technological patterns observed from the data were compared with the chemical groupings of the samples and possible characteristics were attributed to some samples as local and imported. In general, samples from Koukonisi indicated Mycenaean pottery production characteristics while pottery assigned as local to Koukonisi showed different technological attributes.

## 1. Introduction:

The purpose of this research is to identify the technological characteristics of the Late Helladic pottery from Koukonisi, located on the island of Lemnos, which is situated in the northeastern corner of the Aegean Sea. There are two objectives in this study. The primary objective is to identify technological characteristics such as surface decorations, microstructures, and vitrification levels of the samples, which help to determine firing atmosphere, structure and possible temperatures employed in the creation of these potteries, and also to identify the elemental oxide concentrations of the ceramic bodies and surfaces of the decorated samples. The secondary objective is to demonstrate the advantages of using Scanning Electron Microscopy (SEM) in archaeometry for pottery analysis and in the social sciences for the identification of concepts such as movement and agency.

This study is a subset of a larger ongoing project that incorporates different methods of analysis to investigate a Late Helladic pottery assemblage from Koukonisi. For this Master's thesis I was responsible for twenty samples, which I analyzed using SEM-EDS at the National Centre of Scientific Research "Demokritos" under the supervision of Dr. Anno Hein and Dr. Vassilis Kilikoglou. These samples were intentionally selected to represent all of the chemical groups present in the larger assemblage. The chemical groups of the assemblage were identified using Neutron Activation Analysis (NAA) by Hein and Kilikoglou (2016).

As it is indicated above, the methodology employed in this research is SEM with an Energy Dispersive X-ray Spectrometer (SEM-EDS). This analytical method required sample preparation before the analysis conducted. Freshly fractured samples were attached to the target holder with a conducting glue and were carbon coated as a method of conducting surface layer application. Microstructures of the samples were made by using backscattered (BS) and secondary electron (SE) modes and elemental oxide compositions were detected by using EDS. According to the SEM-EDS results scatter plots comparing different elemental compositions were made to aid in the interpretation process.

This thesis research consists of four main chapters. The first chapter introduces the cultural background of Lemnos Island and the site of Koukonisi where the analyzed Late Helladic/Mycenaean pottery were found. This chapter also includes information on the

Mycenaean presence at Koukonisi, and a brief discussion on “Mycenaean presence” studies where some ideological and archaeometric approaches are introduced.

The second chapter introduces the theoretical framework, which is divided in two sections, pottery production and ceramic studies in archaeometry. The pottery production section includes information on the *chaîne opératoire* of pottery production where each step in the process is discussed, separated as collection of raw materials, processing of clay and temper, paste preparation, shaping methods, drying, surface treatments, and firing. The section on ceramic studies in archaeometry is divided into four subsections as petrographic, textural, mineralogical and elemental studies.

The third chapter is devoted to the methodology used in this research, divided in two main sections. The first is applied technology, and the second is research design, sample preparation and description. The applied technology section introduces the technique employed in this research (SEM-EDS) and its working properties. The section on research design, sample preparation and description introduces the way SEM-EDS is applied to the samples, how the samples are prepared for the analysis and their description considering their chemical groupings and fabrics.

The fourth chapter introduces the results of the analysis and a general discussion according to these results. This chapter is divided in two sections as microstructure and surface analysis. Vitrification, firing atmosphere and temperature determination; and the elemental compositions of the ceramic bodies are described under the microstructure section, while chemical composition of the surfaces and bodies are compared under the surface analysis section.

## 2. Cultural Background:

### 2.1. Lemnos Island:

Lemnos Island, situated at the northeastern edge of the Aegean Sea between the two large landmasses of Thrace and Asia Minor, opposite the straits of the Dardanelles and close to the eastern Aegean islands, holds a strategic position in the Mediterranean (**Figure 1**). The island has a regular geology and is divided into two parts by the Moudros and Pournias bays, in the north and south respectively. The strategic position of Lemnos and its welcoming geology with low hills, plains and a large number of bays and peninsulas creating safe harbors made the island suitable for settlement throughout the centuries (Dova, 2008). It could be said that the number of Early Bronze Age sites (**Figure 2**) on Lemnos, which are Axia, Nephthina, Kotsinas Komi, Keros, Kathares, Poliochni, Mikro Kastelli, Progomylos, Angaryones, Trochalia, Agios Ermolaos, Vryo Kastro, Poliochni of Kaspaka, Myrina, Playisos Molos and Koukonisi, indicate intensive habitation of the island due to the favorable conditions mentioned above.

Koukonisi has an important place within these mentioned sites since the excavations there indicated habitation from the Early Bronze Age to the Late Bronze Age, while in the Middle Bronze Age Poliochni and Myrina had already been abandoned (Boulotis, 2013). Moreover, when compared with the evidence from other sites such as Hēphaestia, Poliochni, Myrina and Mikro Kastelli, Koukonisi is separated as having one of the most prominent and continuous Mycenaean connections (Boulotis, 2009).

### 2.2. Archaeological site Koukonisi:

In 1992 Christos Boulotis and the Ephorate of Antiquities first began excavations at the site of Koukonisi (**Figure 3a**), situated on a low islet in the innermost part of Moudros Bay (Boulotis, 2013). Excavations continued in the Koukonos area until 2005 and revealed the successive levels of the EBA, MBA (Koukonisi IV) and early LBA (Koukonisi III) (**Figures 4a and 4b**) (Boulotis, 2009). Boulotis indicated that the geographical position of the site (northeast of Mycenae and west of Troy) was one of the decisive reasons for its longevity and successive levels, since it was situated within the innermost part of largest bay on Lemnos, and one of the largest harbors in the Aegean, which made it optimal for year round navigation in all directions thanks to sea currents

(**Figure 3b**), ensuring safe anchorage for ships heading towards the northern Aegean, Macedonia, Thrace, Troy and the Dardanelles (**Figure 5**) (2009:178-180).

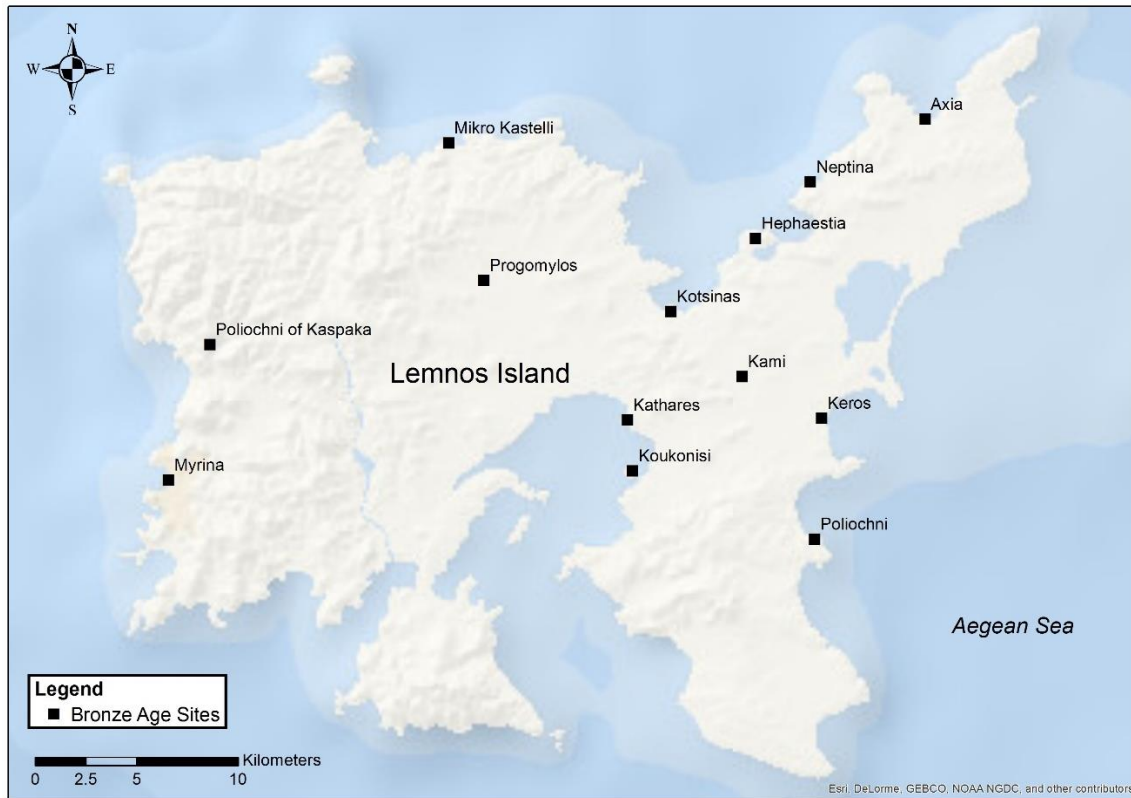
Excavations at Koukonisi have not reached layers earlier than the Early Bronze Age however, but when compared to contemporary sites such as Poliochni and Myrina Boulotis (2013) argued that the earliest layers of Koukonisi would most probably be at the end of the Neolithic Age to the EBA transition. EBA architectural remains and characteristic artifacts such as pottery, bronze, stone and bone tools with animal bones and shells are found right below the Middle Bronze Age layers, from trenches 2-3-5 that have allowed in depth excavation.



*Figure 1: Position of Lemnos Island in its Mediterranean context (map created using ArcGIS by Duygu Ertemin).*

Findings from the MBA layers indicate a wealthy period for Koukonisi, and an earthquake that affected the entire settlement, which was quickly rebuilt at the beginning of the LBA, defined the transition from the MBA to the LBA. Excavations conducted on the LBA layers revealed that the walls were built on the ruins of the old ones, and the use of the identified oldest roads (Zephyros and Voreos) continued. Artifacts from the early stages of LBA, especially painted pottery from Crete, indicated a connection with southern Aegean and Minoan influence at the site (Boulotis, 2013). In addition to these influences on the site, its Mycenaean character was observed from the

cultural materials found during surface survey and from the excavated layers (LBA, Trench 8-Section IX). This influence will be discussed in depth in the next section.



*Figure 2: Web of Early Bronze Age archaeological sites of Lemnos (map created using ArcGIS by Duygu Ertemin; after Dova, 2008:149, fig. 1)*



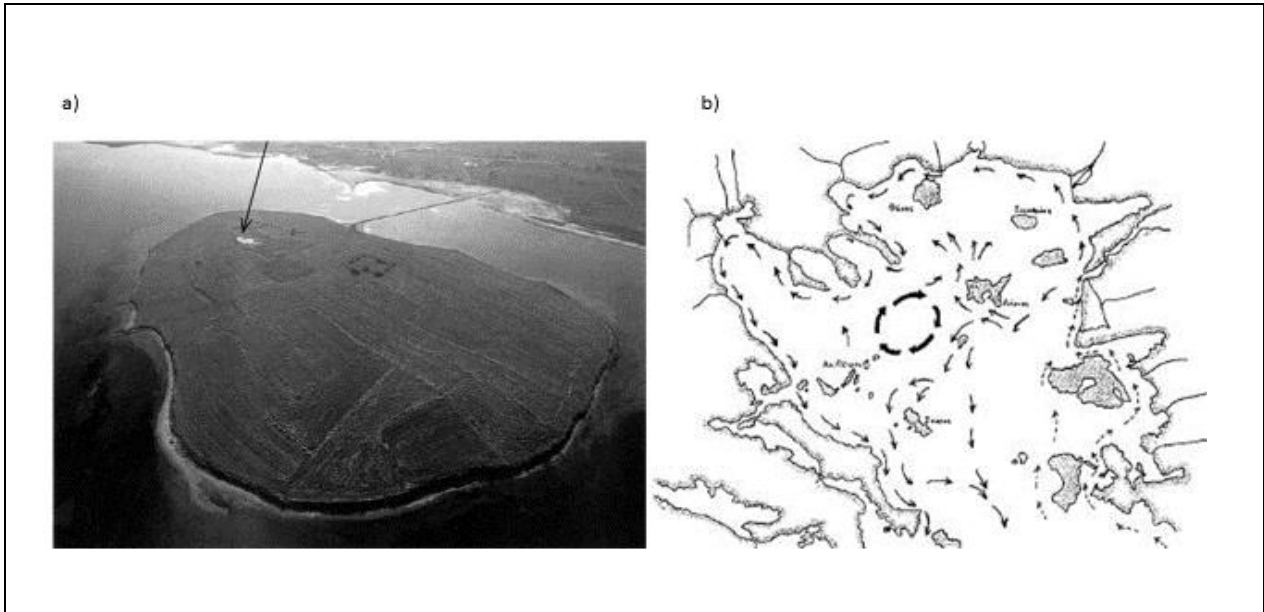


Figure 3: a) Koukonisi from the air; the arrow indicates the main excavation area (Sector B) on the Koukonos plateau. (Boulotis, 2009:179, fig. 3); b) Sea currents in the northern Aegean during the summer (Boulotis, 2009:178, fig. 2).

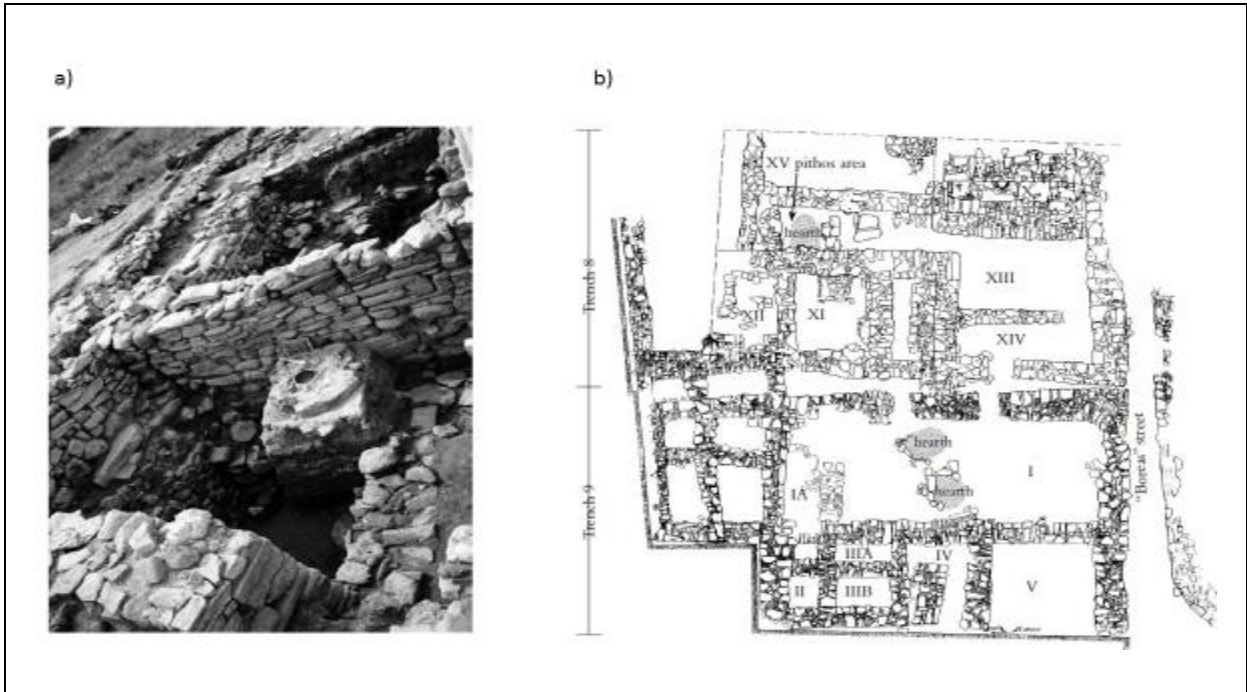


Figure 4: a) Successive phases of the settlement from EBA to early LBA (Room IV, Trench 5 and Room V, Trench 7) (Boulotis, 2009:181, fig. 6); b) Plan of the Minoanising sector of the settlement (Trenches 8 and 9) (Boulotis, 2009:180, fig. 5).

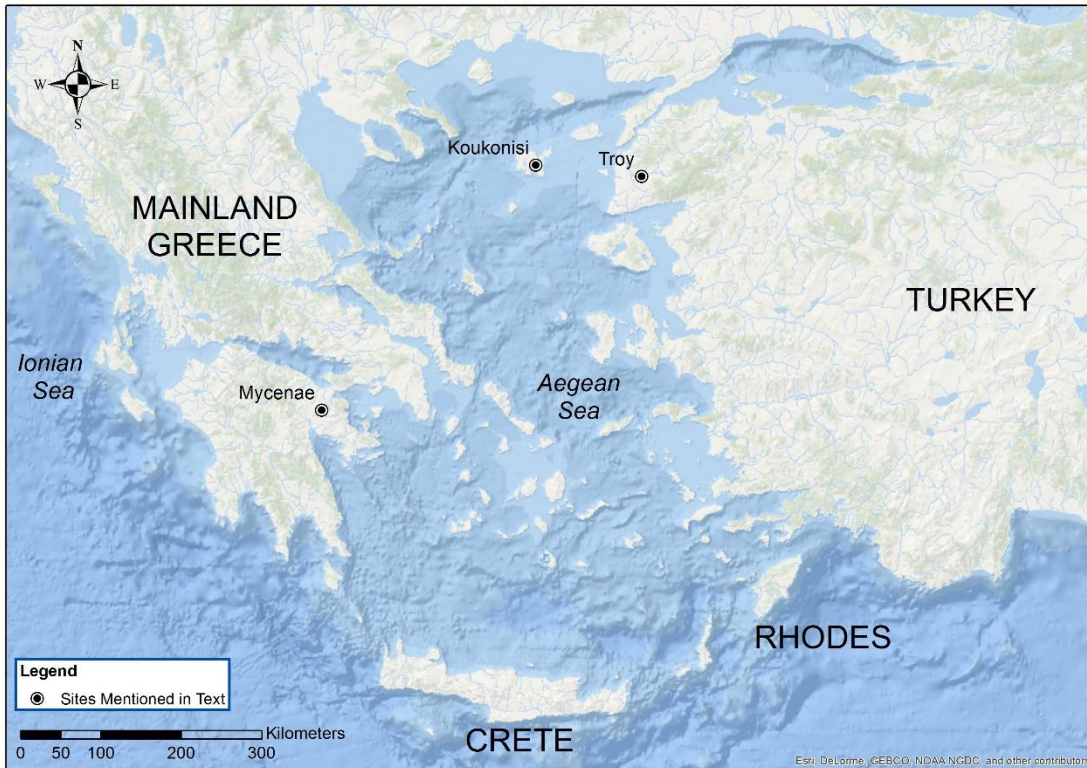


Figure 5: Geographical position of the major sites mentioned text (*Koukonisi, Troy, Mycenae*) in their Aegean context (map created using ArcGIS by Duygu Ertemin).

### 2.2.1. Mycenaean presence on Koukonisi:

Christos Boulotis (2009) began discussions on the Minoanization process in the north Aegean and western Anatolia, including Lemnos Island and Koukonisi, based on material culture found during excavations and survey collections. Following this process, he identified the Mycenaean character of the island and Koukonisi, since Mycenaean presence was also observed on other Bronze Age sites on Lemnos Island. In addition to the material findings that indicated Mycenaean presence on the island, information gathered from the Mycenaean archives of mainland Greece belonging to 13<sup>th</sup> century BC provided information on Lemnian women working as seamstresses, and Linear B tablets that mentioned kings of Lemnos in Mycenaean names was pointed out by Boulotis (2013), and confirmed Mycenaean contact with the island.

Although Minoan presence on the island has been identified, Mycenaean presence and associated pottery on Lemnos Island and Koukonisi have been the focus of attention since the information acquired has assisted in the understanding of movement, technology transfer, and agency, as well

as placed Lemnos within a chronology that covers the Aegean islands and the mainland. It should be mentioned that chronological studies for Aegean archaeology are broad, and have included many techniques over the years that are unfortunately not absolute, and do not enable one to easily procure or provide an accurate and universal chronology. Tartaron (2008: 86-88) reviewed the Aegean chronology studies, which mostly relied on correlating studies of Aegean pottery sequences to the Egyptian historical chronology through the Aegean pottery that has been found by excavations in Egypt. This review referred to Bennet and Galaty (1997) for the absolute chronology of the Bronze Age Aegean, and Manning (1995) for a radiocarbon framework established for the Aegean along with dendrochronological studies. For this study I prefer to use the general pottery phase terms instead of calendar dates, although Tartaron did provide them for Crete and mainland Greece (**Table 1**).

Mycenaean presence on Koukonisi (advanced LBA- Koukonisi II) is understood by its material culture, especially from characteristic Mycenaean pottery and terracotta figurines scattered throughout the islet or in excavated deposits. Mycenaean pottery, despite its regional variations, was prepared with refined calcareous clay and shaped with a potter's wheel. The surface of the pottery is smoothed or polished and generally colored with an iron-rich slip. The firing techniques applied for the production of Mycenaean pottery was oxidation, and/or oxidizing-reducing-oxidizing alternating atmosphere, in updraft kilns that could have controlled atmosphere conditions. Although Mycenaean pottery was sometimes painted, there were undecorated and non-calcareous potteries in Mycenaean pottery assemblages as well (Kiriati and Andreou, 2016:133). As it is indicated above material culture plays a crucial role in understanding cultural relationships in terms of gift exchange, trade and economy. Mainland, south Aegean and Anatolian influences and imports are mostly understood by the diversity in the types of pottery and decoration on Lemnos Island (Boulotis, 2009:208).

Considering the remains of Mycenaean architecture, the discovery of walls built on top of early LBA ruins, for example the one running from southwest to northeast at the westernmost limits of Trenches 8 and 9 (Section IX) that was revealed during the 2005 excavation season, and a curved wall (Trench 6A/'96), were indicated by Boulotis as possible evidence of a shift in settlement from this area to a lower plateau in the southern part of the islet during the Mycenaean period (Koukonisi II) (2009:181). East of the mentioned curved wall a deposit containing LH IIIA:1-2 pottery, including the clay stopper of a stirrup jar, could be an indication of commercial relations

with Mycenae (Kardamaki and Boloti, 2013), along with another one above Room I (Trench 9) in the LM I destruction horizon that was found (Boulotis, 2009).

The 2005 excavation season revealed a hoard of sherds and broken vases just below the surface layer in Trench 6A that mostly belonged to open and closed vessels. Open vessels were mostly drinking vessels (decorated or plain), deep bowls, cups and kraters, while closed ones belonged to large stirrup jars, and they have preliminarily been dated from LH IIIA2 to LH IIIB1, from the middle of 14th to the beginning of 13th century BC (Boulotis, 2009). Also in the 2005 season, west of the settlement in an area called Sector Γ, a 5x5m trial trench was opened where Mycenaean figurines had been found during survey, and numerous Mycenaean sherds were found. Mycenaean pottery collected during surface survey and from excavated layers indicated the presence of Mycenaean on the island and Koukonisi, however the context of the ceramics revealed even more important information. Since Mycenaean ceramics are found in secure deposits related with the LBA, possible Mycenaean architecture, and around Mycenaean figurines that could be related to ritualistic activities, the presence of Mycenaean influence can be considered continuous. Boulotis argues that this influence was most likely permanent, that these findings could not result from acculturation processes of the native population, and in fact that it indicate Koukonisi was a governed colony (2009:208-209). Here it is important to mention the different approaches that have been taken towards interpreting Mycenaean pottery found in different regions and sites.

Crete (Minoan)			Mainland (Helladic)		
	Pottery Phase	Calendar dates	Pottery Phase	Calendar dates	
Prepalatial	Early Minoan (EM) I	3100–2700	Early Helladic (EH) I	3100–2700	
	EM II	2700–2200	EH II	2700–2200	
	EM III	2200–2100	EH III	2200–2000	
	Middle Minoan (MM) IA	2100–1900	Middle Helladic (MH) I	2000–1850	
Protopalatial	MM IB	1900–1800			
	MM II	1800–1700	MH II	1850–1700	
Neopalatial	MM III	1700–1600	MH III	1700–1600	Shaft Grave Era
	Late Minoan (LM) IA	1600–1480	Late Helladic (LH) I	1600–1500	
		LM IB	1480–1425		
Final Palatial	LM II	1425–1390	LH IIA	1500–1440	Mycenaean
			LH IIB	1440–1390	
Postpalatial	LM IIIA1	1390–1370	LH IIIA1	1390–1370	
	LM IIIA2	1370–1300	LH IIIA2	1370–1300	
	LM IIIB	1300–1190	LH IIIB	1300–1190	
	LM IIIC	1190–1070	LH IIIC	1190–1070	
	Subminoan	1070–1000	Submycenaean	1070–1015	

*Table 1: Chronological table of the Aegean Bronze Age, using a modified low chronology (Tartaron, 2008:84, Table 1).*

### 2.3. Brief Discussion on “Mycenaean presence” studies:

Mycenaean pottery found in different regions and sites in the Aegean and Mediterranean, especially from the second half of the second millennium BC, has made it possible to study the different aspects of cultural relations and movement, which has been termed as interregional or intercultural mobility (Kiriati and Andreou, 2016). In addition, studies focusing on trade networks increased attempts to define the Mycenaean core and periphery areas (Tartaron, 2005). According to Kiriati and Andreou, a hypothesis of Mycenaeanisation associated with trade, exchange, migration and colonization was tested by using two approaches: first, acculturation processes involving a high/donor – lower/recipient cultures, and second, core area and periphery cultures, but both approaches assigned a passive role to the recipient or periphery cultures (2016:130). Moreover, Tartaron indicated that the active core and passive recipient model viewed any development in the periphery as a consequence of external forces originating from the core

(2005: 154), and that relations were presented as asymmetrical between the core (Mycenaean) and its periphery (2008:109). However, post-colonial and agency theory helped to understand a more active role of the periphery in adopting Mycenaean cultural elements throughout the Aegean and Mediterranean within the last decade (Kiriati and Andreou, 2016).

In addition to the different ideological approaches used in the studies, archaeometric approaches should be mentioned as well since Mycenaean pottery found in the Aegean, the Mediterranean, Macedonia, Cyprus, the Levant and Egypt drew attention to the importance of identifying if pottery was locally made or imported within the last 20 years. Especially in 2005, during the conference of Aegaeum series (Laffineur and Greco, 2005), many authors focused on the issue of identifying the form of Mycenaean presence through material culture. An important study considering the core-periphery interaction through pottery with the application of archaeometric techniques (neutron activation analysis, petrographic analysis, scanning electron microscopy and X-ray diffraction) has been accomplished in central Macedonia, the central Mediterranean and southern Italy (Buxeda I Garrigo's et al., 2003). This study showed the importance of the integration of archaeometric techniques for the identification of locally produced and imported Mycenaean pottery by correlating chemical analysis of the clays with the technological characters of the ceramics such as the surface decoration techniques, firing techniques and atmospheres.

Another important study applying archaeometric technique to the identification of Mycenaean local and imported pottery from Troia is *Neutron Activation Analysis of Mycenaean Pottery from Troia (1988-2003 Excavations)* (Mountjoy and Mommsen, 2006). This analysis was carried out on 192 sherds found during the Troia excavation seasons between 1988 and 2003. Their broadened spectrum of samples divided the sherds as A-Troy, B-Troy, C-Troy, D-Troy, G-Troy, and most importantly identified that pattern MYBE coinciding with the Argolid imports is very similar to Troy-A, which was identified as local to Troia by the earlier Berlin grouping. Moreover, Mountjoy and Mommsen identified that the Group D-Troy and A-Troy/MYBE showed similarities, although group D-Troy was also close in composition to group Ach-a from NW Peloponnese (2006: 100). This study was an important contribution to the Mycenaean archaeology in two ways. First, it proved that NAA is an important method for the identification of pottery provenance, local production and imported potteries. Secondly, it indicated the use of Bonn Greek Data Bank for the comparison of Troy-A and MYBE chemical patterns (Mountjoy and Mommsen, 2006:98).

As a result of the development in provenance and technological studies of ceramics, large chemical and petrographic databases were produced in different laboratories. Due to the accumulation of data over the years, it has become a problem for archaeometric studies (Waksman, 2016) because the analytical procedures that obtained the results needed to be tested before exchanging in terms of their equivalence. Use of the databases are very helpful since comparative data and reference groups are available; issues concerning the ceramic workshops, the consumption of imported ceramics at the site, diffusion of potteries, commercial networks, and local status of productions can be addressed (Waksman, 2016) as it was the case in Mountjoy and Mommsen's work mentioned above. The Archaeometry Laboratory at the University of Missouri Research Reactor (<http://archaeometry.missouri.edu/datasets/datasets.html>) or the Helmholtz-Institute of Nuclear Physics at the University of Bonn (<http://www.hiskp.uni-bonn.de/gruppen/mommsen/data.html>) providing selected data tables in electronic form via the Internet could be given as an example (Hein and Kilikoglou, 2012). However, availability of the databases and comparison of various data coming from different studies are important issues.

CeraDAT (<http://www.ims.demokritos.gr/ceradat/>) on the other hand provides a relational database for archaeological pottery, with elemental composition of thousands of ceramic artefacts from the Eastern Mediterranean, where one can reach information on the elemental compositions, reference patterns of specific sites, archaeological metadata, geographical distribution, literature references and formal statistical evaluations. Moreover, the CeraDAT database design allows further entries such as petrographical and mineralogical information and advanced study of the material to find links between ceramic assemblages (Hein and Kilikoglou, 2012:142). The ability to reach different kinds of data such as elemental, petrographical and mineralogical is a great advancement since several provenance and technology studies indicated the importance of using more than one technique (ex. Day and Kilikoglou, 2001; Hein et al, 2002). Considering the theoretical and methodological approaches described above for Mycenaean studies, it would be true to say that this thesis study as a technological characterization through SEM-EDS analysis of the Mycenaean pottery from Koukonisi, Lemnos, which is a periphery to the mainland core, provides supplementary results to the NAA data.

### 3. Theoretical Framework:

#### 3.1. Pottery Production:

Fired clay was used for the production of many objects, but ceramics are the most frequently studied by archaeologists due to its high degree of preservation. Not only through its form and style but also its production stages and decorations, pottery gives an enormous amount of information on the potter's mind and how they used the surrounding environment.

According to Maniatis (2009:2) ceramic technology gives important information on the organization of a society including food preparation and storage, the economy, trade and commerce, along with the connections between and competition with other societies. The investigation of ancient ceramic technology is very important for these reasons. The actions performed during the process of ceramic manufacturing are therefore a diverse study of the technology.

The term *chaîne opératoire* was first coined by Leroi-Gourhan (1964:164) for the characterization of techniques as a sequence of gestures and tools, which gave stability and flexibility to the operational series. A ceramic *chaîne opératoire* involves two levels of actions; the main actions and dependent actions involved in the production stages (Roux, 2016).

According to Tite (1999:182), the life cycle, which is similar to the *chaîne opératoire*, starts with the production stage and includes the selection, procurement, and processing of the raw materials, followed by forming, surface treatment, and firing of the pottery, and continues with its distribution, to the consumption stage including the use, maintenance, repair, reuse, and discard phases of the pottery. There are many books (Orton & Hughes, 2013; Rice, 1987; Rye 1981; Shepard, 1956) that provide a comprehensive approach to all the phases of the *chaîne opératoire* in pottery production.

In this chapter the production stage of the ceramic *chaîne opératoire* (**Figure 6**) will be introduced. In general, the production stages of fired clay vessels are as follows (Miller, 2009; Santacreu, 2015):

1. Collection of raw materials such as clay, temper materials, decorative pigments, and fuels.



2. Processing of clay for the desired outcome by cleaning, sifting, soaking and levigation, also preparation of temper by crushing, cutting, sieving, along with preparation of decorative pigments and other materials.
3. Formation of the clay body by paste preparation involving mixing, kneading and maturing.
4. Shaping and forming of clay objects using different production techniques, including hand-forming, molding, use of turning devices, trimming/scraping, and/or paddle and anvil.
5. Drying of objects and surface treatments, including painting and/or slipping, incising or impressing, polishing, smoothing.
6. Firing of objects.
7. Further surface treatments.

### **3.1.1. Collection of Raw Materials:**

Pottery production sometimes requires the use of more than one raw material such as tempers, decorative pigments, fuels and different kinds of clays. Therefore, the first step of a pottery production process is the collection of raw materials. There is a wide range of paste recipes and raw material choices that are part of the production process. These decisions are most probably affected by environmental, geographical and cultural factors and even personal choices of the potter. For example, the use of different clay and temper types can be explained by different desired performance of the materials and their intended uses.

“There are many types of clay that become plastic or malleable when moistened”, as Rice (1987: 36) states they can be both calcareous and non-calcareous. Clays that have more than 5% of CaO in their composition are called calcareous clays, and those with a lower amount of CaO are classified as non-calcareous. Since they have different properties they behave in different ways, such as in their coefficients of thermal expansion (Tite and Kilikoglou, 2002). In contrast to calcareous clays, non-calcareous clays include raw materials without calcium carbonate but of higher siliceous nature (Santacreu, 2015). Cretan ceramics using this type of raw material during the Bronze Age can be given as an example (Hein *et al.*, 2004). Iron-rich calcareous clays were used in pottery production as well. Especially in the Mediterranean basin a certain type of clay

called lateritic can exceed 10-15% in iron content and can be a characteristic of a particular source among different clay deposits (Santacreu, 2015).

Raw materials such as minerals for slips and pigments were sometimes difficult to find since these materials might not be available in the local landscape but at considerable distances. Common coloring minerals used in the making of slips and decorations were red ochre or manganese-iron compounds that were crushed and mixed with fine clay and water to the desired consistency, while grog, rock minerals, or other materials added to slips were often ground and sieved to arrange the desired size range. For glazed surfaces the materials required were more diverse and required trade networks (Miller, 2009).

Another important raw material used for pottery production was the fuel. It was perhaps the most important raw material since without it the clay body could not be fired and become pottery, so maintaining a steady supply of it was an important issue for craftspeople. Moreover, wood from specific species and forms of fuel such as charcoal might have been selected for desired characteristics of heat or smoke production (Miller, 2009).

### **3.1.2. Processing of Clay and Temper:**

Clays that are collected by digging the sediments out of the ground required some processing such as the removal of naturally occurring mineral and organic coarse materials to be used in pottery manufacture (Santacreu, 2015). These stages of processing raw clay, collectively known as “removing the unwanted material”, can be organized into categories of crushing, cleaning, sieving and levigation. Inclusions such as rock and plant fragments were eliminated from the clay by hand or through levigation, which helped to transform the raw clay into a fine one to create a high quality vessel (Miller, 2009). If the levigation process was done well and produced only fine-grained sediments, these clays could also be used for slips (Tite et al, 1982), although the clays used for the slip were generally finer (Rice, 1987). These steps were taken before the process of selection and mixture of the clays and tempers from different sources as a paste choice to give the preferred color and properties. Processing of clays and tempers was done either on the source sites or in the workshop sites where the pottery was created. In addition to clay processing the preparation of tempers were performed by crushing, cutting and sieving, while the preparation of decorative pigments and other materials were also important steps in the production of pottery (Santacreu, 2015).

Rice (1987: 406–413) provided a discussion on the difference between temper and inclusion. Following this, Miller (2009) stated that *temper* refers to any type of material added to the clay, and *inclusion* refers to the presence of non-clay materials in the clay body, whether these materials were found naturally in the clay or added. It may be said that tempers added to clay are the spices added to the dish if we consider the paste as a meal recipe. For example, most common tempers and inclusions are sand, shell, mica, plant materials, other minerals, grog (fragments of fired pottery), dung, salt and sometimes other clays. These materials generally did not require as much processing as clay. Processing that was required before mixing with the clay could be for plant materials such as straw or seeds from domesticated or wild grasses, seed fluff and leaves, which all needed to be cut to the required size. To acquire the desired size of particles, sand, shell, mica and other minerals may have been ground or sieved (Miller, 2009).

### **3.1.3. Paste Preparation:**

During the ceramic paste preparation process potters sometimes did not follow the same procedure. Perhaps it would be true say that each culture or specialized potter created their own paste recipe according to environmental, geological and cultural factors. With this idea the first step for any technological study of ceramics has always been the analysis of the choice and treatment of the raw materials used in their production (Tite, 2008).

As it is explained above, after the extraction and processing of clay and tempering agents the third step in the pottery manufacture is paste preparation. This process involves the procedure of adding desired tempering material to the desired clay and mixing these materials. This procedure can be explained as kneading clay with water and tempering agents to produce a uniform clay body. After this preparation the clay may be wrapped to keep it damp until the potter uses it. Moreover, it is said that storing the final uniformed clay body prior to use improves its working qualities (Miller, 2009).

The choice of clay and tempering agents depends on many factors. One of the most important is perhaps the working properties. Each temper agent has certain technical advantages and disadvantages. Moreover, two different clays may require different tempering strategies (Orton & Hughes, 2013). For example, some clays do not need the addition of tempers but function as desired with what is found naturally in the clay. Other clays require temper additions for the desired working properties. Also there are some types of tempers that affect firing properties such

as plant materials. These materials burn out during firing and leave voids behind which increase the heat resistance of the product. Furthermore, some materials may be added for ritual purposes, beyond what is functionally required for intended working and firing properties (Santacreu, 2015).

#### **3.1.4. Shaping Methods:**

The next step in the pottery production *chaîne opératoire* after forming the clay body is shaping. There are many shaping methods that have been classified according to the clay chunk being worked on, such as a single lump of clay, or successive additions of clay, and whether they are entirely shaped by hand or with the addition of tools or application of rotational force (Rice, 1987). These are the six common techniques for shaping; the three hand-forming techniques (pinching, modelling and coiling methods), the slab technique, the molding technique, and forming with the use of turning devices such as wheel-throwing, or using other turntable devices such as tournette (Rice, 1987; Miller, 2009; Shepard, 1975).

The common *hand-forming* techniques are pinching, modelling and coiling. Pinching and forming or modeling a lump of clay by hand has been used to produce pottery and many other clay objects (Miller, 2009:113). This technique consists of pinching a lump of clay with the thumbs and fingers to open the lump and thin the walls of a vessel by squeezing. This technique is usually reserved for small vessels or the bottom parts of bigger vessels (Rice, 1987).

The second major hand-building technique is *coiling*. For this method potters follow the steps of making cylinders or ropes from clay, winding these on top of each other in a circle to build up the walls of the pottery and then smoothing the joins between the coils (Miller, 2009). Although coiling may be employed from the beginning when there is spiral placement, pottery manufacture usually starts with a basal disc of clay formed by various punching and patting manipulations. The next step would be the construction of the walls of a pot by placing varying size and diameters of coils on top of each other (Shepard, 1965). Additionally, the paddle and anvil technique can be employed together with the coiling technique to apply pressure to bound the coils and thin the walls (Shepard, 1965). This technique is used mostly for large vessels such as storage jars (Rice, 1987).

Apart from these the slab and molding techniques were used as well. In slab building one or more slabs of clay are flattened and used to create the desired shape for vessels (Rice, 1987). As Shepard (1956:63) states, the molding technique may seem to be more advanced compared to hand forming techniques, however pressing clay into a form is not more difficult than a technique such as coiling. This technique is used to form complex shape of pottery or to form and support parts of large pots such as bases of large jars until the clay dries (Miller, 2009). Molds may be formed with plaster and fired clays or large broken vessels and are used for slip casting as well (Rice, 1987).

The *Wheel-throwing* technique is another widely used production method. This term is used for forming techniques using various turning tools such as a tournette or turnable supports, however the term is reserved for when the potter used a fast turntable. It is thus important to distinguish “true” wheel throwing from other turning tool methods. Although the use of turnable tools allows pottery in the process of manufacture to be rotated, “wheel-throwing” is the method where potters use wheels rotating at a rapid speed for a considerable period of time (Rice 1987). These “true” wheels produce centrifugal force as well as sustained momentum about a central pivot thanks to high rotation created by the wheels so that pottery can be produced consistently (Miller, 2009). In wheel-throwing, a lump of clay is placed on the wheel, opened by inserting fingers into the center of mass clay and lifting the walls as it rotates. This rotation creates rilling effects on one or both sides (Rice, 1987). Other turning tools in the making of pottery are called pot rest and tournette. A pot rest is a turnable support on which clay can be placed and formed while the support is rotated by hands or feet. These supports can be anything turnable without a pivot. The term tournette refers to the hand-wheel method that allows rotation like pot rests but also has a pivot. Thanks to the pivot, a tournette can be rapidly rotated for a short period of time, and may even produce surface marks characteristic of wheel-thrown pottery such as rilling.

### **3.1.5. Drying:**

After forming the clay body, the object must dry and come to a leather hard state before the firing stage. Although some surface treatments can be applied while the object is still wet, most of the treatments are performed after the object is dried to some degree (Miller, 2009). The most important variables in the process of drying, which can also be called the dehydration process, are the temperature, humidity and the location where the pottery is stored prior to firing (Santacreu,

2015). This drying phase can take several days or even weeks. It can be a rapid or incomplete process which would affect the final product either during drying or firing (Rice, 1987), so it should be closely monitored since the thicker parts of the pottery would dry slower than the thinner parts. Another important point is the effect of drying on the concentrations of dissolved salt and fine clay particles toward the vessel surface, which in turn would have an effect on the color of the vessel during firing (Orton & Hughes, 2013).

### **3.1.6. Surface Treatments:**

Surface treatments include the application of slips, pigments or other materials, as well as incising, impressing, polishing or smoothing. A few types of pigments are applied after firing, but most treatments are usually done before firing. Rice (1987) divided these treatments into two categories, finishing techniques and surface enhancements. These treatments can be named as secondary forming techniques since they alter the surface characteristics (Rice, 1987). Finishing techniques include applications such as beating, scraping, trimming, smoothing, polishing and burnishing. The surface enhancement type of pottery decoration can be further divided into two categories, penetration of the surface and color addition (Rice, 1987). Here, the surface treatments further discussed will be finishing techniques and color additions.

#### ***3.1.6.1. Finishing:***

Surface finishing techniques depend on the function of the pottery and whether it is going to be decorated or not. It can be done while the pottery is still wet and plastic or leather-hard and dry. These techniques are used to eliminate irregularities left from forming the clay body such as finger depressions or marks left by the edge of the support, or to create a smooth surface for decoration (Shepard, 1956).

The beating technique is applied to roughly made vessels to modify its shape and size. The paddle and anvil technique is the most common beating technique. This technique is mostly applied to pottery shaped with via coiling. Beating the surface has many effects on the pottery such as bonding segments, thinning walls and smoothing surfaces (Rice, 1987). The scraping technique is used to thin the walls of pottery and remove impurities as well. It is mostly used to finish vessels shaped by coiling, molding and pinching with smooth edged tools such as bone, shell, bamboo or sherds. In the trimming technique, which is used for wheel-thrown and molded

vessels, the aim is to trim the excess clay and impurities. Another action that alters the surface of the pottery is called smoothing. It is done with a soft tool such as a piece of leather, cloth or hands by perhaps rewetting or before the vessel is completely dry (Rice, 1987). It can be said that the polishing and burnishing techniques are variants of smoothing. Polishing is used to give a lustrous look to the final product, which can be slipped or not (Shepard, 1956). To give that shiny, glossy look on the surface a hard object such as a pebble or piece of wood can be used to rub back and forth on the leather-hard clay. In this way the clay particles oriented and compacted on the surface (Miller, 2009; Rice, 1987). The distinction between the use of a polishing technique on slipped and unslipped pottery is that the polishing tool would remove the slip easier than the paste when the condition of moisture is not correct (Shepard, 1956).

The burnishing technique is done with a hard tool such as a pebble, bone or horn to a leather-hard or dry clay, and it also gives a shiny look to the surface like the polishing technique, however sometimes with burnishing matte parts on the surface can be observed. The polishing is executed with care to dry pottery creating a lustrous surface whereas burnishing can be done to a leather-hard clay and can be observed by the partially matte look on the surface and parallel facets (Rice, 1987). Apart from these finishing techniques vessels sometimes may be patterned or textured. Vessels incised or impressed with various tools can be an example of patterning and texturing. These techniques may involve complex stamps, be grooved with fingers, combed in wavy lines, or incised with symbols (Miller, 2009). Sometimes these techniques are done for functional purposes such as roughened vessels that could be used for transport or cooking (Rice, 1987).

#### *3.1.6.2. Coloring the surface:*

There are two direct ways to color the surface of vessels. The first one is to coat the whole surface with color, and the second is to only partially color the surface (Rice, 1987). A third way of coloring the surface is to manipulate the vessels via firing conditions. These coloring techniques are defined as painting, slipping and glazing. In this section painting and slipping applications will be introduced briefly, while manipulation of the surface color through firing conditions will be introduced in the firing section.

#### 3.1.6.2.1. Painting:

Painting is the application of pigments or colorants to a vessel to color the surface. Although Shepard (1956: 31-42) used the term paint as a pigment or colorant such as matte painting, carbon paint, iron and manganese paints and clay paints, both Rice and Rye argued that the term paint should only be used for the action of applying the substances, and not the substance used. In this vein, here the term paint will be used to describe the technique and not the colorant.

For successful painting the pigments must retain a desirable color after firing and it must adhere to the vessel surface (Shepard, 1956). These pigments are generally chosen from organic substances such as iron oxides like hematite, magnetite and copper oxides that occur naturally in the environment (Santacreu, 2015). The selections used on the pottery are mostly some kind of mixture consisting of the aforementioned colorants, together with fine clay, water and binder (Rice, 1987). There are three important colorants that can be found as an oxide form in nature and survive through firing. These are iron, manganese and carbon oxides. Although these oxides are used for slipping as well, slips differ from pigments as Rice (1987: 148–149) and Rye (1981: 40–41) give clear definitions for both. Following Rice (1987) it can be said that pigments are fluid suspensions of fine clay and other colorants and applied with a brush made from animal hair, fur, feathers or vegetable fibers since it is viscous before firing, whereas slips are less viscous fluid suspensions of again fine clay, colorants and water that are applied over the pottery to create a thin coating prior to firing. The application of pigments or colorants on the same piece of pottery may be done more than once. For example, decorations made with one colorant is called monochrome, while those with three or more colorants are called polychrome decorations (Rice, 1987). Noll et al. (1975) have detailed research on monochrome and polychrome paintings separated as black by reduction technique, manganese black technique, carbon black technique, black/red and black/red/white dichrome and polychrome techniques. It should also be noted that painting could be done over slips (Miller, 2009).

#### 3.1.6.2.2. Slipping:

Surface color and texture can be altered with slipping. As it is explained above, slips are fluid suspensions of fine clay, colorants and water that are applied over the pottery surface to create a thin coating before the vessel is fired. The successful application of a slip requires some technical



knowledge. Shepard (1956) gives three technical requirements that slips should meet; adhering well to the body, hardening within the same temperature range as the body, and having sufficient covering power to coat the body. Although most of the slips meet these requirements they vary in color, quality, luster and thickness due to the different types of clay used, which affects the particle sizes, the kind and amount of the absorbed ions and the degree of dispersion of the particles in the suspension (Rice, 1987). The most common oxide in slip production is iron, which fires to different colors according to the firing atmosphere. For example, under an oxidizing condition iron based slips fire red, while manganese iron compounds fire black or brown (Miller, 2009).

There are three different ways to apply slips. The first method is dipping, and it gives a uniform look to the vessel by filling in all the holes and grooves. The second method is pouring, which is used for large vessels since they cannot be dipped into the slip, or for vessels that only need to be slipped on the interior. The third method is wiping, when a slip is wiped onto the vessel with a piece of cloth or fur or the potter's hand (Rice, 1987). Apart from these techniques slips can be separated into true slips and self-slips. True slip is the application of a coloring or coating suspension to the surface of a vessel, whereas self-slip is the process that fine clay particles move to the surface via a smoothing action, and the change in surface color depends on the firing atmosphere (Miller, 2009).

Although slips are generally applied for decorative reasons, there are some cases where slips are applied for functional purposes. For example, slips that contain sand and large particles create uneven surfaces that provide thermal shock resistance (Rice, 1987). Also, slips on the interior of vessels may be applied to reduce the porosity so that they can be used for liquid storage (Miller, 2009), or bowls and jars with a slip applied to the interior and extending onto the lip to eliminate drips and splashes (Rice, 1987).

### **3.1.7. Firing:**

Firing is perhaps the most important step in pottery production. The final product depends on the firing technique and other variables such as firing atmosphere, firing temperatures and duration of firing (Rice, 1987). One other aspect affecting the final product is the method of loading the

vessels into the firing structure, the type of structure and assemblage of the vessels (Miller, 2009). Firing causes permanent changes to the natural clay material both physically and chemically. Next, changes in the clay matrix during firing according to the different firing temperatures, structures, and atmospheres and their effect on the color change of clay bodies and surfaces will be briefly introduced.

#### *3.1.7.1. Changes in Clay Matrix during Firing:*

Permanent physicochemical changes to natural clay materials due to firing start with the volatilization of the absorbed water in pores and between particles at low temperatures (100–200°C), and continues with the dehydroxylation process, which is the term for the loss of chemically bound hydroxyl water, as the temperature increases (400–800°C). As the temperature increases solid-state reactions, such as the sintering and vitrification of the clay minerals, occur because the chemical compositions of the clay minerals change (Maniatis, 2009). Sintering begins at temperatures of 600°C and continues until the start of vitrification at higher temperatures of 800°C to 1000°C (Quinn, 2013). Vitrification is the simultaneous formation of an amorphous phase consolidating and cementing the particles together (Maniatis, 2009:3).

It should be mentioned that the presence of fine calcium carbonate in the clay plays an important role in ceramic properties such as microstructure, vitrification, bloating and final color (Maniatis, 2009:8). Decarbonization, which is the process of calcium carbonate ( $\text{CaCO}_3$ ) decomposing to calcium oxide ( $\text{CaO}$ ) with the emission of carbon dioxide in the 750°-850°C temperature range (Tite, 1972:229), has an especially important role in changes to color and microstructure that occur during firing (Maniatis 2009:7). The process of decarbonization is also an indicator of the firing temperature since the presence of calcium carbonate that has not altered to  $\text{CaO}$  or  $\text{Ca(OH)}_2$  indicates firing temperatures below 800°C (Leicht, 1977). Firing temperatures above 800°C can be estimated according to the extent of vitrification in the body due to the different levels of vitrification such as interconnection of mineral particles (initial vitrification), network of interconnecting glass clay phases (extensive, continuous and total vitrification), and bloating of the body (Tite, 1992). Maniatis and Tite (1981) explain that these different levels of vitrification that occur during firing at different firing temperatures and atmospheres depend on the calcium oxide concentrations of the clays used in pottery production. It should be noted that reaching and maintaining firing temperatures in the range between 800 and 1000°C would be an indication that

people knew how to build kilns and control air (Maniatis, 2009), which will be discussed in the following sections.

### 3.1.7.2. *Firing Structures:*

According to Rice (1987) firing structures can be classified as kiln and non-kiln techniques. These techniques are separated according to the firing atmosphere they provide and also the usage of fuels (Rice, 1987; Miller, 2009). Instead of separating the firing structures as kiln and non-kiln, Miller divide these structures into three as ephemeral, single chamber and multi-chamber firing structures (Miller, 2009).

Ephemeral firing structures that are separated into open firing, bonfire and clamp methods are also called non-kiln firing structures, which provide firing in low temperatures over a short time period. Although open firing practices may vary, there are general characteristics that they share. These kinds of firing practices are done with a base from fuel that would fire slowly, and then the placement of the pottery on top of that fuel bed. The third step would be the placement of fast burning fuel around and on top of the pottery. By lighting up the base fuel firing starts, and after the fuel is burnt out the pottery may be taken or left in place until it cools down (Rice, 1987). The fuel used varies and includes charcoal, animal dung, wood, straw, etc. (Rice, 1987).

Single Chamber firing structures are more permanent than open firing systems. Pit kilns, ovens and hearts can be an example for these kind of structures. In single chamber firings, fuel is placed at the bottom like ephemeral structures or one end of the structure. Placement of the objects would be either on top of the fuel or next to it and potsherds or clay objects might be placed between the potteries and the fuel. This would be the main division of the fuel and the object to be fired.

According to Miller (2009), the difference between single and multi-chamber firing techniques is the placement of fuel since *Multi-chamber firing structures* have two separate chambers for the fuel and products. In these structures fire is more controlled so that the final production is evenly fired. Double-chamber updraft or vertical kiln can be the example for this kind of firing structures where the products are placed above the fuel chamber on a floor or supports. This separation reduces the fire-clouding so that objects can have even surfaces whereas in open firings this can't

be achieved. Moreover, kilns provide higher and controlled firing, controlled atmosphere, and efficient use of fuel (Rice, 1987).

### *3.1.7.3. Atmosphere of Firing and its Effects on Color Variation:*

The atmosphere of firing has an important effect on the final appearance of the products. There are three types of atmosphere which are called oxidizing, reducing and neutral atmosphere. According to the conditions provided by these firing atmospheres, firing temperatures, and the clay minerals, and organic tempers; pottery would change in color. An oxidation atmosphere is an oxygen-rich firing atmosphere while reducing is an oxygen poor, carbon monoxide rich atmosphere (Miller, 2009). Third kind of atmosphere is called neutral which is rich in carbon dioxide with the right amount of fuel and air (Miller, 2009). In ephemeral firing structures such as open firings and bonfires, mentioned firing atmospheres cannot be achieved since oxygen cannot be manipulated and fuel and smoke are not separated from the objects. Thanks to kiln structures, single and multi-chamber firings, atmosphere of firing can be controlled consequently the production.

As it is explained above, different atmospheres of firings have different effects on the clay body, surface paintings and slips depending on the firing temperature, clay minerals, pigments, colorant and organic tempers used in the production. For example, iron oxides are the main materials used in the production since the final color of the pottery can manipulated through the kind of atmosphere used for firing such as acquiring red color with oxidation atmosphere and black with reducing atmosphere. Moreover, the combination of the different forms and quantities of iron together with organic materials existing in a clay cause variety of colors in the raw clays such as grey, beige, brown, orange, or red (Maniatis, 2009).

In addition, it should be mentioned that the presence of fine calcium carbonate in the raw clay also plays an important role in the final color. For example, as Maniatis explain the process (2009), clays containing fine CaO less than six percent which is called non-calcareous clays fired at oxidizing atmospheres display red colors and become more intense as the firing temperature increases. In contrast, clay containing fine CaO more than six percent which is called calcareous clays, go through a different process which CaO appearing from the dissociation of calcium

carbonate above about 750– 800°C, reacts with the iron oxides and breaks them down. This process results in the bleaching of the red color to pink, cream or even whitish as the temperature increases above 850°C (Maniatis, 2009). Considering the range of temperature mentioned here, it should be noted that although oxidation requires a good draft and a high temperature to burn off carbonaceous matter, this process should be completed before vitrification starts to eliminate the expansion of gas and consequent bloating in the body (Shepard, 1956).

Considering iron oxides and calcium carbonate in the body or slips and or paintings in reducing atmosphere, it can be said that the final results would be very different than the oxidizing atmosphere. In reduction, iron-rich clays would be fired a black or grey (Miller, 2009).

According to Noll *et al.* (1975) this is the oldest ceramic decoration technique. The reason behind this process is explained by Maniatis (2009:7) as dissociation of Fe-hydroxides and Fe-oxides existing in the raw clay and release of oxygen during firing under reduced atmosphere and above 700°C temperature. Thanks to these process Fe oxides would turn into magnetite (Fe<sub>3</sub>O<sub>4</sub>) or wustite which are black in color and would turn the color of the pottery dark grey to even black.

Considering calcium carbonate, firing of non-calcareous clays in a reducing atmosphere result in dark grey and even black color ceramics, while calcareous ones would result in light grey to even whitish colors. However, as Maniatis states, color of the ceramic body fired under reducing atmosphere, whether calcareous or non-calcareous, would not change in color if the temperature was not above 800°C since dissociation of CaCO<sub>3</sub> and the appearance of the reactive CaO in the clay matrix occurs at about this temperature (Maniatis, 2009).

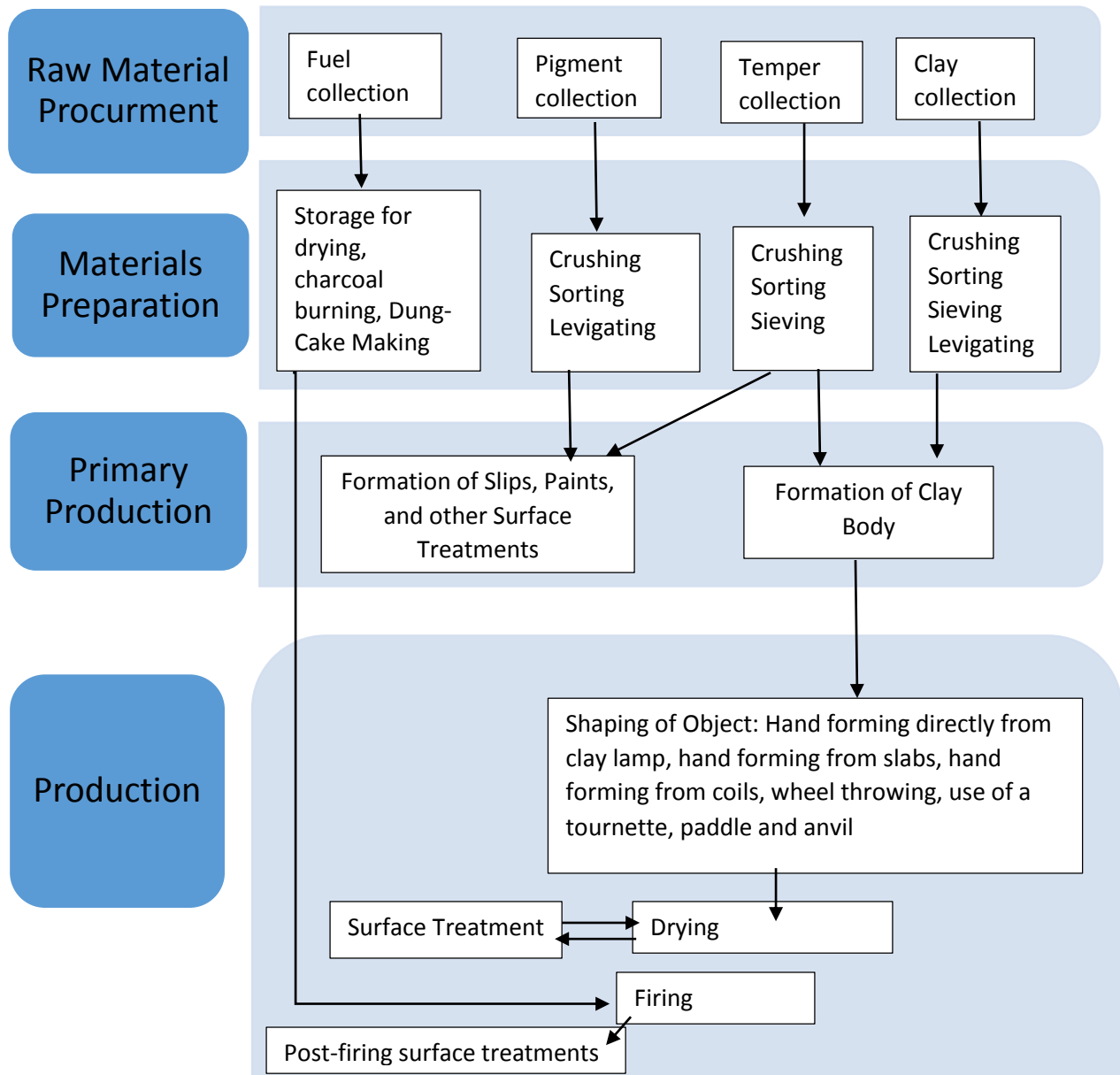


Figure 6: Production Process Diagram for Pottery (after Heather M- L. Miller 2009, 108).

### 3.1.8. Post Firing Surface Treatments:

Post-firing surface treatments can be functional or decorative and it can be done either by the potter or the consumer to prepare it for use (Rice 1987; Miller, 2009). Considering functional purposes. For example, by filling the pottery with liquid foodstuff and heating prior to cooking would seal the inner surface and would prevent sticking or pottery might be lined with resins or oils to decrease the permeability of liquid storage containers. Again coating outer surface with gum or resinous substance is another method mentioned by Shepard (1956:93). Considering decorative purposes, painting with vegetable dyes and other colorants which would not survive firing can be given as post firing surface treatment (Miller, 2009).

## 3.2. Ceramic Studies in Archaeometry

Archaeometry comprehends a group of analytical techniques that can be applied in the study of material culture. Moreover, it is based on the necessary interdisciplinary relationship between different branches of the natural and social sciences (Rice, 1987). Archaeological ceramic is one the study area of archaeometry. The aim of the ceramics studies with these techniques is the investigation of the ceramic *chaîne opératoire* or overall life cycle as Tite (1999, 2008) suggests. After production and technological choice, the second aspect of the ceramic life-cycle requiring interpretation is the distribution of ceramics away from identified production centers or sources of raw material. These interpretations can be made thanks to provenance studies which make a significant contribution to our understanding of trade and exchange, movement, agency, and technology transfer.

Although ceramic production techniques and provenance studies seem like the main concerns in ceramic studies through different types of textural, mineralogical and chemical research techniques in archaeometry; assignment of ceramic function through thermal and mechanical properties, or organic residue analysis and dating of ceramics through thermoluminescence and optically stimulated luminescence techniques are other important archaeometric analysis (Tite, 2016).

### 3.2.1. Techniques of Ceramic Archaeometry:

Application of archaeometric techniques provides a diverse and comprehensive framework of data from cultural materials which scholars would use to identify abstract and social concerns of past societies (Santacreu, 2015). Since ceramics are the most found archaeological materials, their study provides information on various phenomena and social concerns.

Ceramic characterization requires both mineral and chemical methods because each technique provides information the other cannot (Rice, 1987). These techniques used in ceramic research can be divided as textural, petrographic, mineral and chemical analysis (Orton&Huggens, 2013) and each will be introduced in this chapter.

#### 3.2.1.1. Petrographic Studies

Petrographic analysis is a widely used technique in archaeometry, especially in ceramic analysis<sup>6</sup>. Petrographic microscope is used to analyze optical characteristics of the minerals which ceramic is composed of (Rice, 2015). This microscope is a specific type of microscope with many features. Firstly, it has two polarizing lenses. One is below the stage that transmits light only in one direction and the second is attached to move in and out of the microscope tube (Rapp et al, 2006). Secondly, it has a rotating microscope stage that gives the opportunity to identify maximum birefringence point and differentiate the extinct minerals from voids (Quinn, 2013). These features provide enlarged images of the material put on the stage, plane and crossed polarized lights together for the analyses (Rapp et al, 2006) so that mineralogical composition, and structure such as size and distribution, and textural and optical characteristics of the clay matrix, shape and quantity of voids, and many more characteristics (Peterson and Betancourt, 2009) can be obtained. Therefore, this technique allows the determination of specific *petrofabrics*, depending on their particular composition, technology and origin (Quinn, 2013; Tite, 2008).

One of the most important drawback of thin section petrography for ceramic characterization is the study of fine-grained clay minerals (Rapp et al, 2006). Although clay minerals are too fine-grained to be studied in terms of optical mineralogy and does not provide study of the fired clay mineral particles (Rapp et al, 2006), the optical activity of the matrix, which can be observed by rotating the sample under cross polarized light XP, gives important hints for the firing



temperature since it becomes anisotropic and glassy looking above certain temperatures (Quinn, 2013). For example, an anisotropic matrix is non-vitrified and retains its optical properties, and suggests a firing temperature below the vitrification point (Rice, 2015).

#### *3.2.1.2. Textural Analysis*

Textural analysis is concerned with the distribution of mineral sizes and shapes rather than the identity of the minerals in a ceramic body (Orton&Huggens, 2013). The analysis, grain size analysis, mainly refers to the percentage of fine and coarse fractions occurring in the paste and especially to the characterization of its inclusions and tempers by means of variables such as frequency, grain size, particle shape, sorting and roundness (Rice, 1987). Thanks to textural analysis, apart from the information on the mineral sizes and shapes of the paste itself, information on the environment in which the sediment was deposited and its degree of alteration can be acquired as well (Hein *et al.*, 2004).

There are two procedures of grain-size analysis of the coarse fraction. First approach describes the grain-size distribution for all the inclusions together, and the second one describes each identified inclusion type separately (Orton&Huggens, 2013). First approach that describes the grain size distribution considering the entire aplastic coarse fraction as a single phase, distinguishes between mineral and organic non-plastic components occurring in the paste and it can be performed with a binocular microscope. Second approach that describes each inclusion type separately would require the use of petrographic microscope (Sancreu, 2015; Orton&Huggens, 2013).

It should be noted that the sectioning process of the samples for petrographic microscope use may reduce the presence of the larger non-plastic components of the sample and this would cause representational problems (Orton&Huggens, 2013).

#### *3.2.1.3. Mineralogical Studies*

Mineralogical compositions of ceramic can be investigated by optical microscopy of thin sections, scanning electron microscopy and X-ray diffraction techniques. Also Raman spectroscopy can provide information about the structural characteristics of mineral phases (Vandenabeele & Van Pevenage; 2016).

In X-ray diffraction technique ceramic characterization is based on the identification of minerals by their crystalline structure. In this technique X-ray are aimed onto a specimen and the atomic planes of this specimen diffract the X-rays. These diffraction of the X-rays are detected by the detector (Rice,1987). What is important about this technique is the diffraction angle which depends on the crystal structure (Pollard *et al.*, 2007: 113). Although XRD is a traditional method for mineralogical analysis, it cannot detect pseudo-amorphous phases of the fired clay ceramic since they lack distinct XRD peaks. In that case, FT-IR method can be used. FT-IR, fourier transform infrared spectroscopy provides a mineralogical fingerprint and can be used to detect crystalline minerals and pseudo-amorphous phases of fired clay ceramics (Shoval, 2016).

Working principle of infrared spectroscopy is as follows. The absorption of electromagnetic radiation in the infrared range of the spectrum interacts with a material and changes in the vibrational energy of molecule. Also FT-IR is an easy and fast technique with minimal sample preparation which makes the technique very useful (Shoval, 2016). Another useful technique is Raman spectroscopy. It is the fingerprint of the ceramic's molecular structure and can be used for the identification of production technology, such as raw materials processing and paste formation (Vandenabeele & Van Pevenage; 2016).

#### *3.2.1.4. Elemental Studies*

Elemental analyses are used for various purposes in ceramic studies such as provenance and technology studies or determination of reference groups by obtaining the elemental compositions of the ceramics. Instrumental Neutron Activation Analysis (INAA), X-Ray Fluorescence (XRF), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), X-ray Emission Induced by Protons (PIXE) and Scanning Electron Microscopes combined with Energy Dispersive X-ray Spectroscopy (SEM-EDX/EDS) have been used most commonly (Tite, 2016). These techniques assess the elements present in a ceramic body, slips, paintings and glazes and provide quantitative data. These techniques are used most commonly to acquire information on provenance (Orton & Hughes, 2013). Determination of ceramic reference groups and comparison of the chemically characterized ceramics with the control groups are made possible by the elemental analysis (Santacreu, 2015). Moreover, elemental analysis is used for the understanding of the ceramic fabric composition without aiming to create control groups as the primary goal since it is useful for the study of production technology and the identification of post-depositional alterations

(Santecrue, 2015). It should also be noted that elemental analysis supplements the study of petrological, mineralogical and textural composition of ceramics (For example, in the case of fine-grained ceramics or when only the more ubiquitous non-plastic inclusions, such as quartz and shell, were present chemical studies would be better technique than petrography for provenance studies (Tite, 2016). Also characterization of a group of ceramics of known provenance as the basis for further studies is another important study (Kilikoglou et al, 1988). Because when comparative data and reference groups are available; issues concerning the local status of productions, ceramic workshops, the consumption of imported ceramics at the site, diffusion of potteries, commercial networks can be addressed (Waksman, 2016).

Elemental analysis on ceramics provides a compositional fingerprint, signature of raw material sources, defined by Bishop et al. (1982:294) as "... a weighted average of all the mineralogical components of a ceramic specimen" that allows provenance of an artefact to a source site. According to Weigand et al. (1977) provenance of an artefact to a source site through chemical analysis depends on the "provenance postulate". The term interpreted by Glascock and Neff (2003) as that as long as between-source chemical differences exceed within-source differences raw material source of an artefact can be identified. However, here are several studies that are challenging the idea of "provenance postulate". For example, chemical composition differences of Late Helladic (LH) fine wares from the northern Peloponnese (Hein et al., 2002b) and different production regions was difficult to identify and again the examination of the clay deposits on the north-west coast chemically resembled the ceramics from the north-east Peloponnese (Hein et al., 2002b).

From these points onward, it can be said that the starting point for the provenance studies is the identification of compositional groups and the characterization of these groups in term of raw materials and technology (Quinn, 2013). Considering ceramic researches, identification of the compositional groups that allow grouping the ceramics can be achieved with the chemical methods mentioned above (Pollard et al. 2007). However, the NAA technique has been one of the longest and most successful application for provenance studies since it measures both very low and very high concentrations of a wide range of elements with high precision, using small samples (Pollard et al., 2007). Considering ceramic researchs, extensive NAA study has been performed on Bronze Age Mycenaean and Minoan pottery of Greece and Crete, and related areas around the eastern Mediterranean (Mommsen et al. 2002). Especially by 1999, the Bonn NAA

database included measurements of 30 elements from around 2000 shards already (Hein et al. 1999). Until 1980s NAA was the standard method for producing multi-elemental analysis and then ICP and PIXE were developed. Due to development of new methods and the gradual loss of neutron irradiation facilities; ICP-OES and ICP-MS techniques gained importance (Pollard et al, 2007). The techniques provide the quantification of major and trace elements and as a result, it has become essential to conduct researches comparing these techniques to be sure ICP data were compatible with the vast databanks. These researches included comparison of NAA, XRF, ICP-OES and ICP-MS on ceramics (Hein et al, 2002a), (Tsolakidou & Kilikoglou, 2002).

As it is indicated above, elemental analysis on ceramic provide compositional fingerprint and is used for provenance researches along with the “provenance postulate” idea. However, it should be noted that according to Hein and Kilikoglou (2017), elemental variability of the raw material sources must be taken into consideration as well as human factor (potter) in the pottery making, post depositional processes and analytical method choice for the analysis and moreover, these variabilities must be integration into statistical evaluation for the interpretation process for ceramic provenance and formation of compositional reference groups. Without the estimation of the variabilities mentioned above, similarity and dissimilarity among the samples for the formation of a compositional reference groups would be inadequate (Hein and Kilikoglou, 2017) and to be able to study these similarity and dissimilarity of compositional patterns, additional information on the fabric, potential raw materials, production technology and sample conditions must be known. Additionally, the term “fingerprint” must be discussed as well since it can be misleading as the term is used to correspond the meaning of unique. The concept of “signature” assumes that internal variability can be found within a single clay source so that it can be a better term (Hunt, 2012). Considering all the variables effecting the elemental analysis and reference group formations, SEM-EDS technique is one of the best methods providing all the supplementary information and it will be introduced in the methodology section on this paper.

## 4. Methodology:

### 4.1. Applied Technology:

#### 4.1.1. Scanning Electron Microscopy

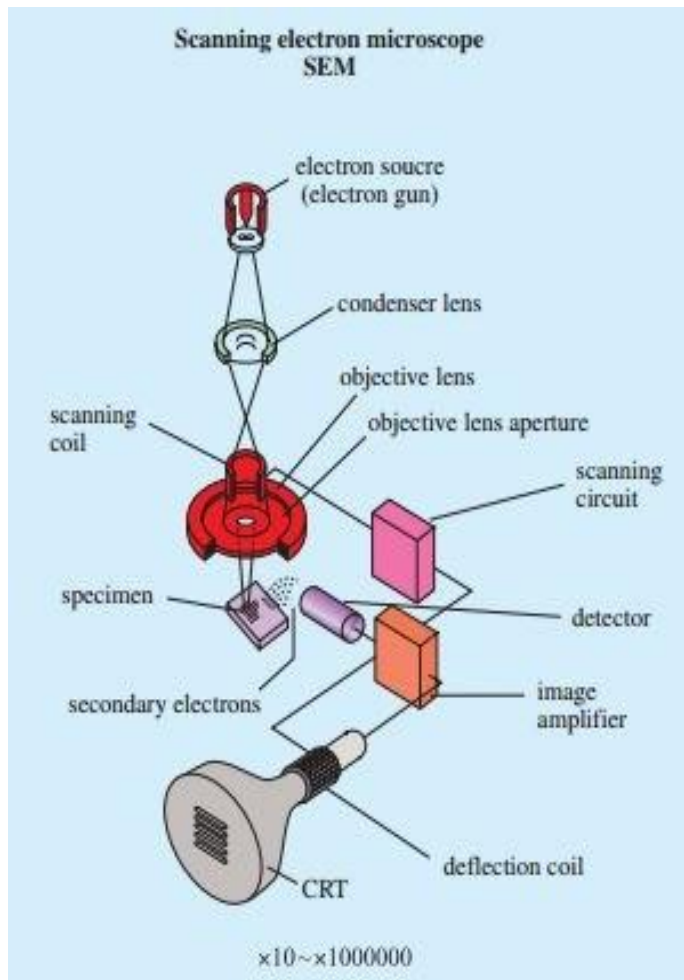
The history of scanning electron microscopy starts in 1930s with the progressive attempts on solid sample imaging and continues with the use on cultural material analysis in 1960s (Mcmullan, 2006). Within these 30 years, the technology became a commercial instrument for analysis thanks to Knoll (1935), Von Ardenne (1938a, b) and a project started in 1948 by Oatley at the Cambridge University Engineering Department (Oatley, 1982).

Starting from the 1960's scanning electron microscopy is used for cultural material analysis. For example, Brothwell indicated the advantages of the use of SEM for ancient bone, stone tools and plant remains (1969: 564-566). Considering ceramic researches, SEM is used to understand the production technology. For example, Tite and Maniatis (1975), Maniatis and Tite (1981), Olsen (1988), Tite and his colleagues (Tite et al, 1992) were the pioneers as ceramic researchers using SEM, and in the last decade, it has been a very common tool for ceramic studies as Renfrew and Bahn (2012, 359) pointed out.

It can be said that the strength of scanning electron microscopy on ceramic studies and on other cultural materials is its ability to combine imaging and analysis such as calculation of quantitative results of elemental composition, and of small analytical spot size whose location can be controlled (Pollard et al., 2007, 113). Considering the sample imaging, SEM provide high resolution image of a sample generally used in the range x100 to x2000 by using highly focused beam of electrons having an energy between the range of 0.5 keV and 30 keV (Froh, 2004). Moreover, the identification of the degree of vitrification in ceramic bodies and consequently the firing temperature estimation, identification of slips and colorants are the other important features that SEM can provide (Tite, 2016). It can be said that the proposed features that SEM provides with attached X-ray spectrometers are the reasons why it is an important technology for studying ceramic provenance and technology.

#### 4.1.1.1. How it Works:

The scanning electron microscope (SEM) uses electrons through an electron source to create a grayscale image with good depth of field at high magnification (Ponting, 2004). It has electromagnetic coils referred to as lenses which focuses the electron beam to move across a sample and analyze a series of areas (**Figure 7**) (Rice, 1987).



*Figure 7: Parts of SEM (Ponting, 2004).*

To eliminate the interaction of electron with air molecules, vacuumed environment is necessary and moreover, samples have to be conducting to avoid the build-up of charge (Ponting, 2004). Because of this reason, samples require a special treatment before SEM examination which will be introduced in sample preparation section in this chapter. As it is explained above, electrons move through an electron gun and hit the sample. This interaction creates backscattered electrons,

secondary electrons and x-rays and the images acquired are called “Secondary electron images” and “Backscattered electron images” (Ponting, 2004).



*Figure 8: SEM used in this thesis research (FEI, Quanta Inspect D8334 SEM coupled with an EDS at the NCSR “Demokritos” in Athens.*

Secondary electron image (SE) is generally used for the study of microstructure and texture such as the identification of the components within the paste such as fine inclusions and clay minerals (Santacreu, 2015) while backscattered electron images (BSE) are used to understand the composition of the materials such as the distribution of areas of different composition within the sample (Ponting, 2004). These different compositions in the samples can be observed from the difference in the grey scale gradients of the images which depends on the atomic number of the different components of the ceramic body (Santacreu, 2015).

Considering the X-rays created through the interaction explained above, they can be analyzed since each element produces a series of peaks in a unique pattern (Ponting, 2004). For the spectroscopy of X-rays in the SEM, there are two techniques that can be used depending on the purpose of the research. First one is called wavelength dispersive x-ray spectrometer (WDS) and the second one is energy dispersive X-ray Spectrometer (EDS) technique. EDS technique is used for archaeological ceramic research (Tite et al, 1992). Although EDS technique is used for this research, it is necessary to introduce Electron Probe Micro-Analysis (EPMA) technique here. This technique was introduced by geologist as a tool in 1975. It is very similar to SEM in function and its primary importance is to provide a chemical analysis primarily by wavelength-dispersive spectroscopy (WDS) at very small "spot" sizes (as little as 1-2 microns) with higher quality precision and detection levels (Henderson, 2000).

#### **4.1.2. SEM-EDS:**

SEM-EDS technique provides elemental quantification by using X-ray spectroscopy. It offers high resolution images for ceramic surfaces and provides compositional information on different areas of the same image and enables analysts to select an area for chemical analysis that is as representative of the original composition as possible. Since, energy dispersive X-ray spectrometers provide a quick determination of the element composition of the target, composition of ceramic fabrics can be acquired. Thanks to these features mentioned above, SEM-EDS can also be used to compare the chemical composition of the matrix and the slips covering the surface of the pottery (Santacreu, 2015). Moreover, it provides evidence to evaluate the presence of a different stages of vitrification and the temperatures reached during the firing process (Tite and Maniatis, 1975; Tite et al., 1982). These are the reasons why SEM-EDS is highly useful analytical tool for ceramic studies.

### **4.2. Research Design, Sample Preparation and Description:**

#### **4.2.1. Research Design:**

The research analysis on twenty Late Helladic ceramic samples from Lemnos island in Greece is conducted through FEI, Quanta Inspect D8334 scanning electron microscope, coupled with an EDS (**Figure 8**) at the NCSR "Demokritos" in Athens. This study included the investigation of



bulk analysis and surface treatments on the selected samples which will be introduced in the following sections. The samples were studied both in secondary and backscattered electron mode for the examinations of the microstructures of the ceramic bodies and surfaces. EDS is used to identify possible compositional differences between the ceramic bodies and the surfaces. In order to provide accurate quantitative results, at least three measurements were taken from the bulk and surface layers. Fabrics and the surface layers of the samples were also studied and photographed under the optical microscope.

#### **4.2.2. Sample preparation:**

Ceramic samples that are going to be used in the SEM can be prepared either as resin-impregnated polished sections from ceramics or as fresh fracture surface pieces which is the most common and simple method (Tite *et al.*, 1982). Although the accuracy of the compositional analysis of fresh fractured sections through SEM-EDS is limited compared to the polished sections, multiple measurements of fresh fractured section provide a basic estimation of precision and assessment of important differences in the compositions (Ferrerias *et al.*, 2016). Fresh fracture surface sample preparation technique starts with separating the fresh fractured pieces from the ceramics to be studied and continues with the attachment of these pieces to the target holder by a conducting glue after flattening the surface of attachment (Froh, 2004) (**Figure 9**). Careful drying is necessary to eliminate outgassing in the SEM due to vacuumed environment. Since ceramic is not electronically conducting specimen, it needs to be covered by a conducting surface layer (1-10 nm thick). This application is required for each sample since only a fraction of the electron charge incident on the target in the SEM is reemitted as backscattered or secondary electrons, the excess charge must be carried off to the metallic target holder. Application of the conducting surface layer cover can be made by sputtering gold, carbon, Pt, Au-Pd alloys in an argon atmosphere (Froh, 2004). For the samples examined in this research, freshly fractured pieces from the sherds were carbon coated as a method of conducting surface layer application (**Figure 10**).



*Figure 9: Samples used in this study being attached to the target holder by a conducting glue.*



*Figure 10: The samples used in this study after being carbon coated.*

#### **4.2.3. Sample Description:**

According to Neutron Activation analysis of Mycenaean ceramic assemblages from Lemnos, Kokounisi which comprised of 77 fragments classified as Mycenaean fine ware, Mycenaean medium ware, decorated and undecorated, local, cooking pots and transport jars, eight chemical groups are identified which are named as A, B1, B2, C1, C2, C3, D and E (Hein, Kilikoglou, 2016) (**Table 2, 3**).

For this thesis research, 20 samples are selected from chemical groupings A, B1, B2, C1, C2, C3 and D in total with the consideration of ware types (**Table 4**). These 20 samples chosen from the 77 fragments are Lem03, Lem06, Lem07, Lem11, Lem14, Lem16, Lem18, Lem27, Lem28, Lem29, Lem36, Lem37, Lem41, Lem45, Lem53, Lem55, Lem58, Lem59, Lem61, Lem62 and will be introduced according to the results on their chemical groupings and fabrics studied by Hein and Kilikoglou (2016).

#### *4.2.3.1. Samples from Chemical Group A:*

Samples used in this research representing chemical group A are Lem11 (**Figure 13**), Lem16 (**Figure 15**), Lem27 (**Figure 17**), Lem36 (**Figure 20**), Lem37 (**Figure 22**), Lem41 (**Figure 23**). According to NAA analysis, chemical grouping A presents a small chemical variation for all element concentrations and it shows similarity with the group D-Troy from Troy chemical reference groups (Mountjoy and Mommsen, 2006). Samples Lem 36, 37, 41 represent fine decorated Mycenaean pottery which belong to fabric group 11a1. This fabric group consist of fine clay with gold mica inclusion. Sample Lem16 which is a medium fine decorated pottery is belonged to same chemical group with Lem 36, 37 and 41. This sample is from fabric group 11a2 which is medium fine clay with gold mica temper. Sample Lem 11 which represents fine decorated Mycenaean pottery belongs fabric group 11. This fabric is similar to fabric 12 which is very fine clay with no inclusion, but the clay of fabric 11 is not as light colored as fabric 12 and there is possibly gold mica in it. Sample Lem27 is belonged to fabric group 11b1 which consists of fine clay with gold mica. According to NAA fabric 11b1 is initially thought to be local.

	Lemnos-A		Lemnos-B1		Lemnos-B2		Lemnos-C1	
	24 +3(-) samples		7 + 1(-) samples		2 samples		16 + 1(-) samples	
	mean	stdev.	mean	stdev.	mean	stdev.	mean	stdev.
As	10.7	3.8	7.9	1.6	5.2	1.3	13.0	7.7
Ba	800	231	767	196	642	95	846	174
Ca (%)	6.0	1.1	<b>9.9</b>	2.0	<b>5.4</b>	0.7	6.0	0.9
Ce	62.2	1.2	63.8	0.7	64.8	0.6	68.5	2.8
Co	<b>23.1</b>	1.0	<b>28.6</b>	1.1	<b>30.2</b>	0.1	<b>20.1</b>	1.5
Cr	231	14	233	5	268	7	218	14
Cs	<b>5.8</b>	0.3	<b>9.2</b>	0.7	<b>17.0</b>	2.3	<b>5.2</b>	0.5
Eu	1.19	0.03	1.18	0.02	1.24	0.02	1.24	0.02
Fe (%)	4.86	0.15	5.27	0.12	<b>6.00</b>	0.08	<b>4.25</b>	0.30
Hf	<b>4.3</b>	0.2	<b>3.4</b>	0.2	<b>3.4</b>	0.2	<b>4.8</b>	0.2
La	29.6	0.7	<b>32.6</b>	0.6	31.0	0.2	<b>33.5</b>	1.9
Lu	0.35	0.02	0.33	0.01	0.40	0.01	0.33	0.02
Na (%)	1.1	0.1	0.5	0.1	0.7	0.0	1.5	0.2
Ni	128	17	146	13	201	15	100	18
Rb	<b>116</b>	5	<b>145</b>	5	<b>141</b>	7	<b>105</b>	6
Sb	0.54	0.04	0.67	0.33	0.78	0.05	0.73	0.16
Sc	18.3	0.5	20.6	0.5	<b>23.2</b>	0.2	<b>15.9</b>	0.9
Sm	5.62	0.09	5.54	0.10	5.71	0.02	5.76	0.10
Sr	351	49	408	69	369	105	487	76
Ta	0.90	0.03	0.92	0.02	0.85	0.02	0.86	0.03
Tb	0.67	0.05	0.62	0.05	0.60	0.01	0.68	0.07
Th	10.4	0.3	10.6	0.2	11.4	0.0	12.2	1.0
U	2.24	0.41	2.34	0.20	2.09	0.24	2.37	0.28
Yb	2.34	0.08	2.43	0.09	2.43	0.04	2.35	0.24
Zn	100	10	108	7	121	3	89	15
Zr	118	18	105	12	109	1	130	19

Table2: Chemical composition of the four groups comprising fine wares (Hein, Kilikoglou, 2016).

	Lemnos-C2		Lemnos-C3		Lemnos-D		Lemnos-E	
	4 samples		3 samples		4+ 1(?) samples		4+ 1(-) samples	
	mean	stdev.	mean	stdev.	mean	stdev.	mean	stdev.
As	8.1	4.3	11.6	0.9	9.7	2.3	6.3	0.8
Ba	855	191	988	186	950	152	1040	93
Ca (%)	2.3	1.8	1.5	0.5	2.5	1.2	2.4	0.1
Ce	80.1	1.3	<b>60.2</b>	0.7	82.7	4.4	<b>112.1</b>	1.5
Co	17.6	1.7	14.3	0.7	14.2	1.1	<b>13.4</b>	0.5
Cr	196	9	253	20	188	32	<b>136</b>	17
Cs	4.5	0.2	4.7	0.3	4.6	0.6	<b>2.8</b>	0.1
Eu	1.36	0.02	1.23	0.02	1.32	0.07	<b>1.78</b>	0.09
Fe (%)	3.87	0.11	3.89	0.12	<b>3.32</b>	0.04	<b>3.20</b>	0.10
Hf	5.9	0.5	5.8	0.4	6.0	0.6	6.9	0.3
La	40.1	0.9	<b>31.1</b>	1.8	43.8	2.2	<b>56.2</b>	3.2
Lu	0.35	0.01	0.34	0.00	<b>0.32</b>	0.02	0.33	0.01
Na (%)	1.4	0.2	1.2	0.0	1.4	0.1	1.9	0.1
Ni	91	19	76	10	57	12	<b>49</b>	5
Rb	94	4	91	4	83	7	<b>65</b>	2
Sb	0.61	0.16	0.96	0.27	1.16	0.54	0.54	0.05
Sc	14.3	0.5	14.1	0.2	<b>12.0</b>	0.3	<b>11.8</b>	0.2
Sm	6.41	0.10	<b>5.65</b>	0.12	6.02	0.19	8.02	0.49
Sr	385	107	265	14	524	116	<b>902</b>	83
Ta	0.86	0.04	0.81	0.02	0.80	0.05	0.87	0.07
Tb	0.69	0.03	0.68	0.02	0.68	0.06	<b>0.79</b>	0.06
Th	14.2	0.7	<b>12.0</b>	0.8	15.8	0.8	<b>18.6</b>	0.5
U	2.49	0.14	1.95	0.12	2.38	0.11	2.39	0.12
Yb	2.44	0.07	2.45	0.01	2.20	0.10	2.30	0.08
Zn	76	4	78	10	<b>66</b>	3	<b>65</b>	1
Zr	158	12	142	6	160	16	185	6

Table3- Chemical composition of the four groups comprising coarse wares (Hein, Kilikoglou, 2016).

#### *4.2.3.2. Samples from Chemical Group B1:*

Samples used in this research representing chemical group B1 are Lem03 (**Figure 11**), Lem06, Lem07 (**Figure 12**), Lem53 (**Figure 21**). According to NAA analysis chemical group B1 element concentrations are close to the concentration of chemical grouping A although significant differences in Ca, Co, Cs, Hf, La, Rb are observed. According to studies on Troy chemical reference groups by Mountjoy and Mommsen (2006), Argolid imports were identified. This chemical group identified by NAA represents 8 samples. Seven of them presenting fabric 12 which three of them used in this research (Lem03, Lem06 and Lem07) and one of them presenting fabric 17 which is sample Lem53 again used in this research.

Sample Lem03, Lem 06, Lem07 representing fine decorated Mycenaean pottery (LH IIIA2) are from fabric group 12. This fabric is very fine clay with no inclusions. Sample Lem 53 represents undecorated Mycenaean pottery and is belonged to fabric group 17 consists of very fine clay. When comparing chemical group B1 with the A-Troy Argolid reference group, it can be said that both of the fabric groups 12 and 17 are representing an Argolid import (Hein, Kilikoglou, 2016).

#### *4.2.3.3. Samples from Chemical Group B2:*

Sample Lem14 (**Figure 14**) representing fine decorated Mycenaean pottery is from fabric group 15 which is similar to fabric 11 while the clay is red and there is no visible mica. This sample is the only one in this research representing chemical group B2 which has lower calcium content while it represents higher Co, Fe, and Sc concentrations.

#### *4.2.3.4. Samples from Chemical Group C1:*

Samples used in this research representing chemical group C1 are Lem18 (**Figure 16**), Lem28 (**Figure 18**), Lem29 (**Figure 19**), Lem45 (**Figure 24**) and Lem55 (**Figure 25**). Although these samples represent the same chemical group, their fabric groups are different. Chemical group C1 represents mainly undecorated fine wares. Compared to chemical group A, the pattern shows lower Co, Fe and Sc concentrations and higher light lanthanides and thorium. Moreover, compared with the reference data from Troy indicates a similarity with the group B-Troy which represents local production (Mountjoy and Mommsen, 2006). As Hein and Kilikoglou (2016, 3)

states, most of the examined undecorated wares shows B-Troy chemical pattern (Mommsen et al. 2001) and this should be considered while interpreting Lemnos C1 group samples.

Sample Lem 55 representing fine decorated Mycenaean pottery is belonged to fabric group 11a1 which has gold mica inclusion indicating local identity. Lem18 representing medium fine decorated pottery belongs to fabric group 11a2. This fabric group has gold mica inclusion and burnished surface. Lem45 is belonged to fabric 11b2. This fabric group has gold mica inclusion and very similar to 11b1 although it is made of lila colored clay which may be indicating local identity. Samples Lem28 and Lem29 are belonged to fabric 11b1. This fabric group has gold mica inclusion and it shows local identity.

#### *4.2.3.5. Samples from Chemical Group C2:*

Sample used in this research representing chemical group C2 is sample Lem59 (**Figure 26**). This chemical group represents lower calcium, Co, Fe, Sc concentrations than C1 pattern but higher concentrations of lanthanides and actinides. This sample represents a medium coarse red slipped local pottery with gold mica inclusion.

#### *4.2.3.6. Samples from Chemical Group C3:*

Sample used in this research representing chemical group C3 is sample Lem58 (**Figure 27**). This chemical group represents lower lanthanide and actinide concentrations compared to chemical group C2. Fabric group of this sample which is local red slipped is the same fabric group with Sample Lem59 belonging to chemical group C2 and Sample Lem61 and Lem62 belonging to chemical group D.

Fabric		A	B1	B2	C1	C2	C3	D
Fine to medium fine wares	11	Lem11						
	11a1	Lem36, Lem37 Lem41			Lem55			
	11a2	Lem 16			Lem18			
	11b1	Lem27			Lem28, Lem29			
	11b2				Lem45			
	12		Lem3,Lem6 Lem7					
	15			Lem14				
	17		Lem53					
Coarse ware	red slipped local					Lem59	Lem58	Lem61, Lem62

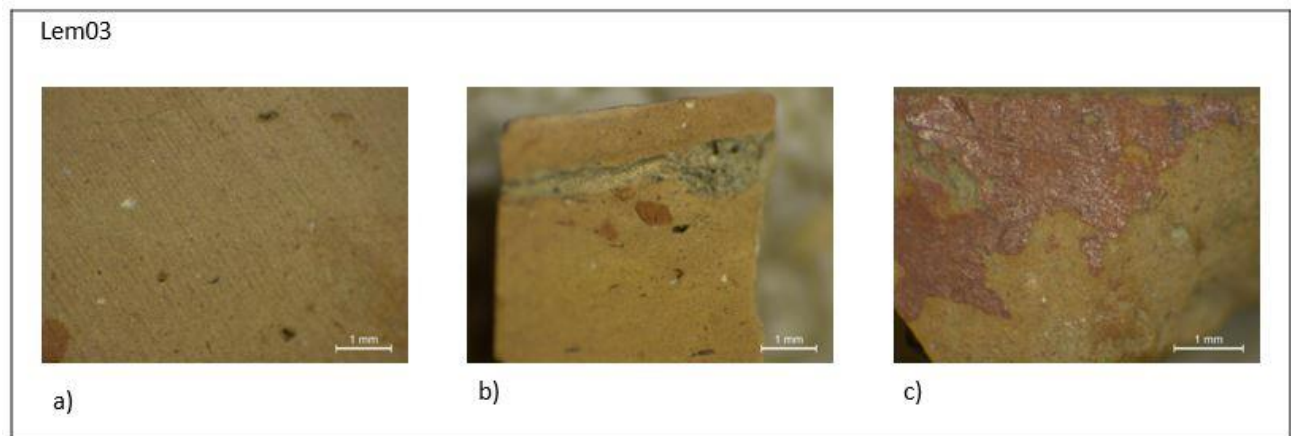
Table 4: Chemical and Fabric groups of the samples according to ware types used in the research.

#### 4.2.3.7. Samples from Chemical Group D:

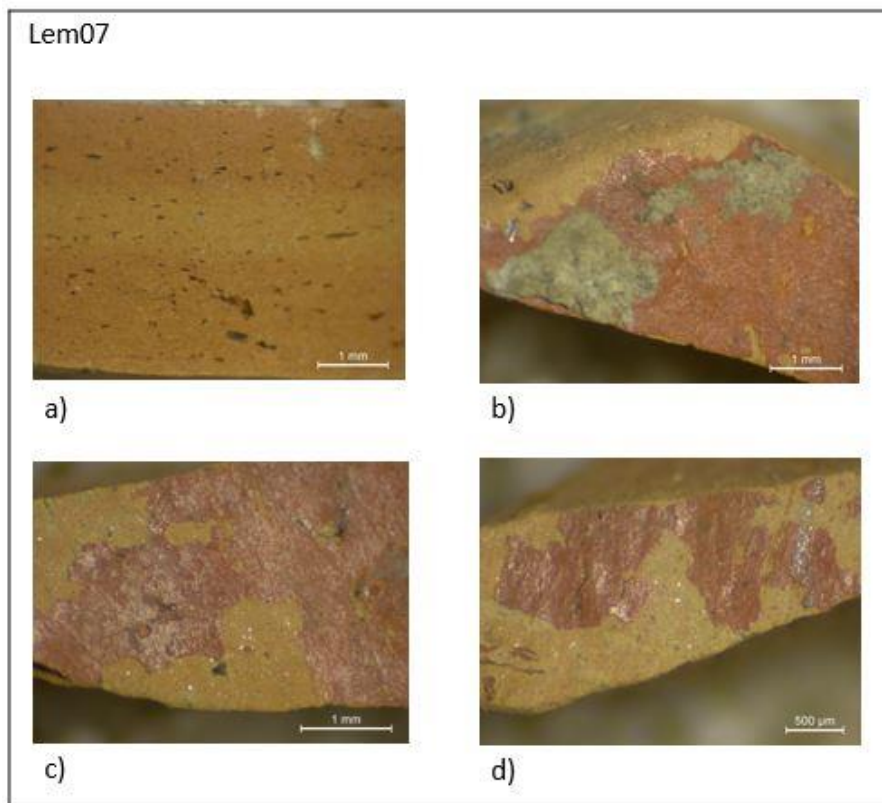
Chemical group D is represented by sample Lem61 (**Figure 28**) and Lem62 (**Figure 29**) in this research. These samples belong to red slipped local fabric group with gold mica inclusion.

According NAA, chemical pattern of this group is not well defined and it shows large variation of most of the element concentrations. However, by comparing Fe, Co and Sc concentrations with other examined ceramics, clear distinction is identified.

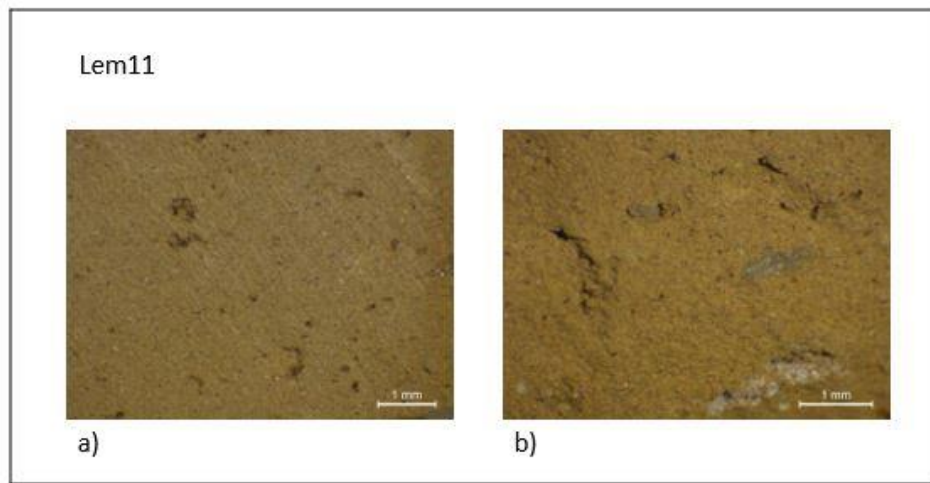




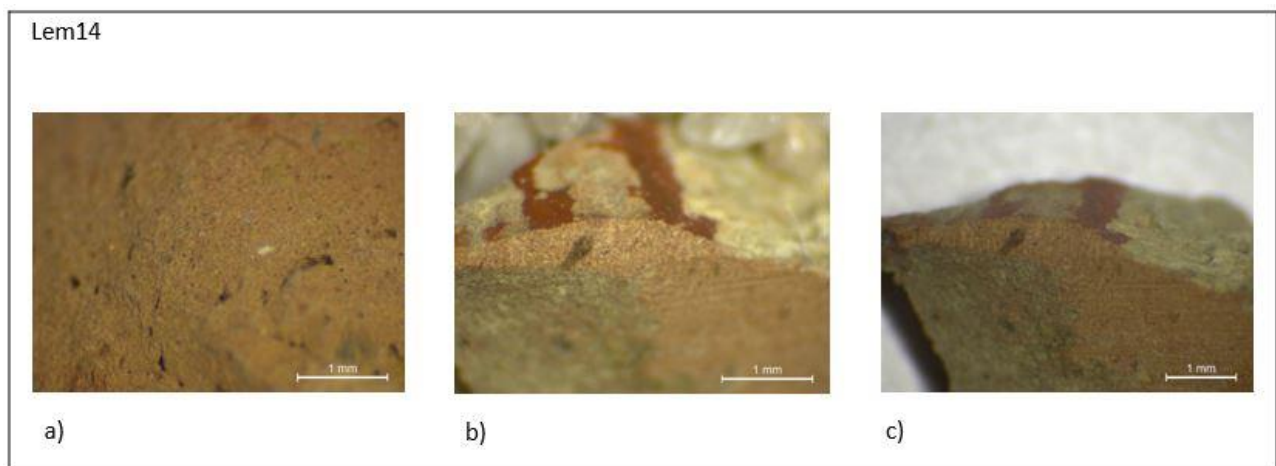
*Figure 11: a) Fabric representation of the sample (objective 2), b) Crust on the sample (objective 2), c) Paint on the sample (objective 3.2).*



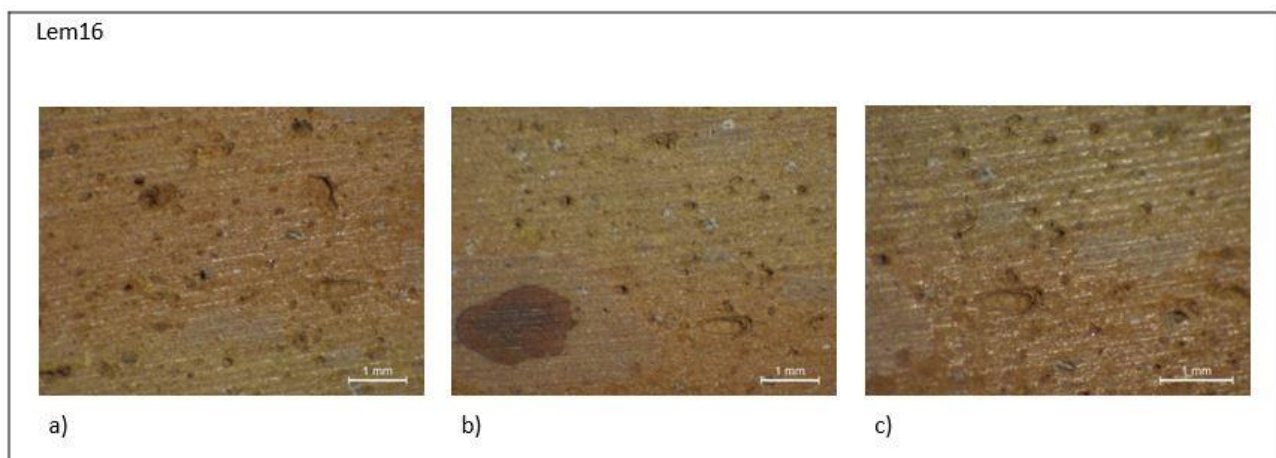
*Figure 12: a) Fabric representation of the sample (objective 2.5) b) Crust on the sample (objective 2.5) c) Representation of the paint on the sample (objective 3.2) d) Paint on the sample (objective 4).*



*Figure 13: a) Fabric representation of the undecorated sample (objective 2) b) Fabric representation of the undecorated sample (objective 2.5).*



*Figure 14: a) Fabric representation of the sample (objective 3.2) b) Representation of the paint on the sample (objective 3.2) c) Paint on the sample (objective 2.5).*



*Figure 15: a) Fabric representation of the sample (objective 2) b) Fabric representation of the sample (objective 2) c) Gold mica focused fabric representation of the sample (objective 2.5).*

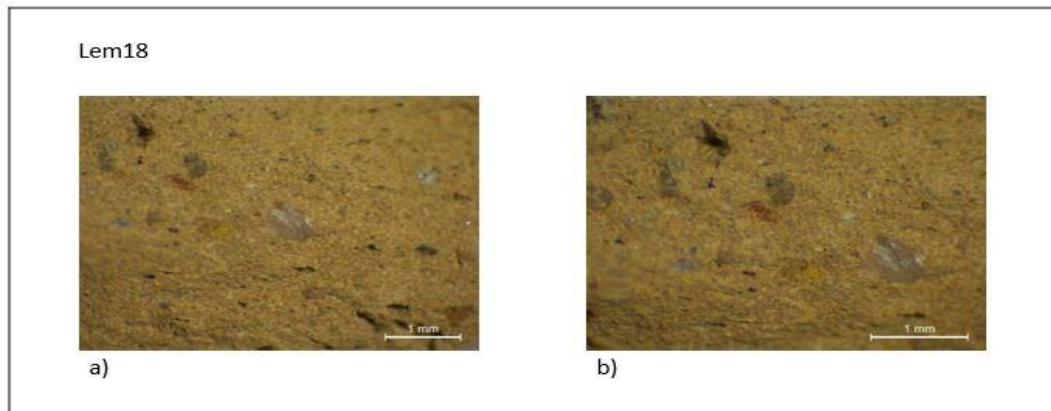


Figure 16: a) Fabric representation of the undecorated sample (objective 2.5) b) Fabric representation of the undecorated sample (objective 3.2).

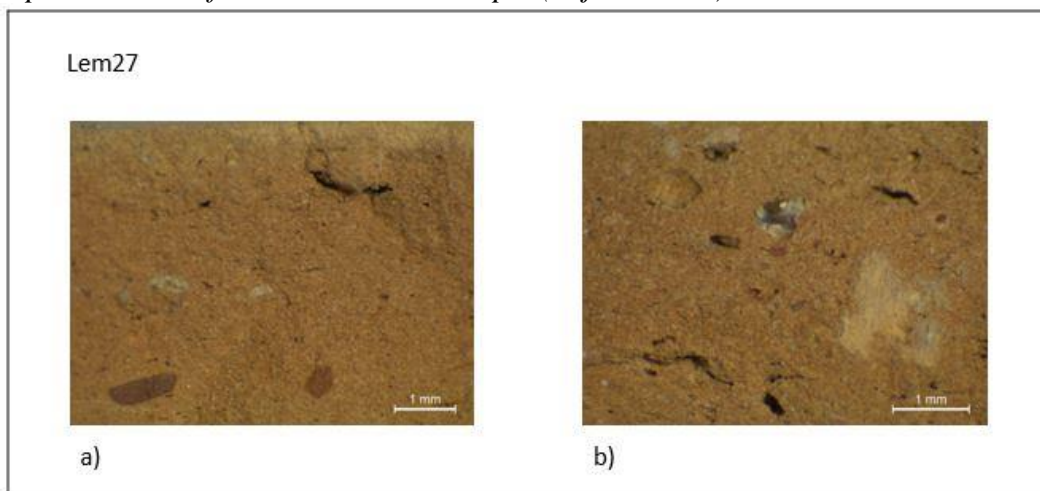


Figure 17: a) Fabric representation of the undecorated sample (objective 2) b) Fabric representation of the same sample (objective 2.5).

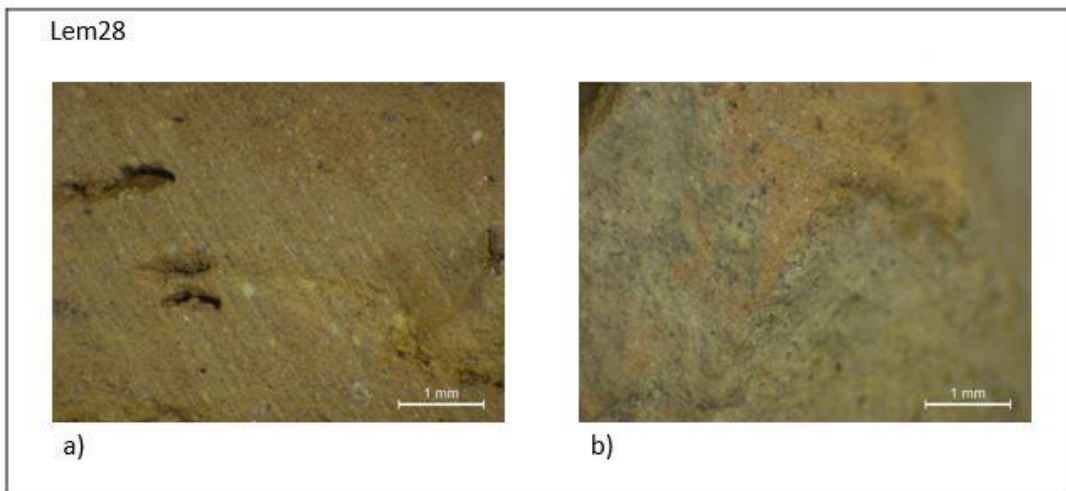
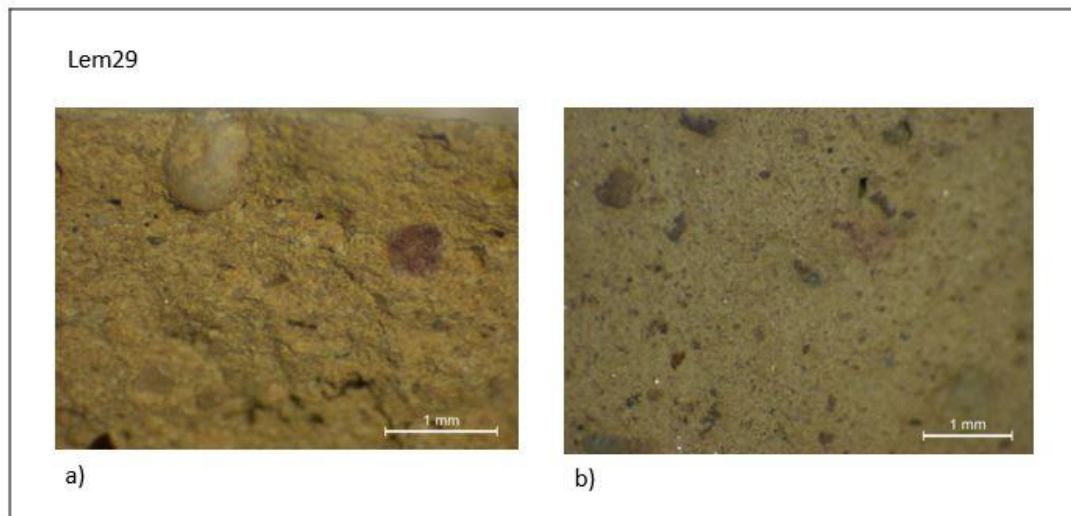
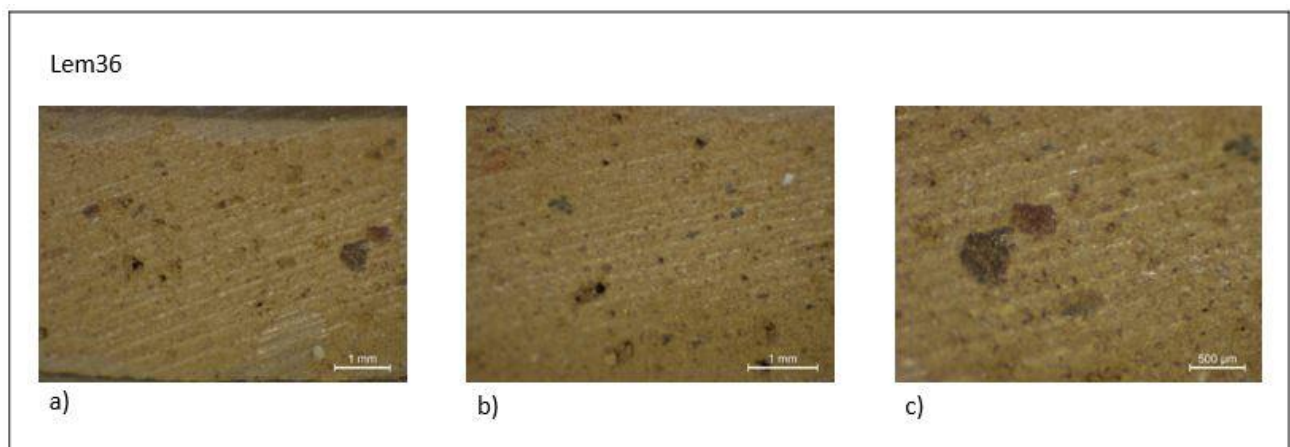


Figure 18: a) Fabric representation of the undecorated sample (objective 2.5) b) Crust on the sample (objective 2.5).



*Figure 19: a) Fabric representation of the undecorated sample (objective 3.2) b) Fabric representation of the undecorated sample (objective 2.5).*



*Figure 20: a) Fabric representation of the decorated sample (objective 2) b) Fabric representation of the same sample (objective 2.5) c) Fabric representation of the same sample with gold mica focus (objective 4).*

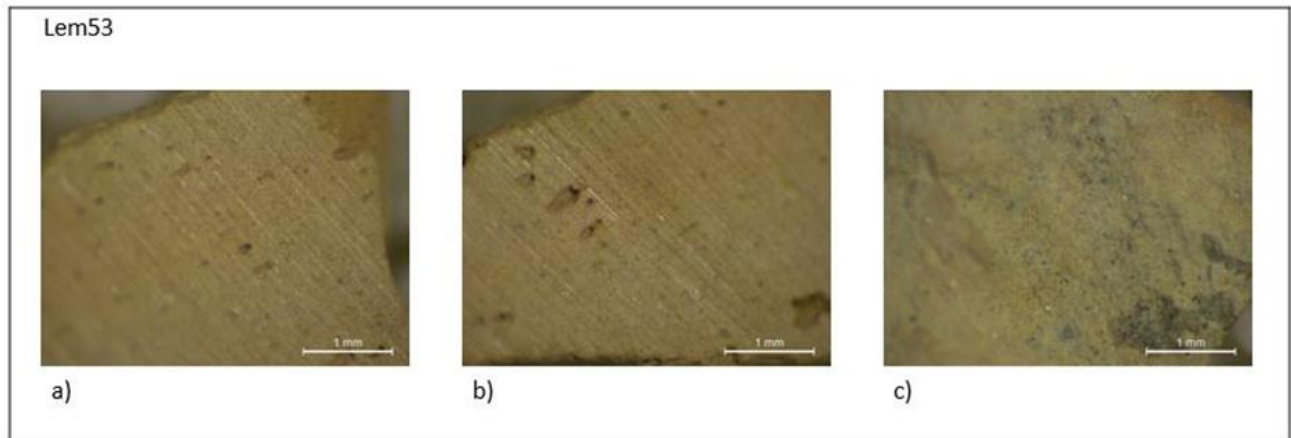


Figure 21: a) Fabric representation of the undecorated sample (objective 3.2) b) Fabric representation of the same sample (objective 3.2) c) Crust on the sample (objective 3.2).

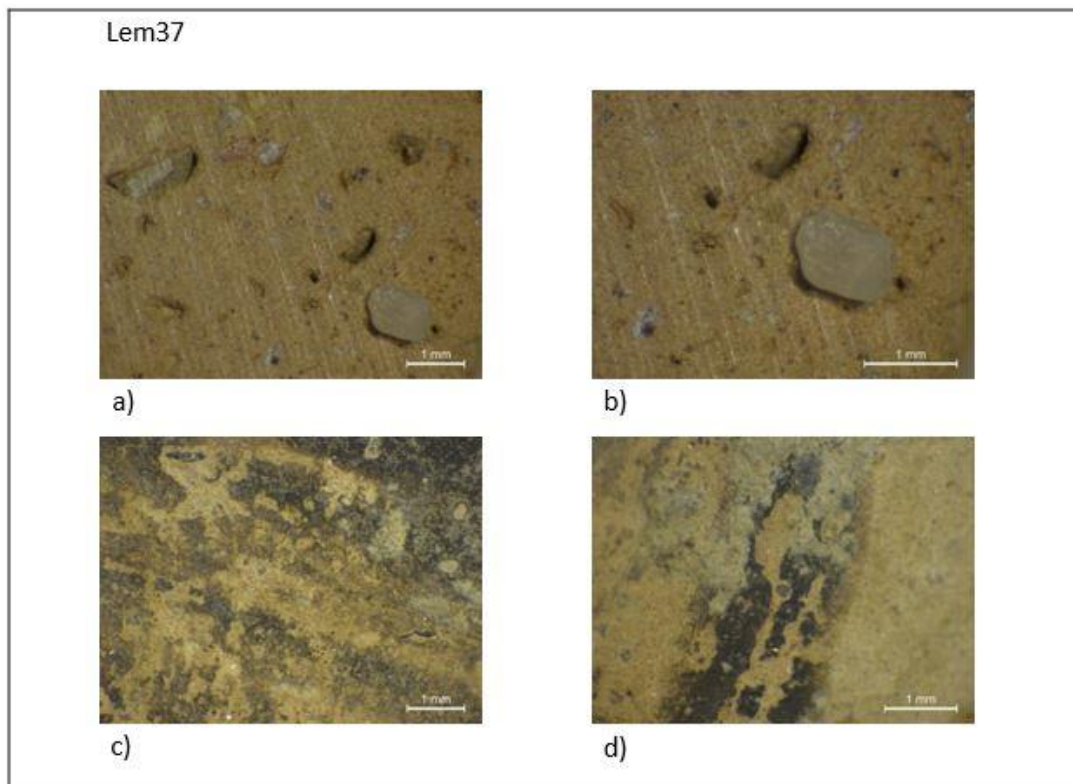
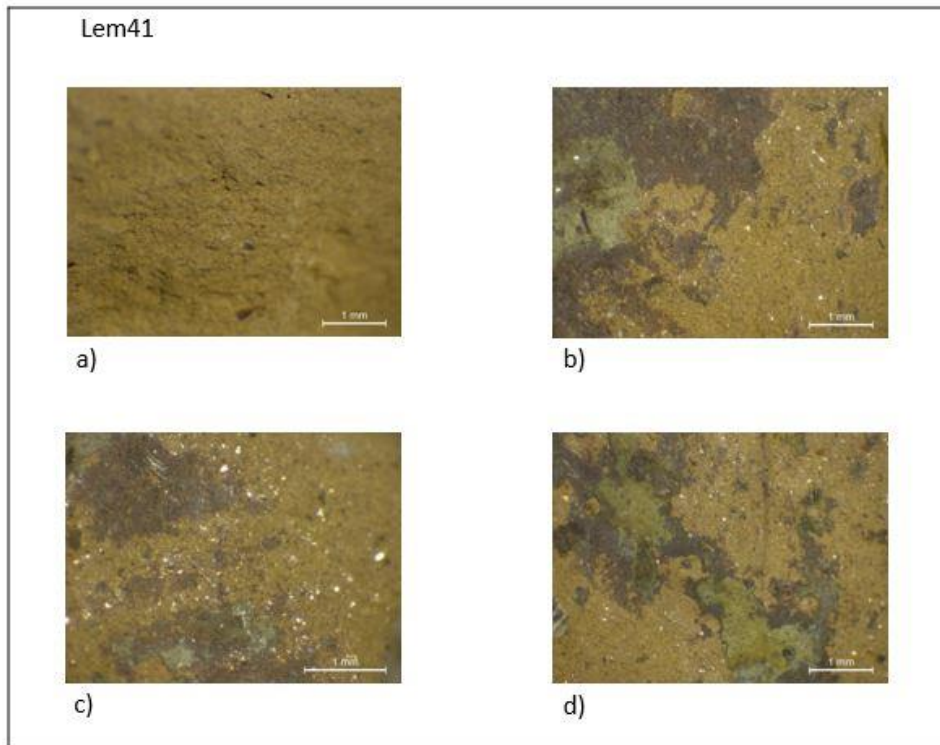
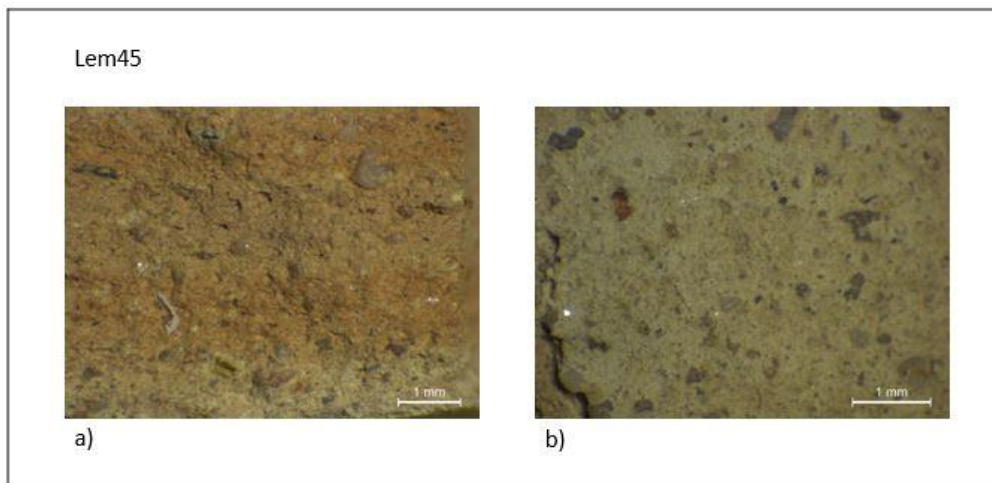


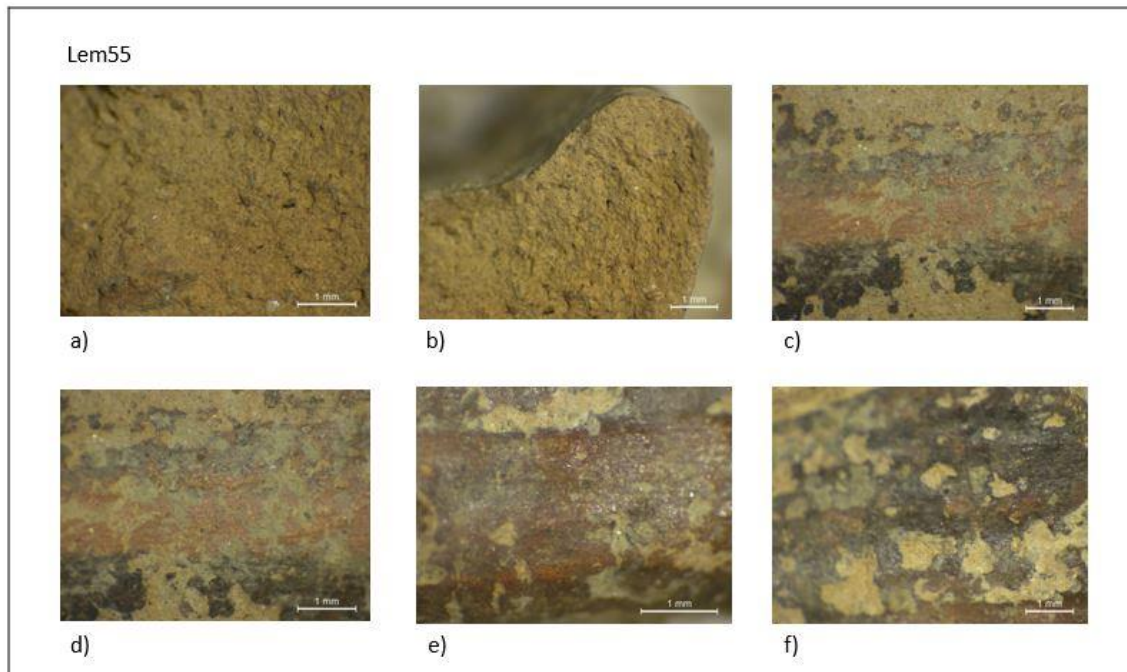
Figure 22: a) Fabric representation of the decorated sample (objective 2) b) Fabric representation of the same sample (objective 3.2) c) Representation of the paint on the sample (objective 2) d) Representation of the paint on the sample (objective 2.5).



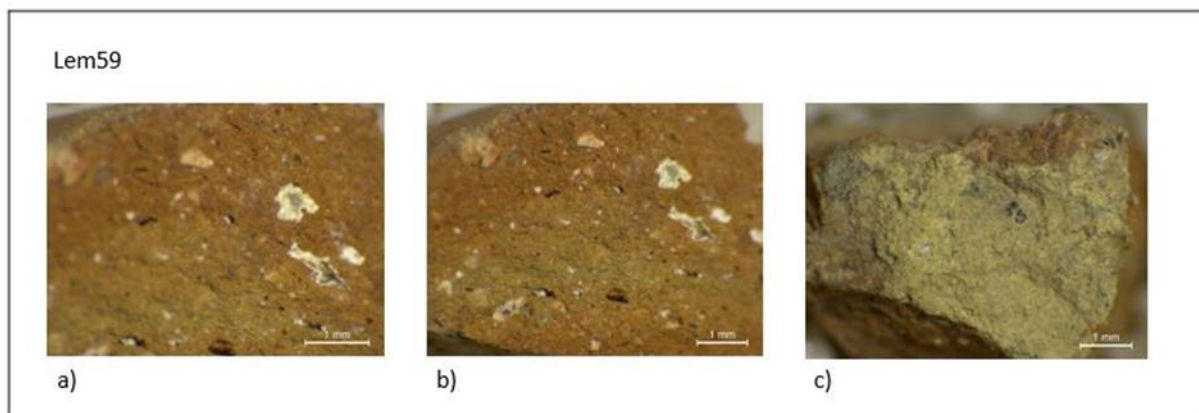
*Figure 23: a) Fabric representation of the fine decorated sample (objective 3.2) b) Representation of the decoration on the sample (objective 2.5) c) Representation of the paint layer with gold mica focus in the fabric (objective 3.2) d) Crust on the paint layer of the sample (objective 2.5).*



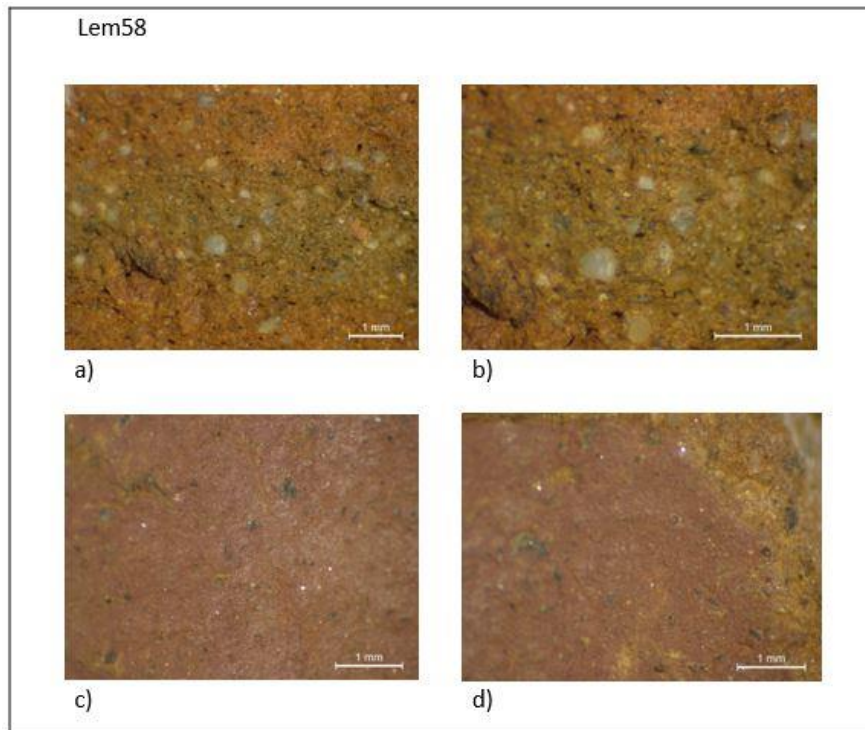
*Figure 24: a) Fabric representation of the undecorated sample (objective 2) b) Crust on the sample (objective 2.5).*



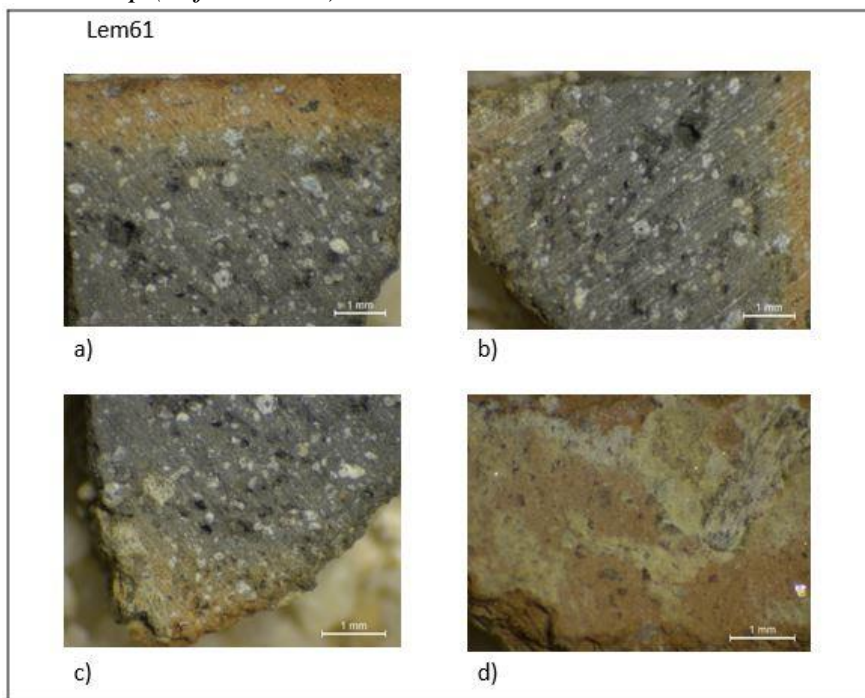
*Figure 25: a) Fabric representation of the fine decorated sample (objective 2.5) b) Fabric and decoration representation of the sample (objective 2) c) Representation of the decoration (objective 2) d) Representation of the decoration (objective 2.5) e) Representation of the red color on the sample (objective 3.2) f) Representation of the black color on the sample (objective 2).*



*Figure 26: a) Fabric representation of the sample (objective 2.5) b) Fabric representation of the same sample (objective 2) c) Crust on the sample (objective 2).*

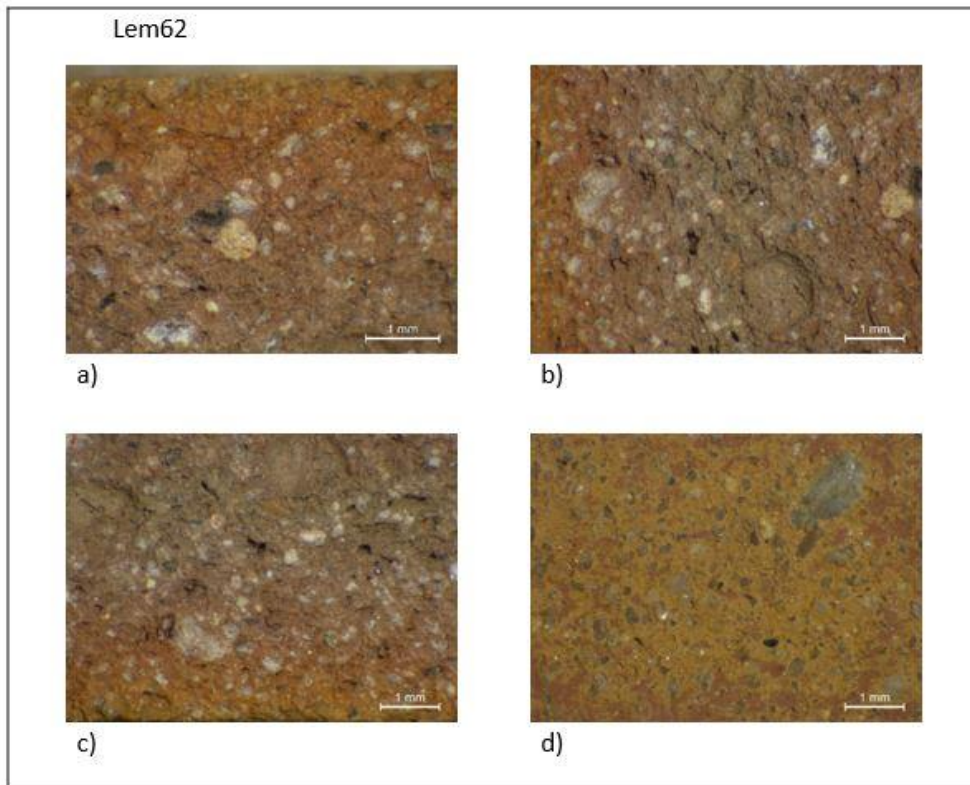


*Figure 27: a) Fabric representation of the sample (objective 2) b) Fabric representation of the same sample (objective 2) c) Representation of the red slip (objective 2.5) d) Representation of the red slip (objective 2.5).*



*Figure 28: a) Fabric representation of the red slipped sample (objective 2) b) Fabric representation of the same sample (objective 2) c) Fabric representation of the same sample dark core emphasized (objective 2.5) d) Crust on the red slip (objective 2.5).*





*Figure 29: a) Fabric representation of the sample (objective 2.5) b) Fabric representation of the sample (objective 2) c) Fabric representation of the same sample (objective 2) d) Representation of the red slip (objective 2).*

## 5. Results and Discussion:

The samples were analyzed with SEM-EDS in order to understand body microstructures, surface coatings and chemical differences between the ceramic surfaces and bodies. Although the chemical groupings of the samples are categorized through NAA (Hein, Kilikoglou, 2016), the oxide concentrations of the ceramic bodies are measured through EDS (**Table 5**). According to these measurements it can be said that samples representing chemical Group A correspond to calcareous pottery (9-11% CaO), with high SiO<sub>2</sub> (52-56%), high Fe<sub>2</sub>O<sub>3</sub> (9-11%) and medium Al<sub>2</sub>O<sub>3</sub> (16-17%). Chemical Group B1 corresponds to calcareous pottery (12-16% CaO), with high SiO<sub>2</sub> (49-52%), high Fe<sub>2</sub>O<sub>3</sub> (9-10%), and medium Al<sub>2</sub>O<sub>3</sub> (15-17%). Group B2 is represented only by sample Lem14 that corresponds to calcareous pottery (10 % CaO), with high SiO<sub>2</sub> (49 %), high Fe<sub>2</sub>O<sub>3</sub> (13 %) and medium Al<sub>2</sub>O<sub>3</sub> (16 %). Group C1 corresponds to calcareous pottery (12-14%), with high SiO<sub>2</sub> (50-56%), high Fe<sub>2</sub>O<sub>3</sub> (9-13%) and medium Al<sub>2</sub>O<sub>3</sub> (14-16%). Group C2 is represented only by sample Lem59 that corresponds to low calcareous pottery (2%), high SiO<sub>2</sub> (60%), high Fe<sub>2</sub>O<sub>3</sub> (9%) and relatively high Al<sub>2</sub>O<sub>3</sub> (19%). Group C3 is represented only by sample Lem58 that corresponds to non-calcareous pottery (2%), with high SiO<sub>2</sub> (62%), high Fe<sub>2</sub>O<sub>3</sub> (9%) and medium Al<sub>2</sub>O<sub>3</sub> (17%). Group D corresponds to non-calcareous pottery with high SiO<sub>2</sub> (61-64%), high Fe<sub>2</sub>O<sub>3</sub> (9%) and medium Al<sub>2</sub>O<sub>3</sub> (16%).

A majority of the samples have calcareous clay, with Groups A and C1 exhibiting the highest CaO concentrations (**Figure 30**). Lem58, 59, 61 and 62 are low to non-calcareous samples and have relatively higher SiO<sub>2</sub> concentrations (**Figure 30**). Although all of the samples are high in Fe<sub>2</sub>O<sub>3</sub>, calcareous samples with high CaO concentrations (10-14%), samples from chemical group B2 (Lem14) and C1 (Lem18, 28 and 29) show relatively higher Fe<sub>2</sub>O<sub>3</sub> concentrations (**Figure 31**). Considering the Al<sub>2</sub>O<sub>3</sub> concentrations, non-calcareous sample Lem59 from chemical Group C2 is the highest among the samples analyzed in this study and Group C1 calcareous samples (Lem18, 28, 29, 45 and 55) have the lowest Al<sub>2</sub>O<sub>3</sub> concentrations (**Figure 32**).

## 5.1. Microstructure:

The microstructural characteristics of the samples are investigated through SEM backscattered and secondary electron modes and through EDS; additionally, the elements of the observed inclusions are analyzed and measured. In general, it can be said that most of the samples display a homogeneous matrix, although some of the studied samples have an inhomogeneous matrix with dispersed inclusions of different grain sizes and shapes. The degrees of vitrification observed in the ceramic bodies show difference. Pores, different in size and frequency, in the matrix seem to occur due to this vitrification process, which resulted in all of the samples displaying a porous structure.

Samples from chemical Group B1 (Lem03 [**Figure 33**], Lem06 [**Figure 34**], Lem07 [**Figure 35**] and Lem53 [**Figure 47**]), and Group B2 (Lem14 [**Figure 37**]) present fine, homogeneous and porous matrices, while those from Group C3 Lem58 [**Figure 49**], Group C2 Lem59 [**Figure 50**], and Group D Lem61 [**Figures 51 and 52**] and Lem62 [**Figures 53 and 54**]) present an inhomogeneous, coarse matrix with dispersed inclusions of different grain sizes and shapes. For example, sample Lem59 has some inhomogeneous iron inclusions while Lem61 and Lem62 have some coarse organic inclusions (**Figure 51c, Figure 52a, b and c; Figure 54a**). It can be said that all of the studied samples were manufactured via wheel throwing, based on the elongated parallel voids and orientation of the inclusions that are observed in the matrix (Courty, Roux, 1995). Moreover, Lem61 and Lem62 show fissures and random orientation of coarse grains with large size aggregates, which could be an indication of pottery thrown rapidly on the wheel (Courty, Roux, 1995). It should be noted that a possible apatite inclusion (56% CaO, 32% P<sub>2</sub>O<sub>5</sub>, 4% SiO<sub>2</sub>) within the matrix of Lem61 very close to surface is observed (**Figure 51c**). This could indicate the addition of bone ash (Ferrerias et al. 2016).

Samples from Group C1 (Lem18 [**Figure 39**], Lem28 [**Figure 41**], Lem29 [**Figure 42**], Lem45 [**Figure 46**] and Lem55 [**Figure 48**]) show different characteristics. Sample Lem18 has a homogeneous matrix with iron rich inclusions. An iron rich inclusion in a void and a crack in the body matrix can be observed (**Figure 39c**).

Samples	Body	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	Cl2O	K2O	CaO	TiO2	V2O5	Cr2O3	MnO	Fe2O3
Lem03	body ave.	0.3	3.0	14.9	50.3	0.4	0.3	0.2	3.4	16.0	1.0	0.2	0.2	0.4	9.4
	std	0.1	0.2	0.5	2.1	0.3	0.2	0.1	0.3	1.3	0.3	0.1	0.1	0.2	0.6
Lem06	body ave.	0.58	3.39	15.74	50.16	0.40	0.26	0.15	2.59	16.33	0.88	0.15	0.18	0.27	8.97
	std	0.2	0.6	0.8	4.6	0.0	0.2	0.1	0.4	3.6	0.3	0.0	0.1	0.0	1.4
Lem07	body ave.	0.2	4.4	17.0	48.5	0.2	0.2	0.1	2.5	15.3	1.2	0.1	0.1	0.3	9.7
	std	0.1	1.1	1.1	5.2	0.2	0.2	0.1	0.9	3.9	0.3	0.1	0.1	0.1	1.3
Lem11	body ave.	1.09	2.44	15.97	56.47	0.09	0.39	0.61	3.41	9.28	1.08	0.20	0.11	0.17	8.72
	std	0.1	0.1	0.2	1.1	0.1	0.1	0.0	0.2	1.5	0.3	0.2	0.1	0.2	0.4
Lem14	body ave.	0.68	4.34	16.03	48.94	0.28	0.43	0.41	3.15	10.31	1.20	0.32	0.32	0.27	13.33
	std	0.1	0.2	0.8	1.7	0.2	0.3	0.2	0.1	1.5	0.3	0.1	0.2	0.1	1.6
Lem16	body ave.	1.19	3.01	16.23	53.63	0.29	0.41	0.32	3.90	9.67	1.21	0.25	0.24	0.33	9.34
	std	0.1	0.3	1.3	0.6	0.1	0.3	0.3	1.0	1.8	0.3	0.1	0.1	0.1	1.4
Lem18	body ave.	1.04	2.77	13.92	49.71	0.36	0.24	0.19	2.85	12.68	1.17	0.57	0.47	0.59	13.43
	std	0.1	0.2	0.4	0.9	0.3	0.2	0.0	0.1	1.1	0.2	0.2	0.1	0.1	0.6
Lem27	body ave.	1.7	4.0	15.6	53.2	0.5	0.1	0.0	2.7	10.5	0.8	0.0	0.1	0.2	10.6
	std	0.2	0.0	0.0	0.7	0.2	0.2	0.1	0.1	0.4	0.1	0.0	0.1	0.0	0.7
Lem28	body ave.	1.0	2.8	13.8	51.6	0.3	0.2	0.1	3.1	14.0	1.2	0.2	0.3	0.4	11.3
	std	0.1	0.3	0.6	1.1	0.2	0.3	0.1	0.3	0.4	0.0	0.0	0.1	0.1	1.6
Lem29	body ave.	1.55	2.73	15.13	51.80	0.44	0.23	0.19	2.94	11.23	1.18	0.24	0.23	0.55	11.57
	std	0.1	0.0	0.5	1.5	0.1	0.1	0.0	0.3	1.0	0.2	0.1	0.1	0.2	1.8
Lem36	body ave.	1.28	4.19	16.48	55.00	0.25	0.27	0.09	2.37	9.37	0.93	0.20	0.17	0.27	9.14
	std	0.4	0.8	1.8	2.3	0.1	0.0	0.0	0.5	1.0	0.2	0.1	0.1	0.1	0.9
Lem37	body ave.	1.20	3.13	16.05	52.10	0.37	0.13	0.10	3.15	11.13	1.20	0.24	0.18	0.32	10.70
	std	0.3	0.4	0.6	2.3	0.3	0.1	0.1	0.8	2.1	0.3	0.1	0.0	0.1	1.2
Lem41	body ave.	0.97	3.28	16.41	54.45	0.31	0.11	0.15	2.95	9.58	1.00	0.10	0.11	0.17	10.40
	std	0.2	0.3	2.3	2.2	0.1	0.2	0.0	0.3	2.1	0.1	0.1	0.1	0.2	2.0
Lem45	body ave.	1.52	4.02	13.72	53.89	0.34	0.33	0.31	2.96	10.97	1.15	0.22	0.31	0.40	9.85
	std	0.1	0.1	0.3	1.2	0.1	0.1	0.0	0.1	0.3	0.2	0.1	0.0	0.1	1.0
Lem53	body ave.	0.54	3.78	16.94	52.26	0.24	0.00	0.07	3.16	12.04	1.05	0.12	0.17	0.28	9.35
	std	0.1	0.1	0.2	0.9	0.1	0.0	0.1	0.0	0.5	0.1	0.1	0.1	0.0	0.5
Lem55	body ave.	1.1	2.7	15.0	55.5	0.3	0.3	0.2	2.3	12.7	1.0	0.2	0.2	0.3	8.2
	std	0.2	0.4	1.8	2.5	0.1	0.3	0.2	0.5	1.7	0.3	0.1	0.1	0.1	1.4
Lem58	body ave.	1.50	2.74	17.45	62.33	0.14	0.24	0.10	2.80	1.77	1.04	0.00	0.26	0.21	9.45
	std	0.2	0.6	2.5	2.1	0.2	0.2	0.1	0.4	0.3	0.2	0.0	0.1	0.1	0.7
Lem59	body ave.	1.38	3.08	18.18	61.69	0.28	0.04	0.01	3.09	1.83	0.95	0.00	0.00	0.00	9.33
	std	0.3	0.2	1.2	1.6	0.3	0.1	0.0	0.3	0.2	0.1	0.0	0.0	0.0	0.6
Lem61	body ave.	1.1	2.9	15.7	61.2	0.2	0.2	0.1	2.8	5.2	1.1	0.2	0.2	0.3	8.8
	std	0.4	0.2	0.8	1.6	0.2	0.1	0.1	0.1	1.1	0.2	0.0	0.1	0.1	0.9
Lem62	body ave.	1.2	2.8	16.0	64.3	0.1	0.1	0.1	3.0	1.6	1.0	0.2	0.2	0.3	9.0
	std	0.4	0.2	0.8	1.6	0.2	0.1	0.1	0.1	1.1	0.2	0.0	0.1	0.1	0.9

Table 5: Elemental composition of the ceramic bodies measured with SEM-EDS (in w%).

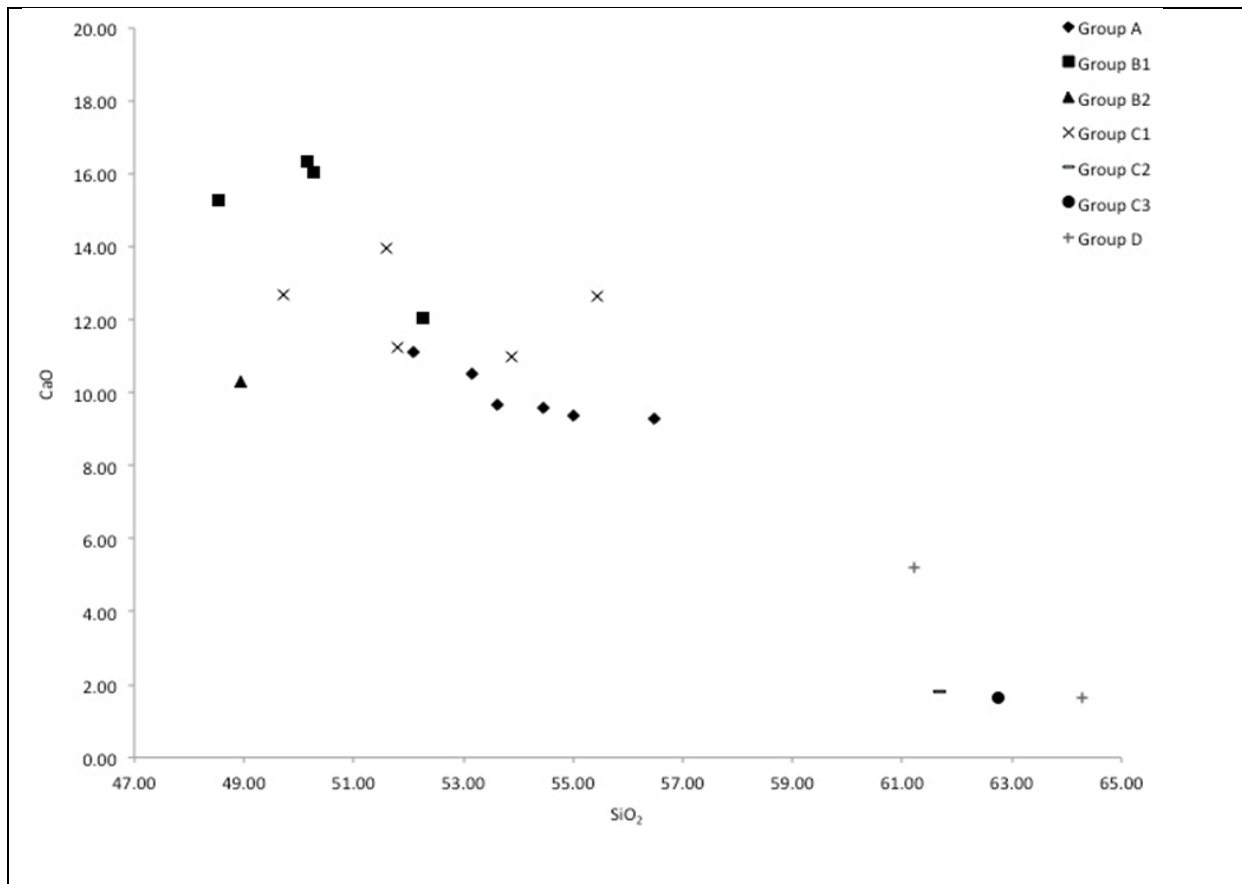


Figure 30: Scatter Plot of SiO<sub>2</sub> vs. CaO concentrations of the chemical groups.

Sample Lem28 has a fine homogeneous body with very scattered inclusions of different shapes and sizes. Lem29 has a homogeneous and porous body with dispersed inclusions in different shapes and sizes. It should be noted that deformation on the grain size boundary is observed on a layered inclusion due to non-continuous vitrification (**Figure 42c**) and deep voids (**Figure 42d**). Sample Lem45 has an inhomogeneous, relatively coarser and more porous matrix. Sample Lem55 has a homogeneous and porous matrix with dispersed inclusions of different shapes and sizes. Elongated parallel voids, which are an indication of the wheel throwing forming technique, are also observed (**Figure 48c**) (Courty, Roux, 1995). Samples from chemical Group A (Lem11 [**Figure 36**], Lem16 [**Figure 38**], Lem27 [**Figure 39**], Lem36 [**Figure 43**], Lem37, [**Figure 44**] Lem41 [**Figure 45**]) have homogeneous and porous matrices with a fine texture. Samples from this group have parallel voids and inclusions situated in the matrix, which again indicates the shaping method. Lem41 has especially elongated parallel voids with very homogeneous and fine texture indicating manufacture using the wheel thrown shaping method.

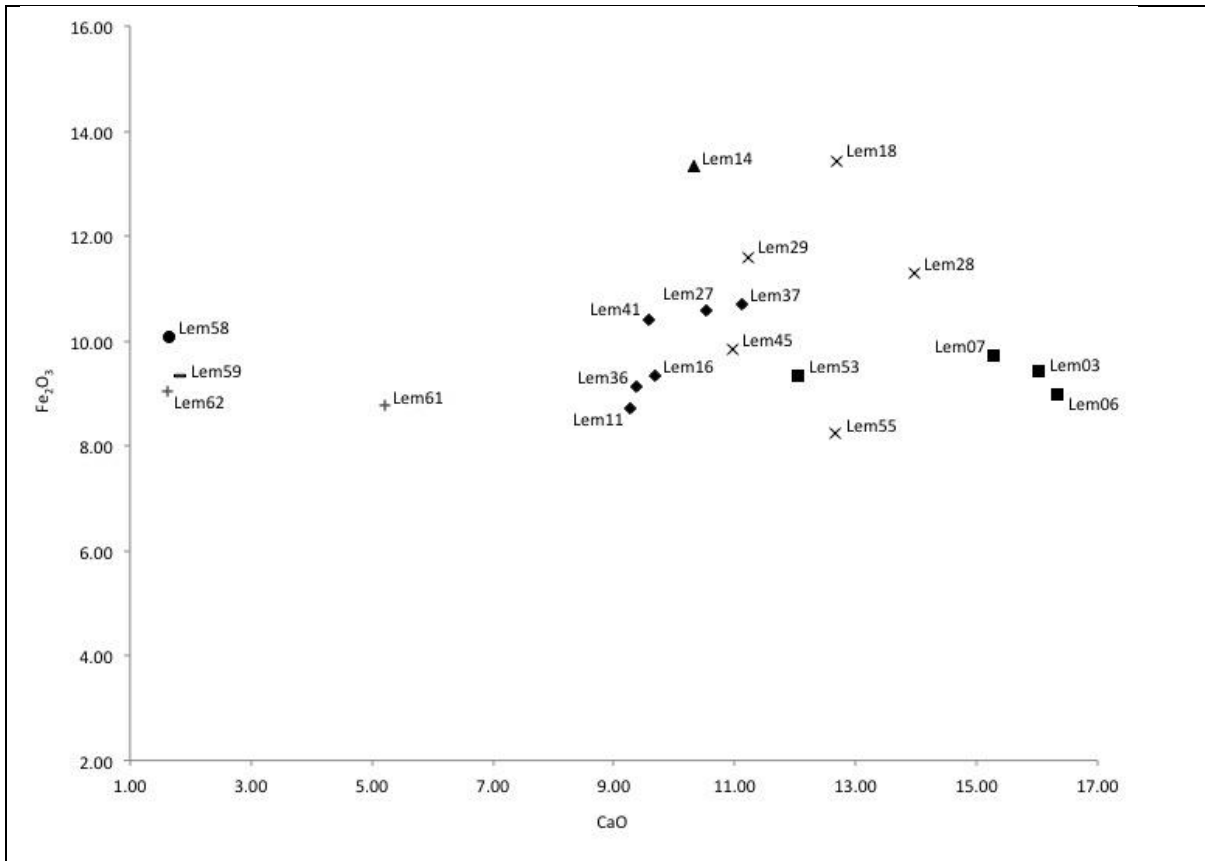


Figure 31: Scatter Plot of CaO vs. Fe<sub>2</sub>O<sub>3</sub> concentrations of the ceramic bodies observed for each sample.

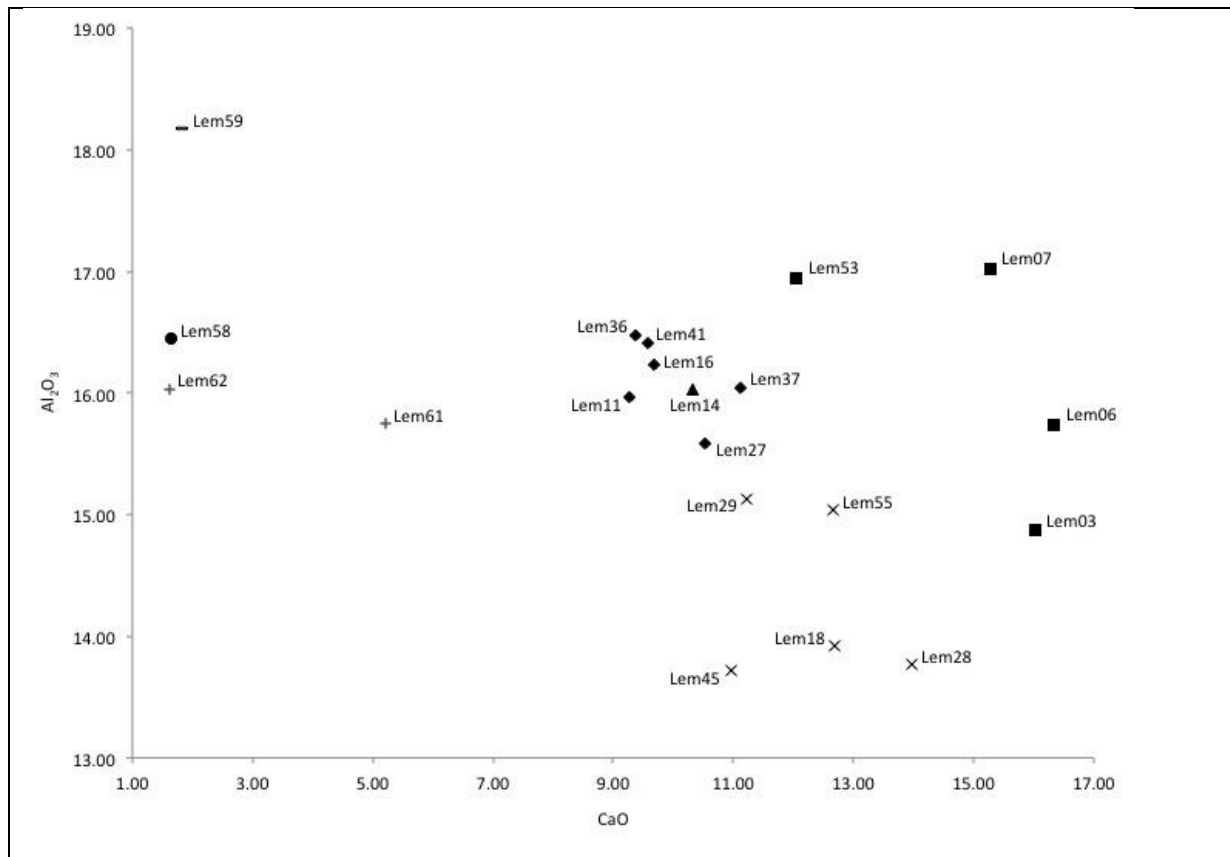


Figure 32: Scatter Plot of CaO vs. Al<sub>2</sub>O<sub>3</sub> concentrations of the ceramic bodies observed for each sample.

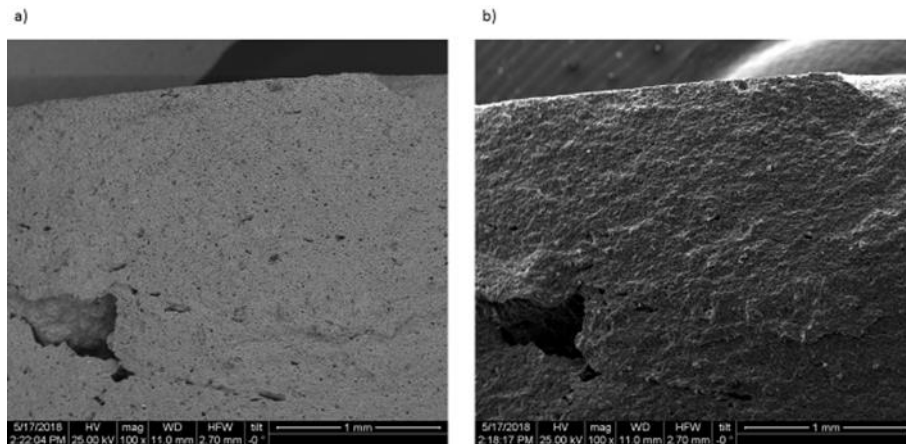


Figure 33: Sample Lem03, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X.

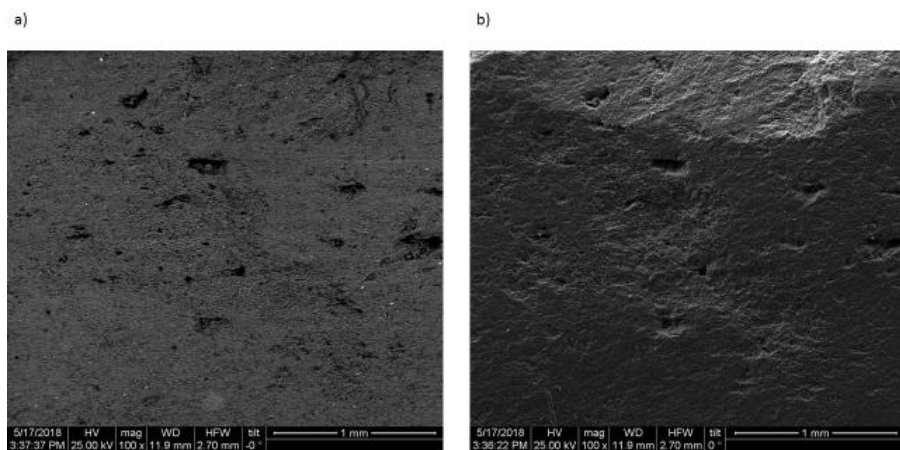


Figure 34: Sample Lem06, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X.

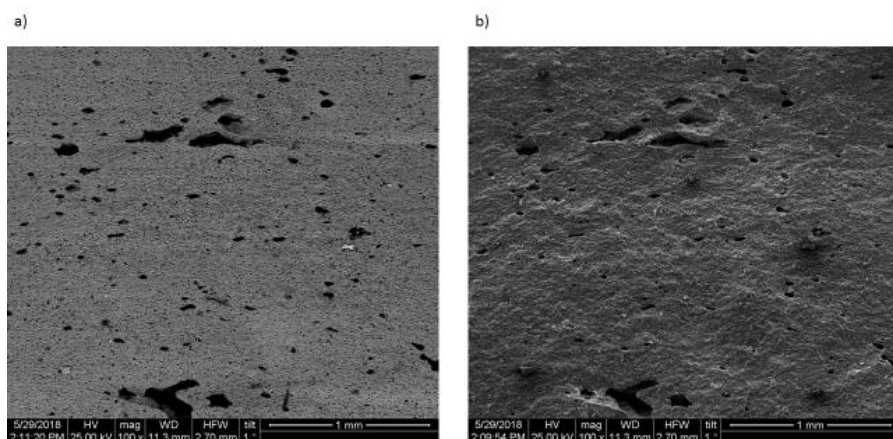


Figure 35: Sample Lem07, scale shows 1mm a) BS of the matrix 100X b) SE image of the matrix 100X.

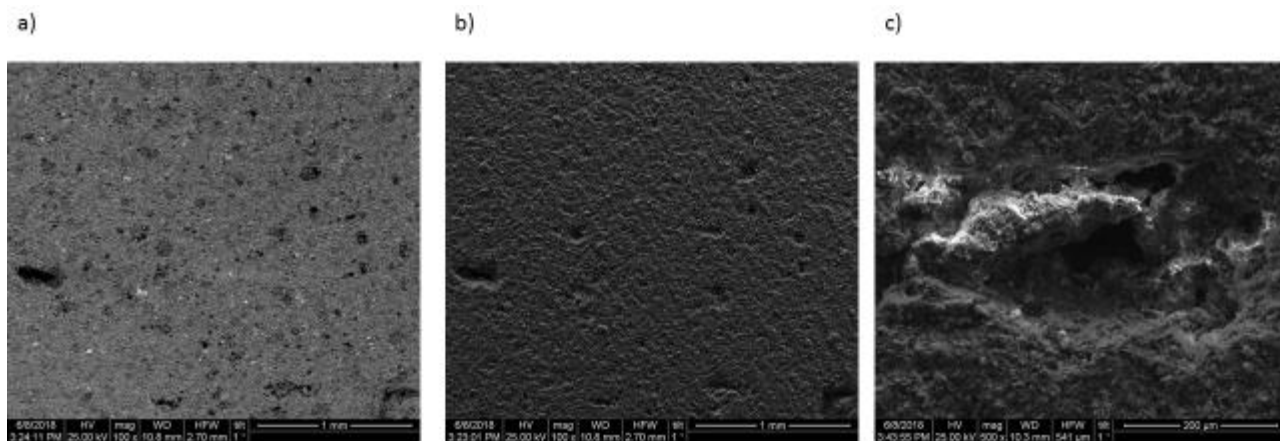


Figure 36: Sample Lem11, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X c) iron rich inclusion 500X, scale shows 200 µm.



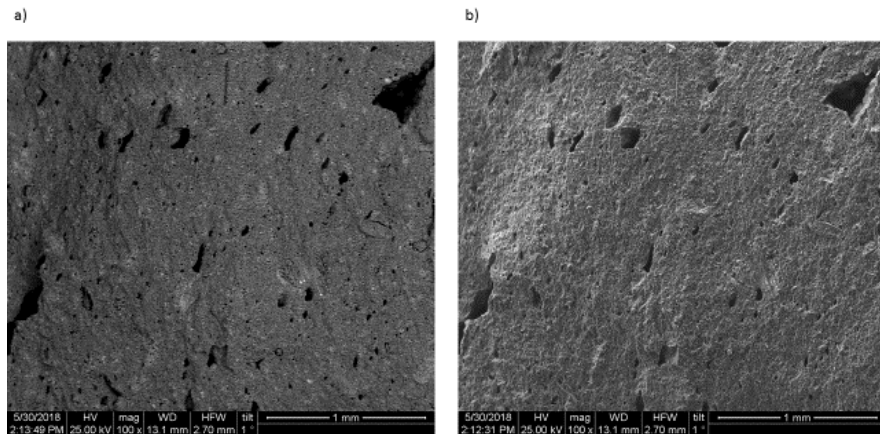


Figure 37: Sample Lem14, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X.

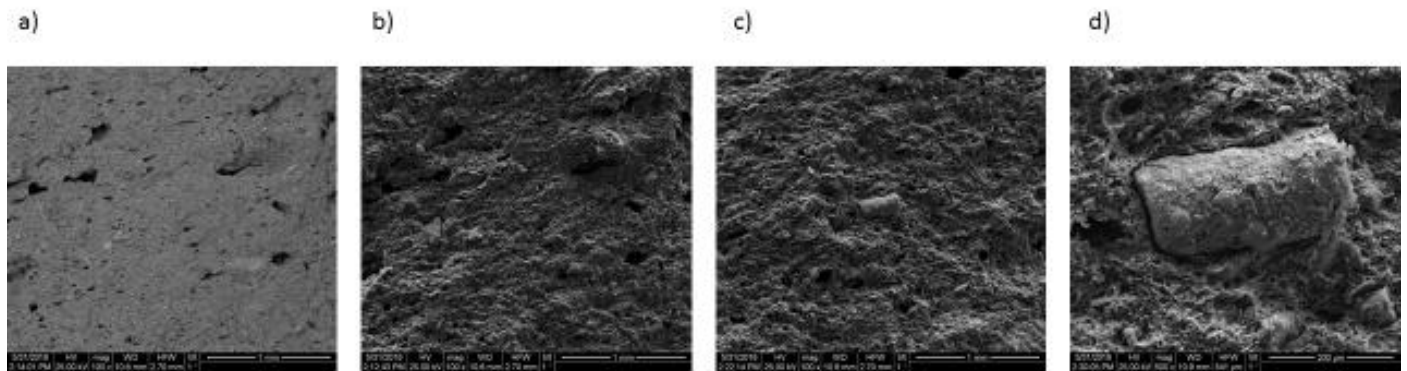


Figure 38: Sample Lem16 a) BS image of the matrix 100X, scale shows 1mm b) SE image of the matrix 100X c) SE image of an iron rich inclusion 100X d) SE image of the iron rich inclusion 500X, scale shows 200  $\mu$ m.

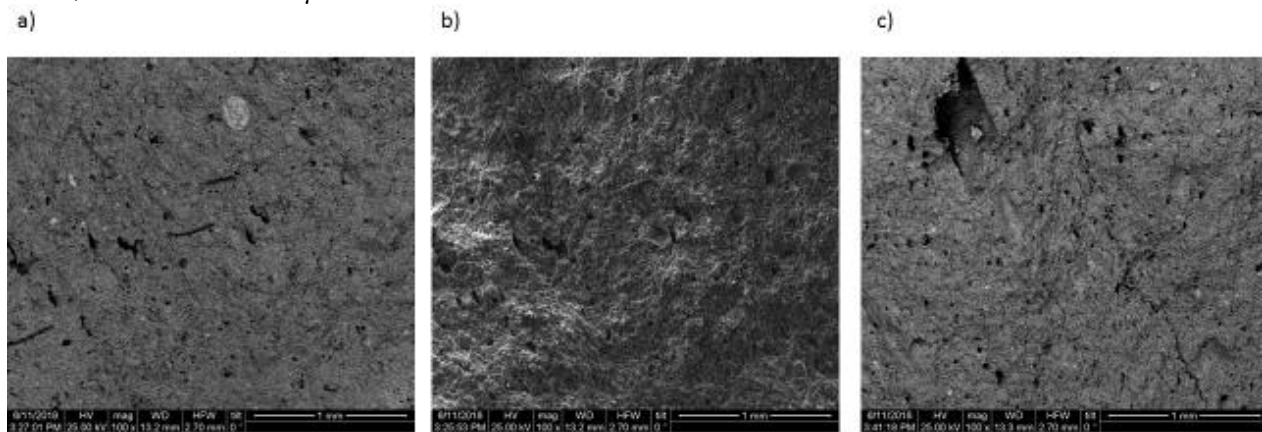


Figure 39: Sample Lem18, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X c) BS image of an iron inclusion in a void and a micro crack 100X.

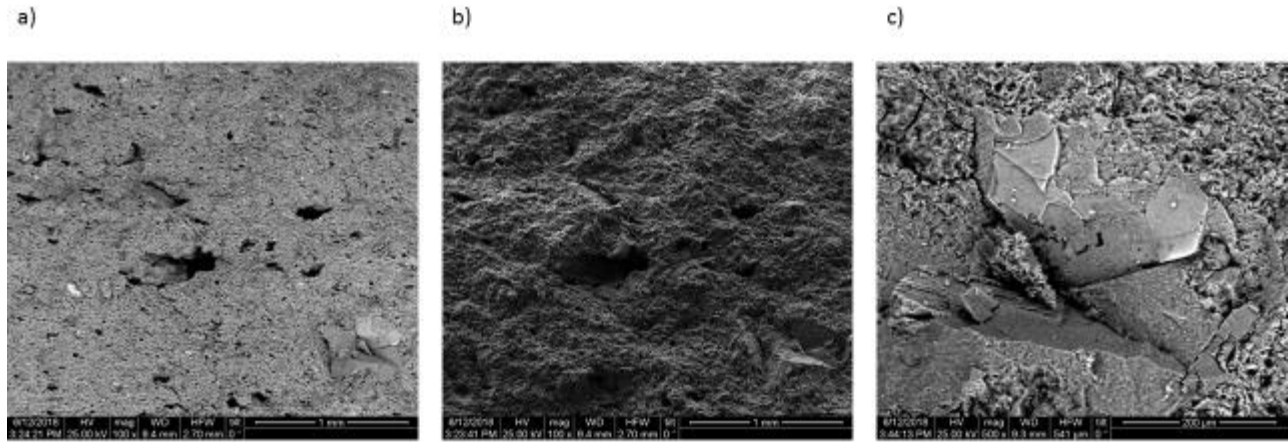


Figure 40: Sample Lem27, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X c) BS image of a mica inclusion in the matrix 500X, scale shows 200  $\mu\text{m}$ .

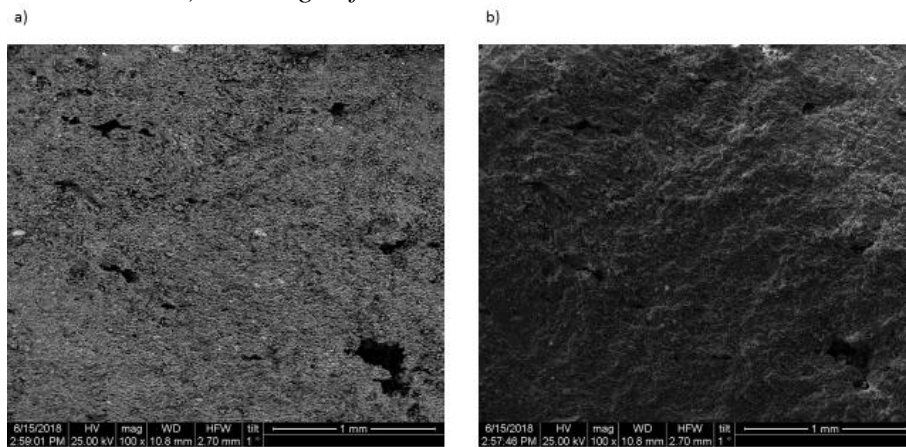


Figure 41: Sample Lem28, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X.

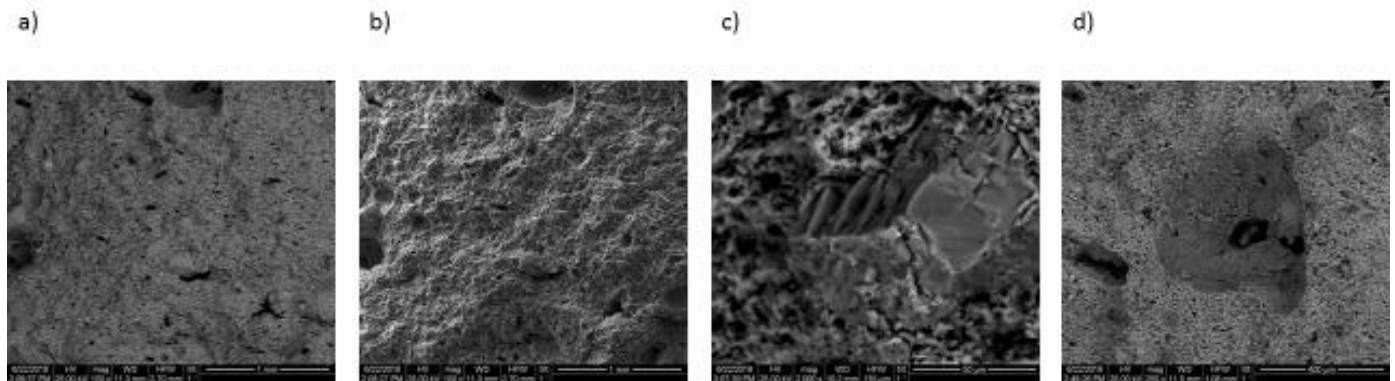


Figure 42: Sample Lem29 a) BS image of the matrix 100X b) SE image of the matrix 100X c) BS image of a layered inclusion 2000X d) voids in the matrix 250X. scale shows 1 mm for a) and b), 20  $\mu\text{m}$  for c), 400  $\mu\text{m}$  for d).

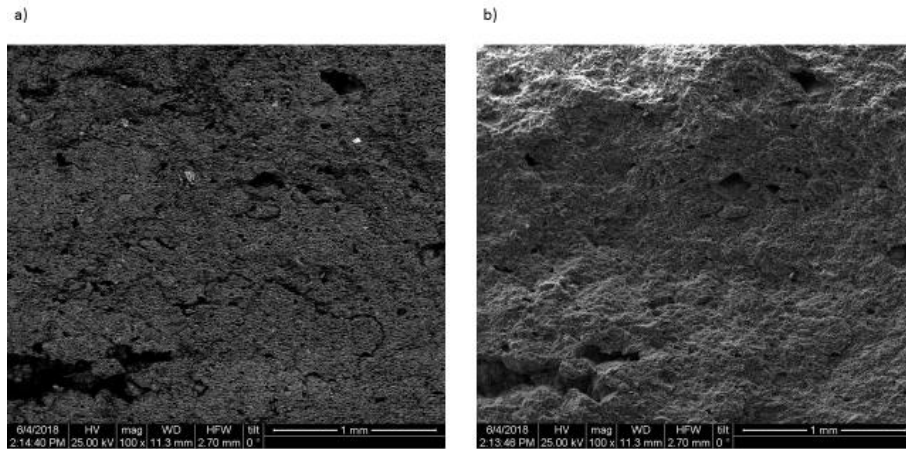


Figure 43: Sample Lem36, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X.

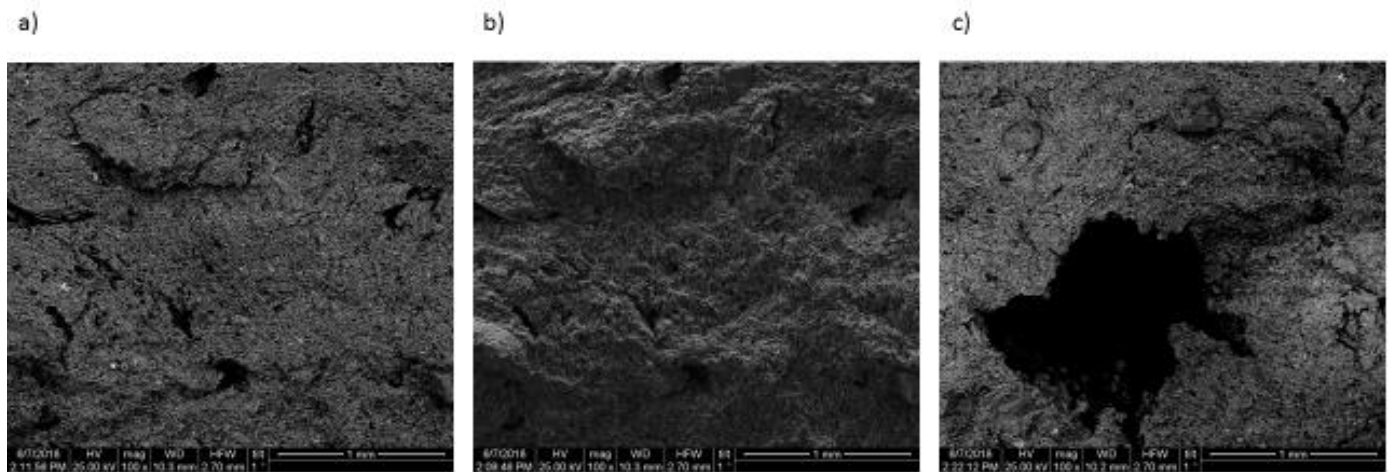


Figure 44: Sample Lem37, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X c) Representation of a void 100X.

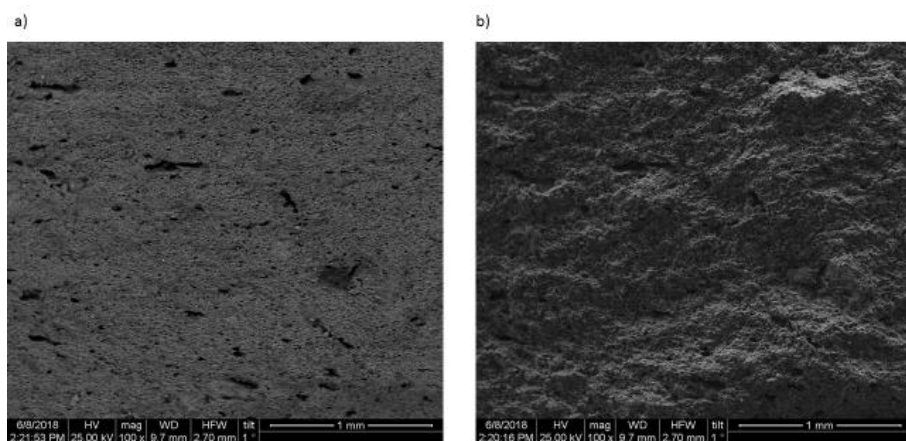


Figure 45: Sample Lem41, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X.

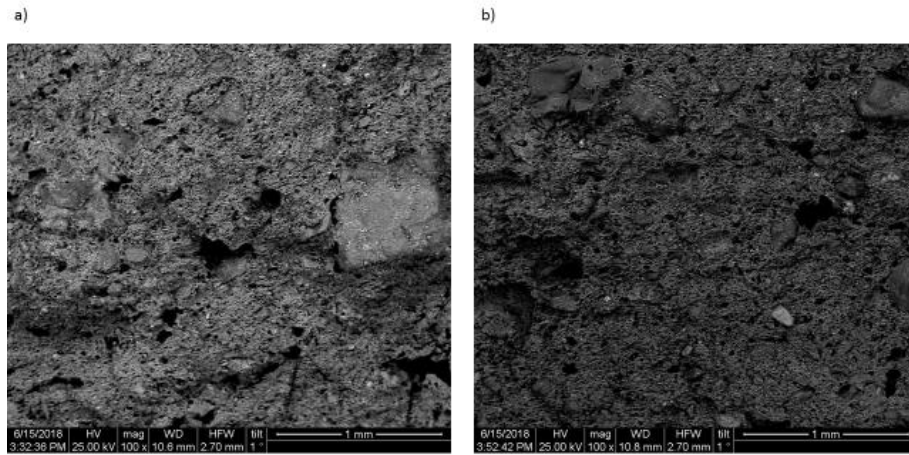


Figure 46: Sample Lem45, scale shows 1mm a) BS image of the matrix and a feldspar inclusion 100X b) SE image of the matrix 100X.

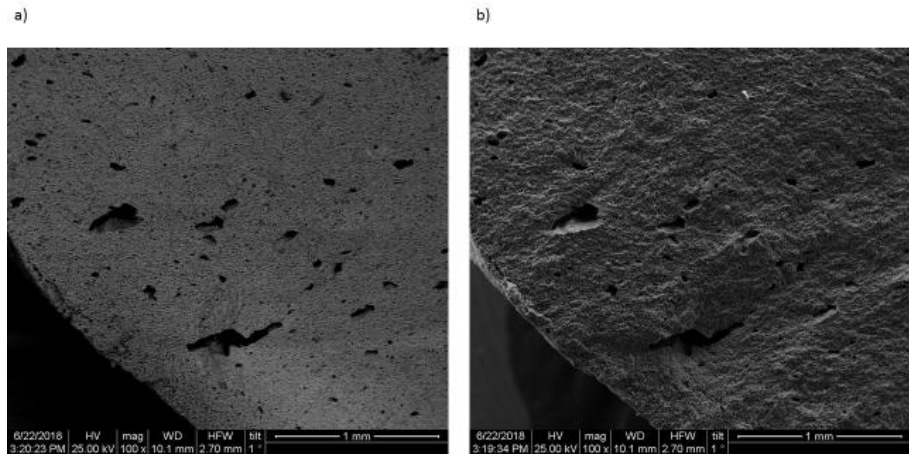


Figure 47: Sample Lem53, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X.

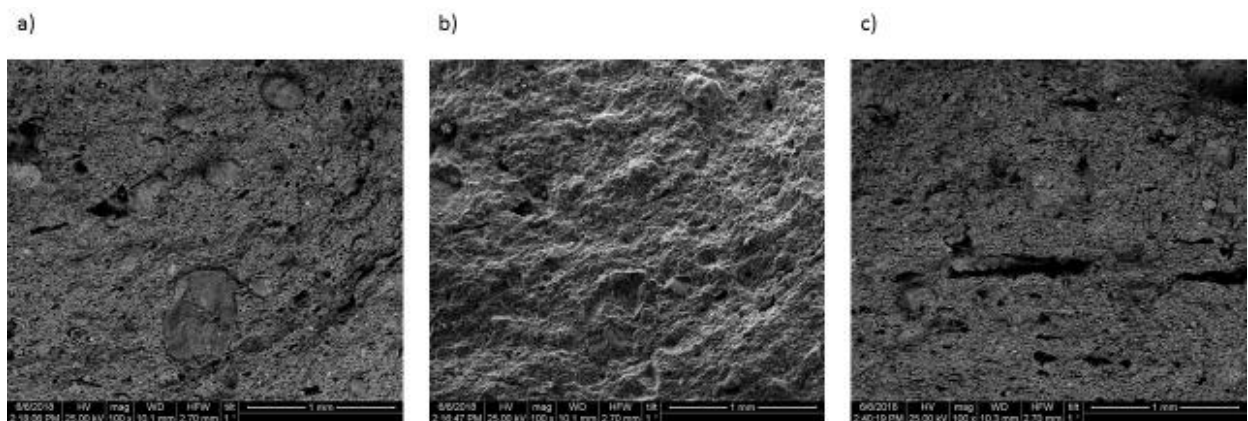


Figure 48: Sample Lem55, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X c) Representation of the horizontal voids 100X (indication of the forming technique).

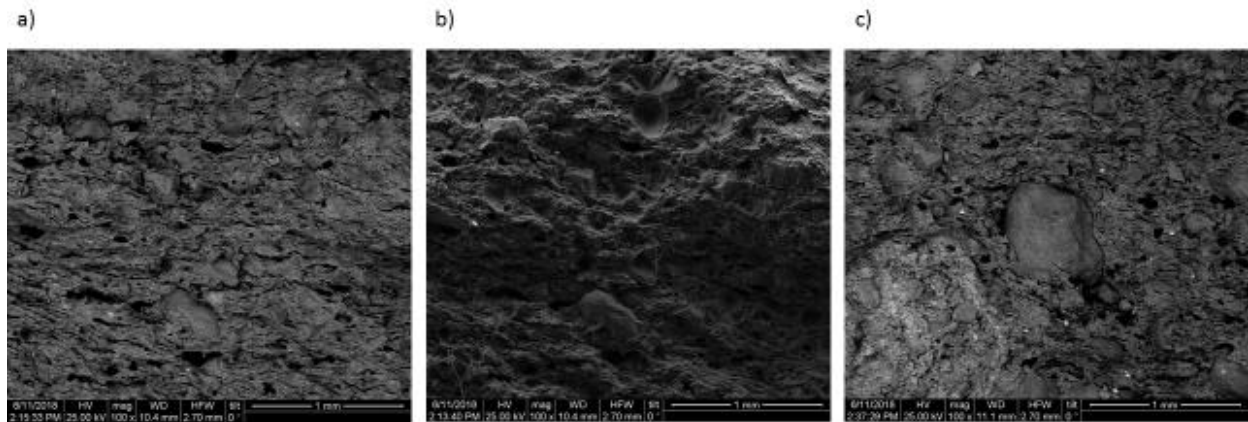


Figure 49: Sample Lem58, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X c) BS image of a round inclusion 100X.

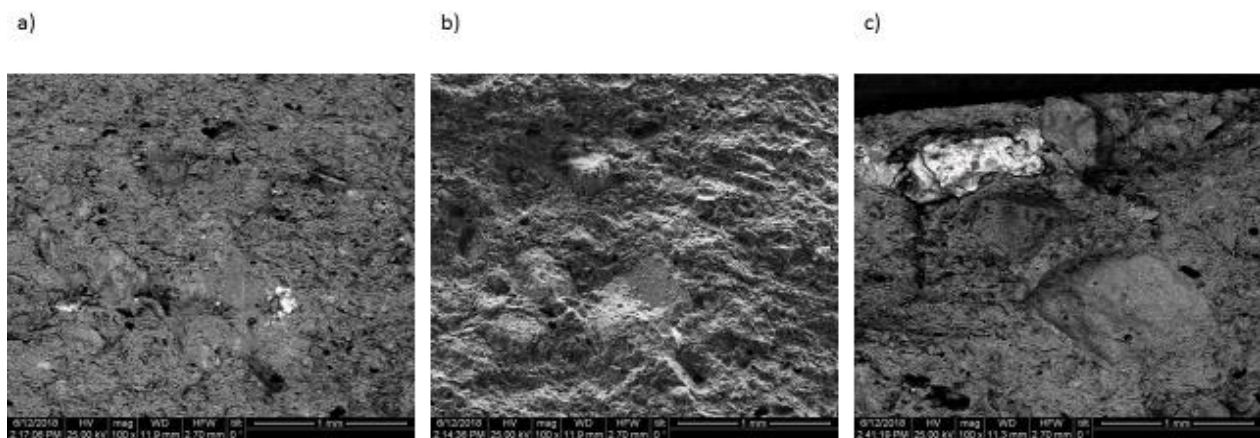


Figure 50: Sample Lem59, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 1000X c) BS image of an iron inclusion 100X.

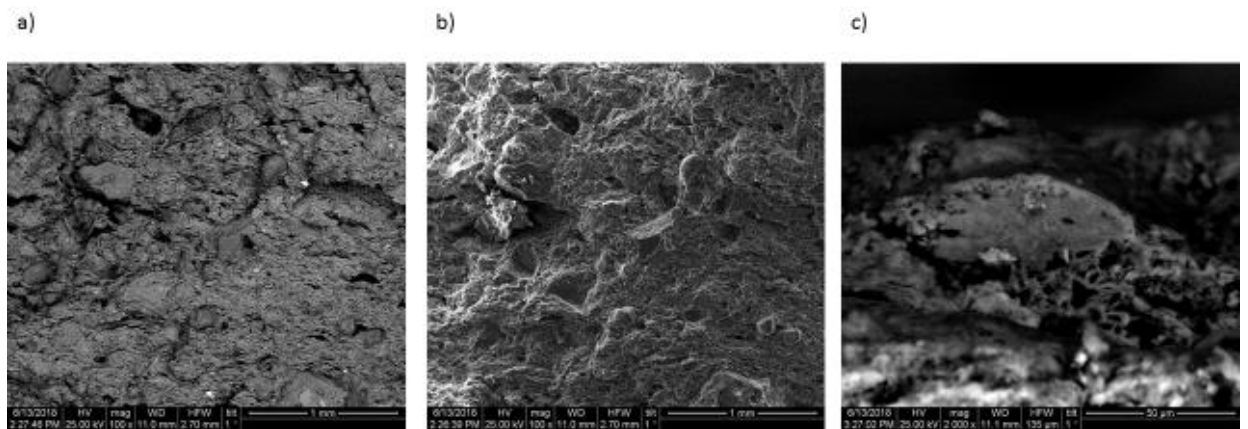


Figure 51: Sample Lem61, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X c) BS image of a possible apatite 2000X, scale shows 50 µm.

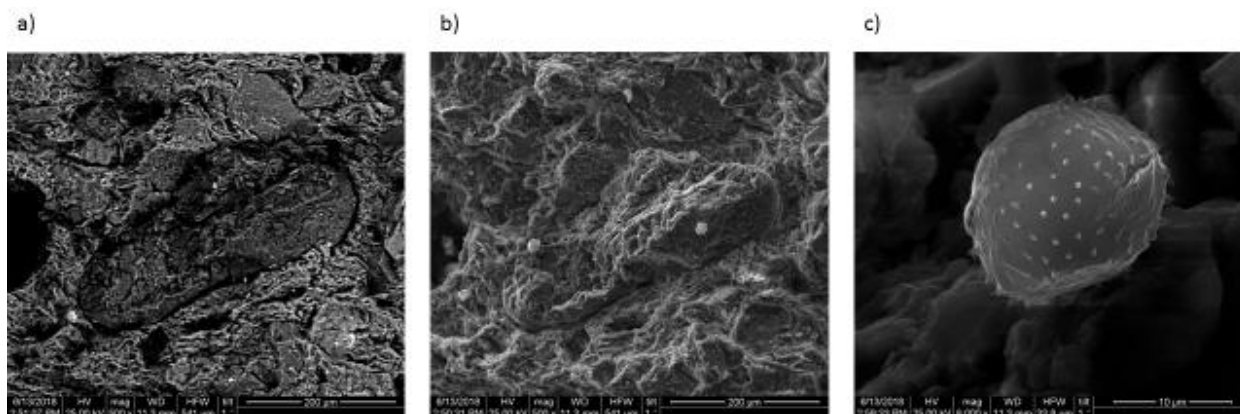


Figure 52: Sample 61 a) BS image of a possible microfossil 500X, scale shows 200  $\mu\text{m}$  b) SE image of the possible microfossil 500X, scale shows 200  $\mu\text{m}$  c) SE image of the microfossil 8000X, scale shows 10  $\mu\text{m}$ .

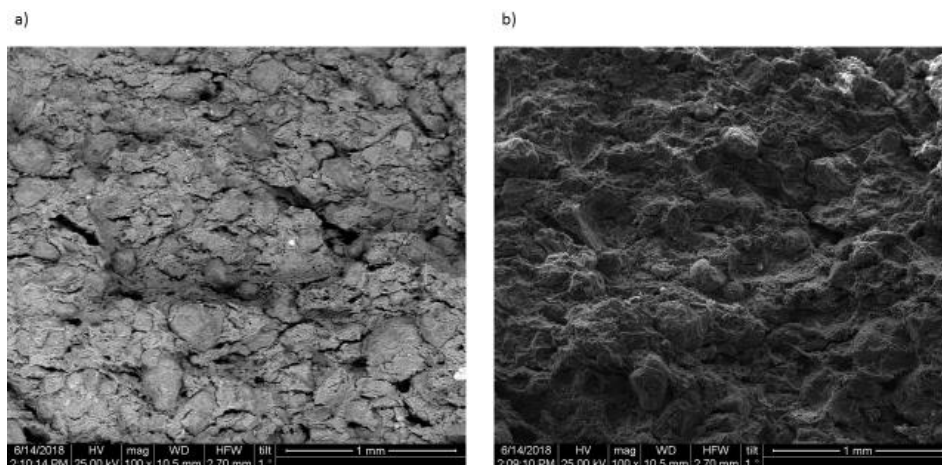


Figure 53: Sample Lem62, scale shows 1mm a) BS image of the matrix 100X b) SE image of the matrix 100X.

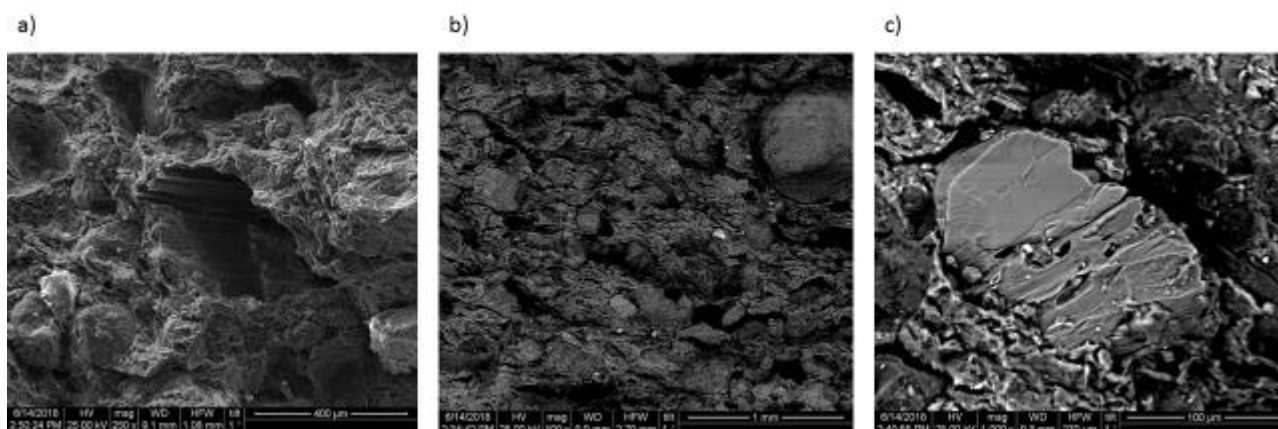


Figure 54: Sample 62 a) SE image of a possible microfossil 250X, scale shows 400  $\mu\text{m}$  b) BS image of dispersed inclusions 100X, scale shows 1mm c) BS image of an  $\text{SiO}_2$  and  $\text{CaO}$  rich inclusion 1000X, scale shows 100  $\mu\text{m}$ .

### 5.1.1. Vitrification, Firing Atmosphere and Temperature Determination:

Determination of the vitrification levels of the sherds is important to understand the changes that occur to the microstructures during firing, and to identify the possible maximum temperatures reached during firing. The vitrification levels of the samples analyzed in this study were determined by considering the CaO content in the matrix together with the firing atmospheres employed during firing, and according to this information the possible maximum firing temperatures are proposed (**Table 7**) (Maniatis, Tite, 1981). The firing atmosphere for the samples with a reddish brown body and no decoration is considered as oxidizing, while for the same bodies with black (iron-rich) decoration the oxidizing-reducing-oxidizing (O-R-O) technique is evident. The single firing technique using a reducing atmosphere was not observed for any of the studied samples considering both the body colors and surface decorations, but it was observed for the oxidizing atmosphere. Although surface decorations will be discussed in the next section, it is important to first indicate the clay types for the surface decorations (**Table 6**) in this section since this information assists in determining the atmosphere and maximum temperatures reached during firing.

As mentioned above, CaO content within the samples and firing atmosphere are important features for the determination of vitrification and maximum firing temperatures reached during firing. The samples are classified according to these characteristics as; no vitrification (NV), initial vitrification (IV), extensive vitrification (V) and continuous vitrification (CV). Samples that are between initial and extensive vitrification are shown as (IV+), while samples between extensive and continuous vitrification are shown as (V+). Lem11 presented a NV characteristic, and because the sample had a reddish brown colored, iron-rich calcareous body with no surface decoration, the firing atmosphere used for the manufacture of this sherd was determined to be oxidizing with a maximum firing temperature below 800°C, since after 800°C the body would have presented as IV (Maniatis & Tite, 1981).

Lem18 (**Figure 58a**), Lem28 (**Figure 59a**), Lem36 (**Figure 60a**) and Lem59 (**Figure 63b**) presented as IV with reddish brown colored calcareous bodies, with the exception of sample Lem59. Although sample Lem59 had a reddish brown body with a lighter core color, it also had a non-calcareous body and slipped surface. According to the body color and surface decoration

(**Table 7**), it was determined that the oxidation technique was employed for this sample. Since it presented as IV, the maximum temperatures reached during firing for this non-calcareous sample must have been between 800°C and 850°C. The firing atmospheres of undecorated samples Lem18 and Lem28 were oxidizing, with the maximum firing temperatures reached between 800°C and 850°C. The firing atmosphere of Lem36 was a three step firing system (O-R-O). This sample was slipped on both surfaces as red and black. Since the body color is reddish brown and it is a relatively iron-rich and calcareous sherd, it is understood that the O-R-O atmosphere was applied during manufacture for surface coloring with higher temperatures between 800°C and 850°C reached during firing.

Samples Lem06 (**Figure 55b**), Lem16 (**Figure 57b**), Lem37 (**Figure 60b**), Lem41 (**Figure 61a**) and Lem45 (**Figure 61b**) presented as IV+. These samples have calcareous bodies. Lem16 and Lem37 have black surface decoration, Lem41 has red surface decoration, while Lem06 and Lem45 have no surface decoration but Lem06 has a polished surface. Since Lem16 and Lem37 have black iron-rich decoration with reddish brown bodies, their firing atmospheres were O-R-O, while Lem06, Lem41 and Lem45 were fired in an oxidizing atmosphere. The maximum temperature reached during firing for these samples was between 800°C and 900°C since the samples are IV, but on some spots non-continuous V is observed, hence the IV+ classification.

Lem03 (**Figure 55a**), Lem07 (**Figure 56a**), Lem14 (**Figure 57a**), Lem27 (**Figure 58b**) Lem29 (**Figure 59b**) and Lem53 (**Figure 62a**) are defined as V. These samples have calcareous, relatively iron-rich bodies of reddish brown color. Lem03, Lem07 and Lem14 have red surface decoration, while Lem27, Lem29 and Lem53 have no surface decoration. The firing atmospheres for these samples were oxidizing, and the maximum temperatures reached during firing were between 850°C and 1050°C. It should be noted that the 200°C difference in this estimated range is because of the stabilized microstructure occurring due to the appearance of CaO from the disassociation of calcium carbonate above 750°C and its reaction with iron oxides. This process leads to the crystallization of new calcium aluminosilicate minerals that stabilize the microstructure of calcareous clays for these 200°C (Maniatis, 2009).

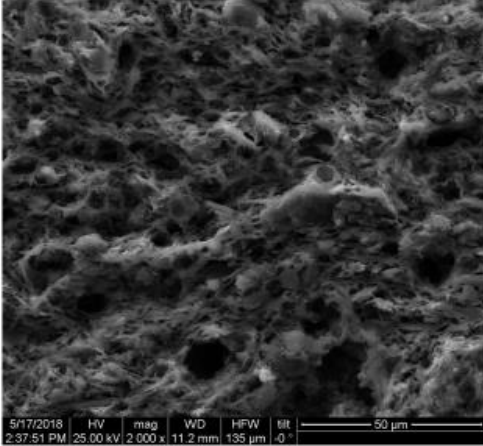
The vitrification levels of samples Lem55 (**Figure 62b**) and Lem58 (**Figure 63a**) are V+, while Lem61 (**Figure 64a**) and Lem62 (**Figure 64b**) are CV. Lem55 has a reddish brown colored calcareous body with relatively high iron, while Lem58 has a reddish brown colored non-



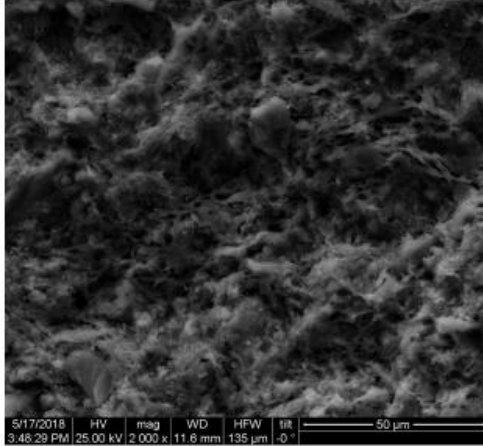
calcareous body with relatively high iron content. Lem55 has red and black surface decoration with non-calcareous clay, while the body of the sherd is reddish brown with calcareous clay. For this sample the O-R-O system is assigned for the firing technique since non-calcareous clay in an oxidizing atmosphere would turn red, like the calcareous clay used for the body, and then under a reducing atmosphere both non-calcareous and calcareous clays would turn grey or even black. During the final step, in an oxidizing atmosphere, a porous calcareous body would turn back to a reddish color while a non-calcareous clay, which had turned black in a reducing atmosphere, would have stayed the same. The maximum temperature reached for this sample was between 900°C and 950°C. Lem58 has a non-calcareous body with red decorated surface made from non-calcareous clay, and was fired in an oxidizing atmosphere. The maximum firing temperature reached was between 900°C and 950°C, since between 850°C and 950°C a non-calcareous body in an oxidizing atmosphere would have extensively vitrified. Lem61 and Lem62 have non-calcareous bodies and red surface decoration, and were fired in oxidizing atmospheres with maximum temperatures reaching between 950°C and 1000°C.

Sample Lem61 and Lem62 should be discussed further in terms of firing atmospheres due to their layered body colors with darker colored cores especially sample Lem61 with a dark grey core. As Orton and Hughes (2013:152) discusses in their book "*Pottery in Archaeology*" layered colored bodies with darker cores can occur under both oxidizing and reducing atmospheres. Most clays contain organic matter that will burn out during firing process in oxidizing atmospheres, however sometimes the carbon does not burn out entirely due to short firing times and turns the core to a dark grey or black, as was the case for the samples Lem61 and Lem62. Thus it is determined that samples Lem61 and Lem62 were fired under oxidizing atmospheres for a short time (Maniatis and Tite, 1975). It should be noted once more that the maximum firing temperatures proposed here were made according to CaO concentrations, color of the body and decorations, microstructure and vitrification characteristics of the samples. As Maniatis (2009:4) discusses, firing rate and soaking time can also affect the mineralogical changes and the degree of vitrification. **Figures 52** and **54a** show the possible microfossils situated in the matrix of these samples and further study on them would be helpful for the identification of the provenance (Quinn and Day, 2007).

a)

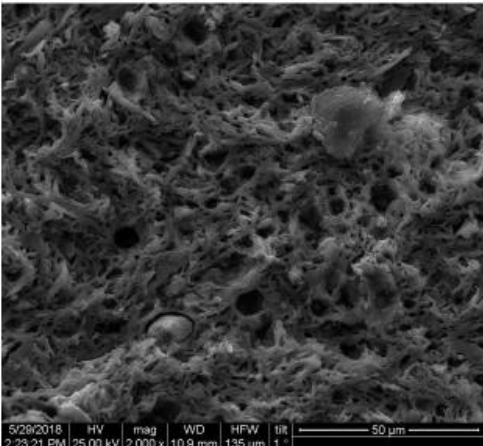


b)

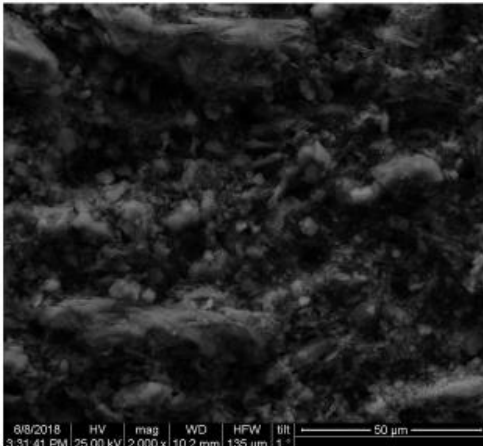


*Figure 55: a) Lem03 representative image of the body vitrification (V) b) Lem06 representative image of the body vitrification (IV+)*

a)

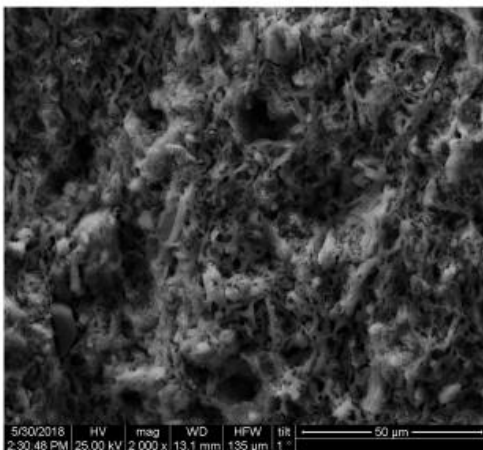


b)

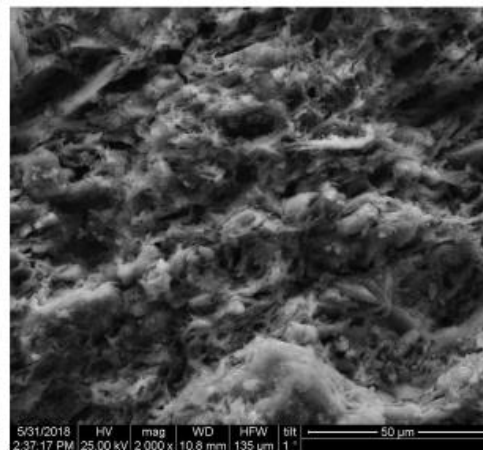


*Figure 56: a) Lem07 representative image of the body vitrification (V) b) Lem11 representative image of the body vitrification (NV)*

a)



b)



*Figure 57: a) Lem14 representative image of the body vitrification (V) b) Lem16 representative image of the body vitrification (IV+)*

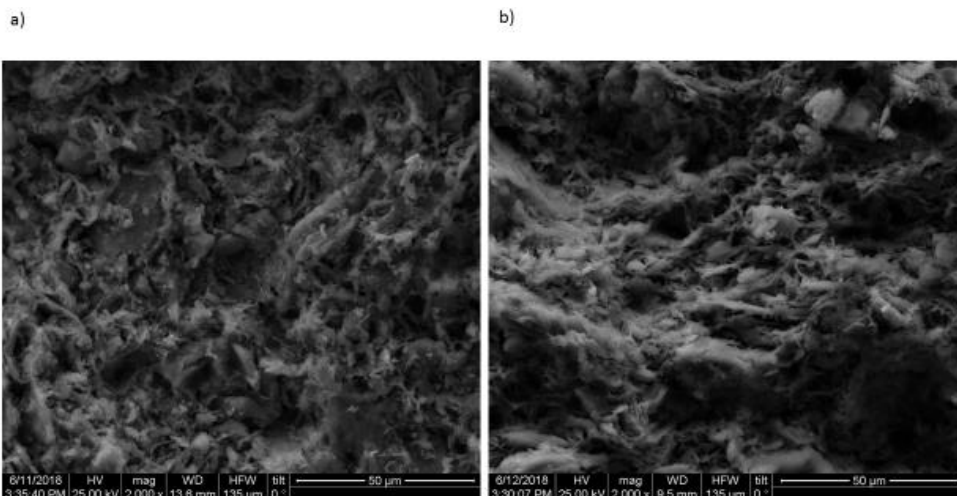


Figure 58: a) Lem18 representative image of the body vitrification (IV) b) Lem27 representative image of the body vitrification (V)

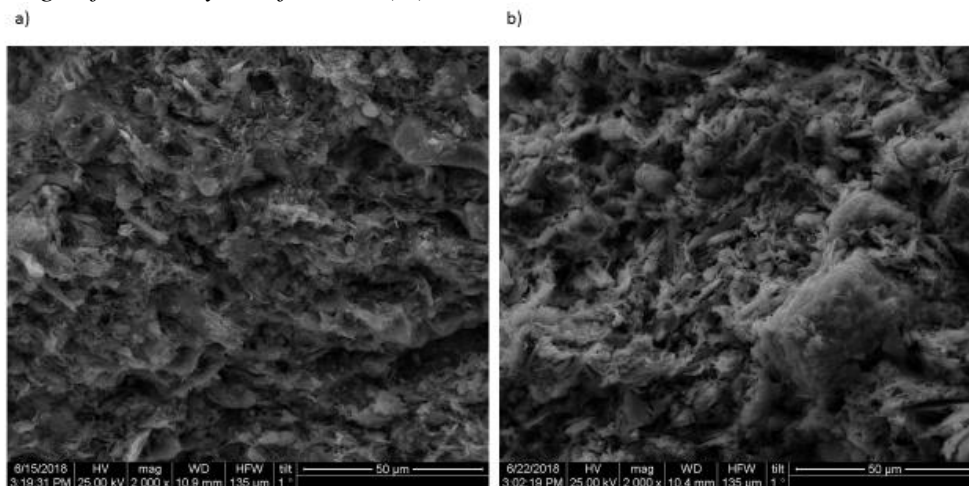


Figure 59: a) Lem28 representative image of the body vitrification (IV) b) Lem29 representative image of the body vitrification (V)

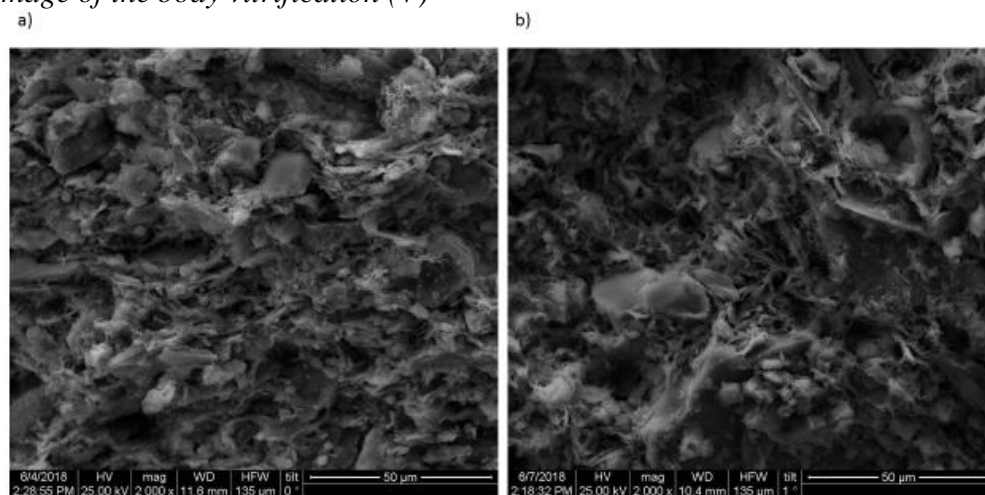


Figure 60: a) Lem36 representative image of the body vitrification (IV) b) Lem37 representative image of the body vitrification (IV+)

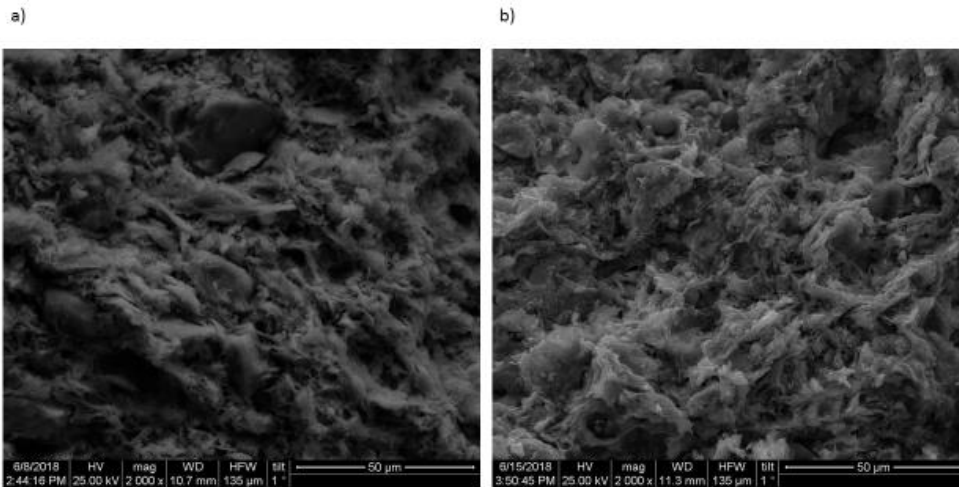


Figure 61: a) Lem41 representative image of the body vitrification (IV+) b) Lem45 representative image of the body vitrification (IV+)

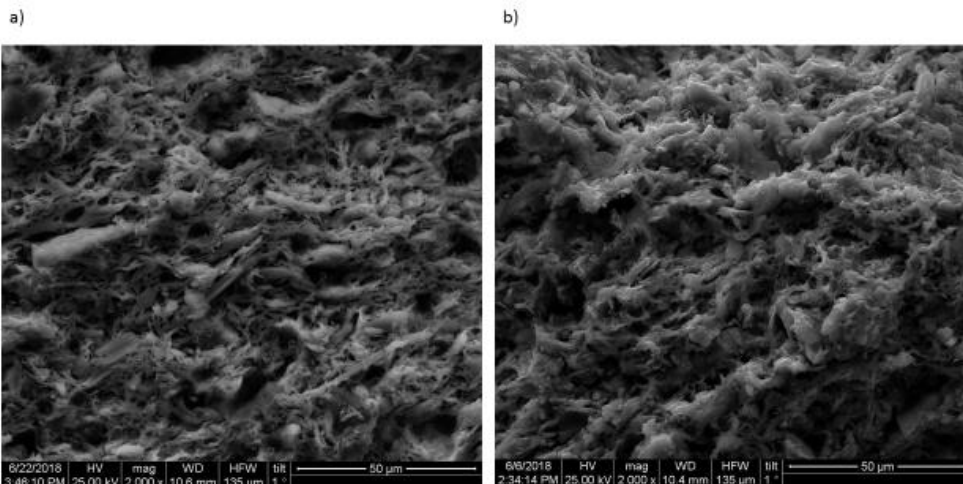


Figure 62: a) Lem53 representative image of the vitrification (V) b) Lem55 representative image of the body vitrification (V+)

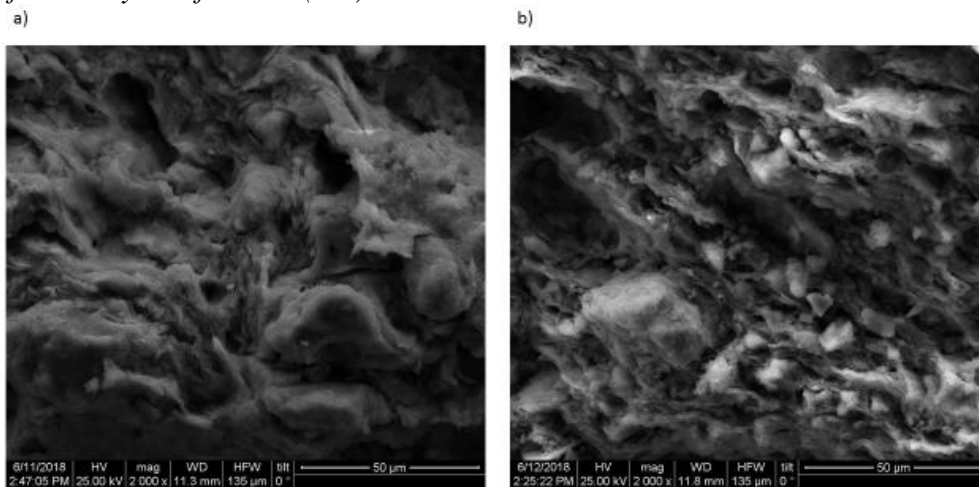


Figure 63: a) Lem58 representative image of the vitrification (V+) b) Lem59 representative image of the body vitrification (IV)

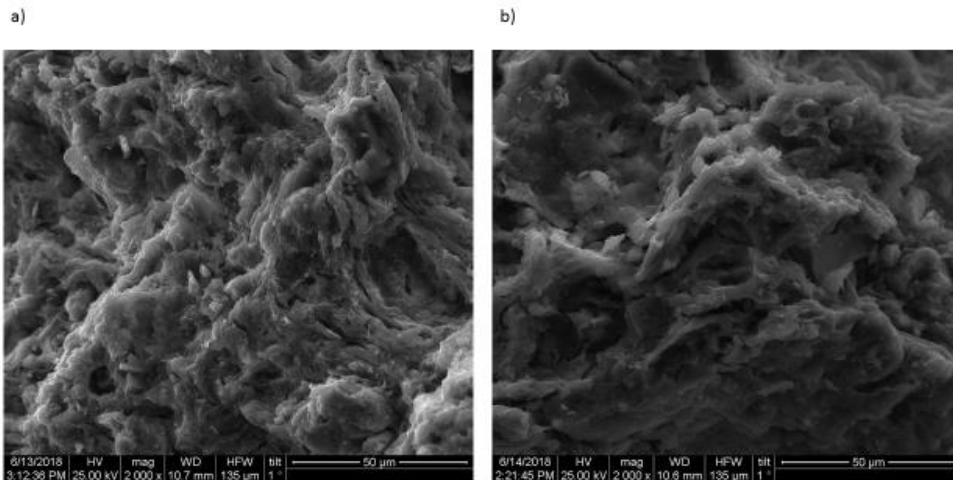


Figure 64: a) Lem61 representative image of the vitrification (CV) b) Lem62 representative image of the body vitrification (CV)

## 5.2. Surface Analysis:

The samples with surface decorations are Lem03 (**Figure 66**), Lem07 (**Figure 67**), Lem14 (**Figure 68a**), Lem16 (**Figure 68b**), Lem36 (**Figure 69**), Lem37 (**Figure 70a**), Lem41 (**Figure 70b**), Lem55 (**Figure 71**), Lem58 (**Figure 72**), Lem59 (**Figure 73a**), Lem61 (**Figure 73b**) and Lem62 (**Figure 74**). The surfaces of these samples exhibit slip layers. During analysis the samples are positioned on the chamber in a way that both sides of the fresh fractured sherd surfaces and the body would be observed, measured and compared at once. The samples with surface decorations on just one surface are Lem14, Lem16, Lem37, Lem41, Lem59 and Lem61, while Lem03, Lem07, Lem36, Lem55, Lem58 and Lem62 have surface decorations on both sides of the samples (**Table 6**). Lem59 and Lem61 have red surface decoration with a slip layer on one surface and polishing applied to the other surface. The thicknesses of the slipped surfaces did not present a uniform picture, and the majority of them were considerably low. They were always between 5 to 20  $\mu\text{m}$ , and generally less than 10  $\mu\text{m}$  (**Table 8**).

Secondary electron and backscattered electron modes showed that slip layers bonded well to the bodies, most likely due to the prior polishing treatment, although sample Lem07 and Lem36 exhibited poor bonding. If the pottery was not moist enough when the slip was applied, due to differential shrinkage of the slip and the body during drying, the slip layer would not have bonded well to the body (Webb, 1994), which could be the case for samples Lem07 and Lem36. Microstructural characteristics of the slips show that they have fine, compact textures. Samples

present mostly homogeneous microstructures except Lem61 and Lem62. Surface layers show higher vitrification characteristics than the bodies due to slip layers containing relatively high concentration of potassium (Ferrerias et al, 2016), which will be discussed further in the following section.

### 5.2.1. Chemical Composition:

Elemental compositions of the surfaces (**Table 6**) were measured through EDS. According to these measurements it was determined that almost all of the slip layers are non-calcareous, as well as potassium- and iron-rich. For each sample at least three average measurements of surface layers and body compositions were compared. The observed differences presented four patterns (**Figure 65**). In order to assess significant enrichment or depletion of element concentrations,  $\text{CaO}+\text{MgO} / \text{K}_2\text{O}$  ratios were considered for the comparison of ceramic body and slips (**Figure 65c**). According to the results of these ratios it was observed that  $\text{CaO}+\text{MgO}$  depletion in the slip layers coincided with  $\text{K}_2\text{O}$  enrichment for most of the samples, which could be explained by the refinement of the clay via elutriation (Ferrerias et al, 2016).

The samples belonging to the first pattern are Lem03, Lem14, Lem16, Lem37, Lem55 and Lem59 (see **Table 9** for elemental composition comparisons between the ceramic body and surface layers). This pattern shows enrichment of  $\text{K}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  in the slip layers (**Figure 65a**) while  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$  ratios show lower concentrations than the bodies (**Figure 65b**). It should be noted that Lem03 has slips on both sides of the sherd, and the elemental composition of the second analyzed surface of this sample revealed that the clay used for the slip is the same as the one used for the body construction, while the first surface decoration is made with a different non-calcareous clay paste. The slip layer of Lem37 showed an increased MnO concentration on some spots, however it was inhomogeneous and elemental mapping showed that MnO was not used for the surface decoration. Lem55 is similar to Lem03, with different decorations on either side of the sherd. The first (inner) surface of this sample has a black decoration that was made with non-calcareous clay, while the second (outer) surface has a red line made with calcareous clay. Both surface layers showed relatively higher  $\text{Na}_2\text{O}$  concentrations. Lem59, with a non-calcareous ceramic body, also has a slip layer made with non-calcareous clay although relatively higher in concentration of CaO. In addition, the slip layer of this sample also shows a relatively higher potassium concentration. It can be said that the clay used for the body construction is also

used for the slip layer after being further refined. Samples Lem14 and Lem16 that constructed with calcareous clay have slip layers that reveal the use of different, non-calcareous clay. The surface layer of Lem16 shows an increased  $\text{Na}_2\text{O}$  concentration, as was also the case for Lem55.

The samples from the second pattern are Lem07, Lem36 and Lem41 (see **Table 9** for elemental composition comparisons between the ceramic body and surface layers). For these samples  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3/\text{SiO}_2$  concentrations were compared between the body and slip layers, and it was observed that, although  $\text{Al}_2\text{O}_3$  enrichments were observed for the slip layers, the  $\text{K}_2\text{O}$  concentration displayed no significant difference between the body and slip layers (**Figure 65a**), and the  $\text{Fe}_2\text{O}_3$  concentrations decreased in the slip layers (**Figure 65b**). Lem07 had surface decorations on both sides of the sherd, and the elemental characterization of these surface layers revealed that the same non-calcareous clay was used for both surfaces, while the body was constructed with calcareous clay. Lem36 had surface decorations on both sides of the sherd as well, and their elemental compositions revealed that the first surface was composed of non-calcareous clay while the second was calcareous. When compared to the ceramic body the second surface (black decoration) had the same iron and potassium concentrations and relative increase in  $\text{Na}_2\text{O}$ . The first surface (red decoration) of the same sample had non-calcareous clay with increased iron and potassium. This determined that the clay used for the body construction was different than the clays used for the slips while each slip layer differed in  $\text{CaO}$  concentrations. The clay used for the slip layer of Lem41 was non-calcareous and elemental characterization revealed increased iron and potassium.

The third pattern consists of samples Lem58 and Lem62 (see **Table 9** for elemental composition comparisons between the ceramic body and surface layers). These samples exhibited enrichment of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  (**Figure 65b**) in the slip layers while the  $\text{K}_2\text{O}$  concentration decreased (**Figure 65a**). Lem58 had surface decorations on both sides of the sherd and elemental characterization of these surface layers showed non-calcareous, iron-rich clay pastes with no difference in potassium. Moreover, the ceramic body was constructed from non-calcareous clay as well. Comparison of the elemental composition of the body and surface layers revealed that the first and second surface layers were from the same clay, which was also used for the ceramic body though it was higher in iron. This could be explained by the use of the same clay but with the addition of ochre for a red surface decoration in an oxidizing firing atmosphere (Freestone & Middleton, 1987). Sample Lem62 was similar to Lem58, with a body constructed from non-

calcareous clay and the slip layers on both sides of the sherd also from non-calcareous clay type. The clay paste used for the slip layers was same with the body, but with an ochre addition that was revealed by a high increase in iron content in the slip layers compared to ceramic body.

The fourth pattern has just one sample, Lem61 (see **Table 9** for elemental composition comparisons between the ceramic body and surface layer). This sample was different than all the others, showing enrichment of  $K_2O$ ,  $Al_2O_3$  and  $Fe_2O_3$  (**Figure 65a and b**) in the slip layer with no difference of  $CaO+MgO$  concentration (**Figure 65c**) between the slip and body layers.

In general, according to these diverse chemical patterns related to the elemental enrichment and depletion identified among the slips and discussed above, it is possible that the technological practice focused heavily on the processing of raw clay material. This highly advanced method is apparent because almost all of the studied samples indicated fine to medium calcareous fabrics with homogeneous matrix except samples Lem58, Lem59, Lem61 and Lem62, which had non-calcareous, coarse fabrics. Concerning the iron over aluminum concentrations of the slips, only three samples showed a higher iron concentration, Lem58, Lem61 and Lem62. Even though the clay could have been refined to enrich the iron (Ferrerias et al, 2016), these samples indicate the use of specific iron-rich clay with an ochre additive. The same clay was used for the slips on both surfaces as for the construction of the body for only two samples, Lem58 and Lem62, while Lem36 and Lem03 had refined second surfaces that showed no considerable impact on the chemical composition. Almost all of the samples indicated  $CaO+MgO$  depletion and  $K_2O$  enrichment in the slip layers, which could be explained by the refinement of the clay by elutriation except for Lem58, Lem59, Lem61 and Lem62, although low  $CaO$  concentrations are generally related with the use of non-calcareous clay in the slip layers while calcareous clays were used in the ceramic bodies. Another important observation was the difference in firing structure employed for the production. Although most of the samples are fired in kiln structures which provide control of the changes in the atmospheres during firing, low calcareous samples Lem61 and Lem62 (similar to low calcareous local Mycenaean pottery from Macedonia (Buxeda et al., 2003:273)) indicates fast firing with a dark core sandwiched between two brownish red layers, and red surface decoration which would be achieved with oxidizing atmosphere, indicates the use of a different structure other than a kiln (Buxeda et al., 2003). Low calcareous samples, Lem58, Lem59, Lem61 and Lem62 show absence of black decoration, fast firing (Chemical group D samples Lem61, Lem62) and red surface decoration could be explained by the



production of these sherds with a non kiln structure such as bon fire, pit or a pit kiln (Buxeda I Garrigo's et al. 2003: 280). Samples with black decorations (Lem16, Lem36, Lem37, Lem55) shows O-R-O episodes during firing indicated the use and knowledge of kiln firing.

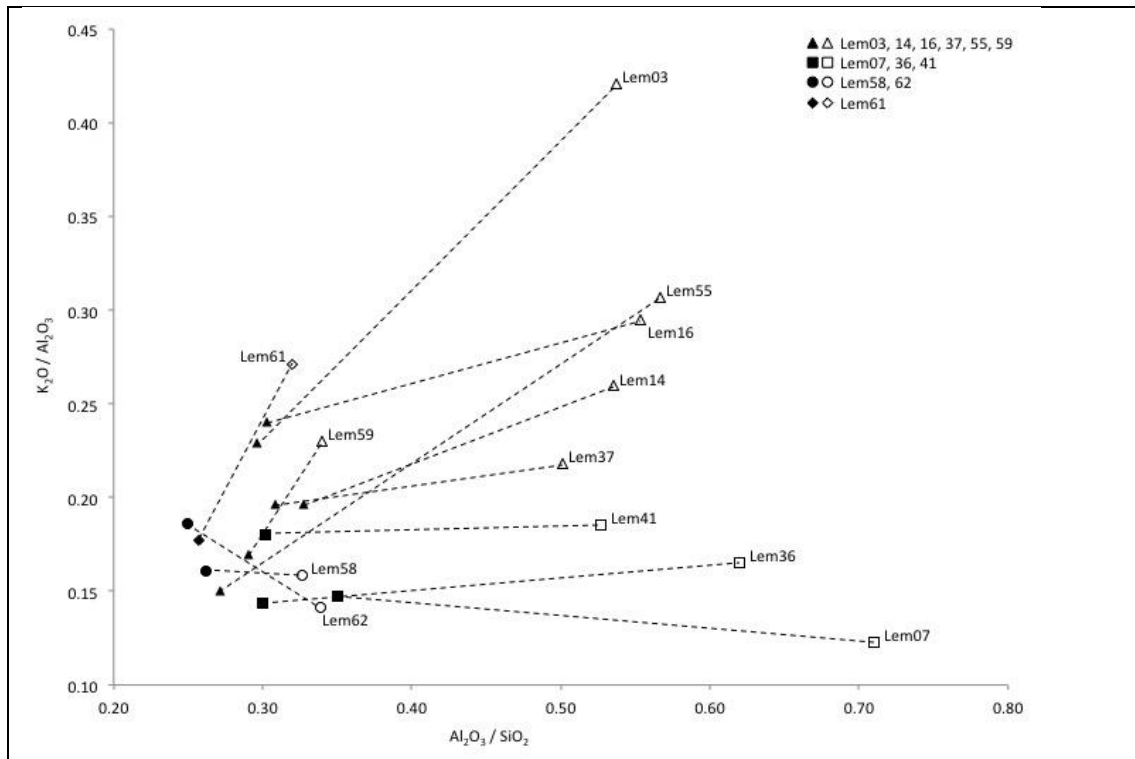
According to the surface analysis four different technological patterns are observed (**Figure 65a and 65b**) and discussed above. Comparison of these patterns with the chemical groups indicates that samples belonging to different chemical groups belong to the same technological patterns. For example, Chemical Group D represented by Lem61 and Lem62 belonged to slightly differing technological patterns, although they showed the same firing technology and structure use. Lem58, belonging to chemical group C3, is within the same technological pattern as Lem62. These samples were identified as local pottery (Hein, Kilikoglou, 2016). Another sample identified as local is Lem59 made with non to low calcareous clay as well. The technological pattern identified for the surface decoration is different from the other locals (Lem58, 61, 62). These results indicate that local pottery is produced with slightly differing surface technology patterns even though they all have red slipped surfaces. Moreover, sample Lem07 belonging to Chemical Group B1 is similar to the imported wares from the Argolid (A-Troy) (Hein and Kilikoglou, 2016) which is similar to (D-Troy) (Mountjoy and Mommsen, 2006). This sample is in the same technological pattern observed for Lem36 and Lem41 that both belong to Chemical Group A.

It should be noted that Lemnos Chemical Group A shows similarities to Chemical Group D-Troy (Kilikoglou, Hein, 2016) which is considered a local paste from Troia (Mountjoy and Mommsen, 2006). Hein and Kilikoglou observed in their NAA analysis that Lemnos B1 and Lemnos A show small differences, similar to the small differences observed between A-Troy and D-Troy Chemical Groups (2006:2). According to these findings it is possible to say that Lem36 and Lem41 are similar to the A-Troy Argolid imports along with Lem07, or alternatively they could be local Mycenaean imitations from Troy. The identification of technology transfers between Argolid, Troy and Lemnos should be investigated further to understand the Mycenaean presence on Koukonisi in detail.

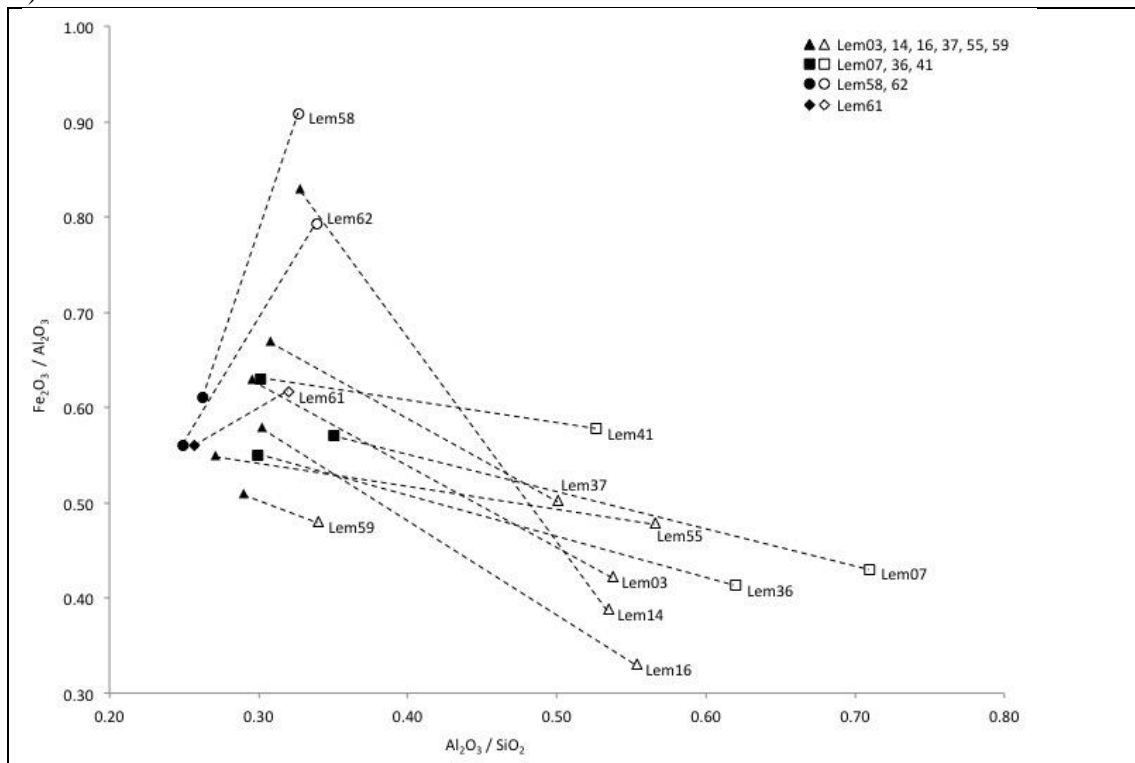
Samples	Surface	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	CaO	TiO2	V2O5	Cr2O3	MnO	Fe2O3
Lem03	1st surface average	0.81	2.25	24.25	45.11	0.26	0.41	4.87	0.83	0.29	0.19	0.18	10.25
	std	0.16	0.08	0.07	2.07	0.15	0.04	0.08	0.08	0.00	0.00	0.06	1.08
	2nd surface average	0.60	3.75	15.29	46.33	0.60	1.89	16.93	1.33	0.18	0.14	0.29	8.86
	std	0.22	0.09	0.32	4.04	0.07	0.86	3.03	0.17	0.25	0.08	0.02	1.25
Lem07	1st surface average	0.6	3.1	31.3	39.0	0.2	0.3	2.3	1.3	0.1	0.2	0.2	17.7
	std	0.09	1.01	3.00	0.33	0.26	0.05	0.66	0.33	0.07	0.15	0.06	1.92
	2nd surface average	0.9	2.8	30.8	43.1	0.1	0.3	2.7	1.2	0.2	0.2	0.2	13.5
	std	0.06	0.18	1.31	0.72	0.13	0.25	1.41	0.07	0.10	0.02	0.08	1.51
Lem14	average	1.0	2.3	25.8	48.2	0.5	0.2	3.3	1.1	0.3	0.3	0.3	10.0
	std	0.34	0.12	0.75	2.49	0.01	0.24	0.74	0.07	0.20	0.11	0.16	1.15
Lem16	average	3.5	2.8	26.1	47.1	0.3	0.3	1.9	0.8	0.2	0.2	0.1	8.6
	std	0.66	0.54	0.00	0.06	0.14	0.09	1.32	0.02	0.13	0.10	0.13	0.83
	1st surface average	1.5	3.1	28.5	46.0	0.2	0.0	2.6	1.1	0.2	0.2	0.2	11.8
	std	0.06	0.08	1.85	2.07	0.05	0.00	0.16	0.03	0.15	0.09	0.06	0.13
Lem36	2nd surface average	2.43	3.25	24.57	47.45	0.75	0.47	7.69	0.73	0.08	0.10	0.14	9.56
	std	0.64	0.47	1.67	0.97	0.67	0.22	1.93	0.20	0.12	0.12	0.09	0.76
	slip average	2.75	2.54	22.38	44.69	0.78	0.32	5.65	1.00	0.23	0.25	3.02	11.24
	std	0.67	0.57	2.33	1.26	0.56	0.12	1.25	0.06	0.02	0.08	3.58	1.89
Lem41	slip average	0.5	3.4	24.2	45.9	0.4	0.5	3.8	1.7	0.2	0.2	0.2	14.0
	std	0.17	0.71	1.65	6.30	0.29	0.46	0.78	0.95	0.23	0.19	0.18	6.77
Lem55	int. slip average	3.0	2.1	24.9	43.9	0.3	0.5	3.6	0.9	0.2	0.2	0.2	11.9
	std	0.69	0.54	1.61	2.47	0.20	0.46	0.55	0.20	0.06	0.07	0.05	2.60
	out. slip average	3.1	1.9	23.5	44.2	0.2	0.7	6.5	1.1	0.3	0.3	0.3	11.2
	std	0.66	0.12	1.87	4.64	0.09	0.40	4.76	0.40	0.18	0.13	0.15	3.05
Lem58	1st surface average	0.6	3.4	17.9	54.9	0.3	0.3	1.7	0.9	0.2	0.2	0.3	16.3
	std	0.06	0.32	0.67	3.45	0.11	0.18	0.23	0.10	0.08	0.10	0.07	3.61
	2nd surface average	0.4	3.1	18.6	56.5	0.2	0.3	1.9	1.0	0.2	0.2	0.2	14.7
	std	0.01	0.16	2.45	1.04	0.20	0.20	0.55	0.18	0.03	0.04	0.03	2.09
Lem59	average	1.2	2.6	19.4	57.0	0.3	0.4	3.7	0.7	0.2	0.1	0.1	9.3
	std	0.19	0.11	0.78	1.33	0.08	0.21	0.54	0.06	0.06	0.13	0.05	0.24
Lem61	average	1.5	2.7	15.9	58.0	0.1	0.3	5.3	1.2	0.2	0.2	0.2	9.9
	std	0.6	0.7	3.0	5.5	0.1	0.3	0.3	0.2	0.2	0.2	0.1	1.6
Lem62	1st surface average	1.2	3.1	18.5	54.7	0.9	0.3	1.8	1.5	0.1	0.0	0.2	14.7
	std	0.21	0.50	2.54	4.11	0.25	0.04	0.01	0.98	0.11	0.06	0.13	6.72
	2nd surface average	0.8	2.8	19.3	58.3	0.5	0.4	2.1	0.9	0.3	0.3	0.2	10.0
	std	0.0	0.0	2.8	0.7	0.1	0.1	0.8	0.2	0.2	0.2	0.0	2.6

Table 6: Elemental compositions of the surface layers of slipped samples measured with EDS (in w%).

a)



b)



c)

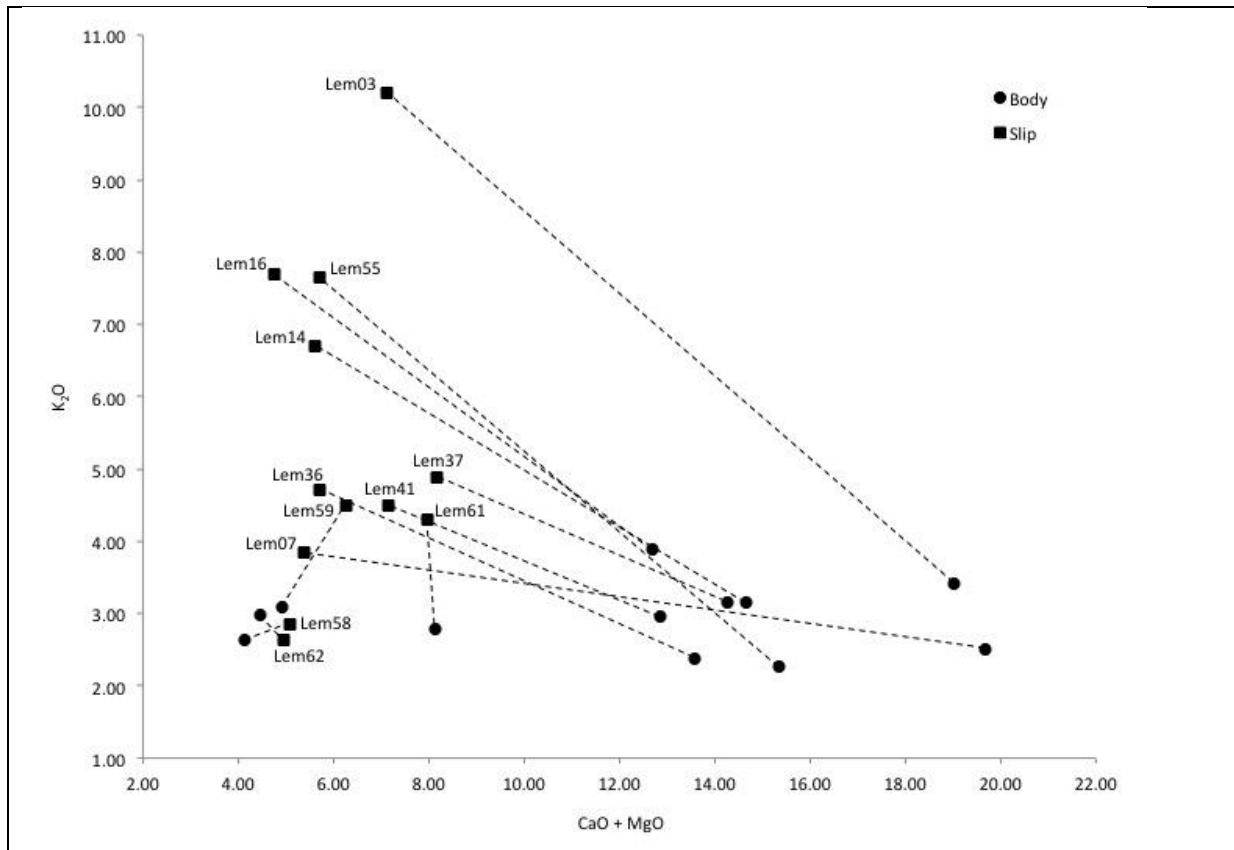
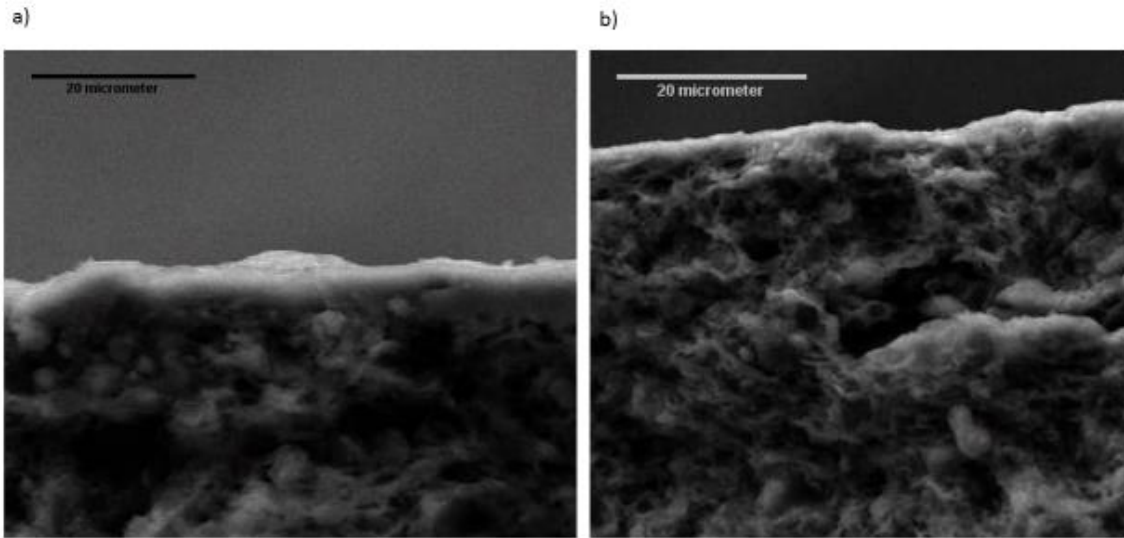


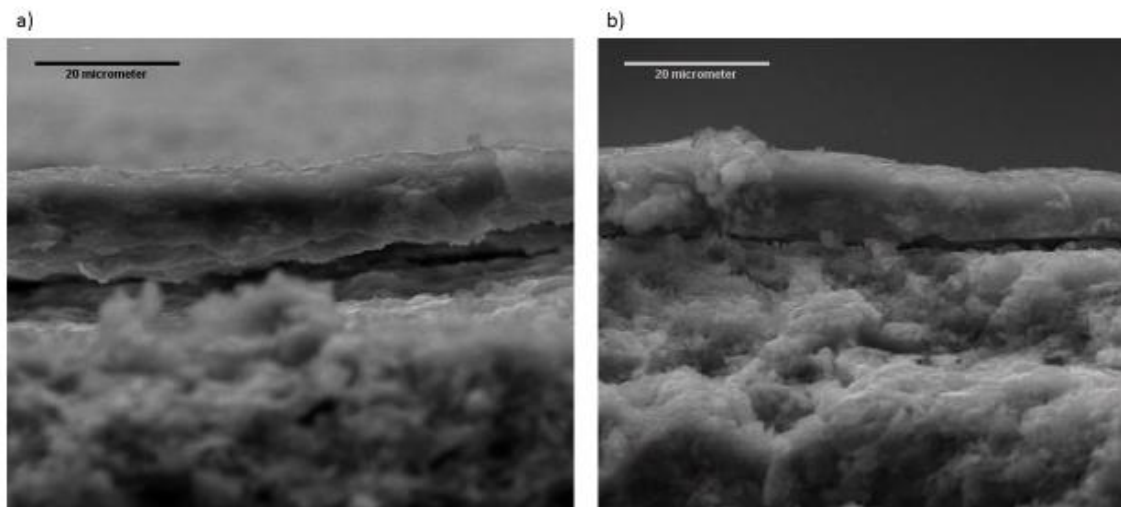
Figure 65: a) Scatter Plot comparing the ratios of the K<sub>2</sub>O over Al<sub>2</sub>O<sub>3</sub> concentrations and the Al<sub>2</sub>O<sub>3</sub> over SiO<sub>2</sub> concentrations b) Scatter Plot comparing the ratios of the Fe<sub>2</sub>O<sub>3</sub> over Al<sub>2</sub>O<sub>3</sub> concentrations and the Al<sub>2</sub>O<sub>3</sub> over SiO<sub>2</sub> concentrations. The symbols represent patterns in terms of compositional differences between the surface and body of a specific sample: white, surface measurements; black, measurements of the ceramic body. Symbols presenting the same sample are connected with lines. c) Scatter Plot of CaO+MgO over K<sub>2</sub>O concentrations of the decorated samples showing differences between the slip and body of a specific sample.

Samples (Chemical Group)	Calcareous	CaO % (in w)	Body Color	Surface Treatment	Firing Atmosphere	Body Vitrification	Firing Temperature (C)
Lem03 (B1)	High	16.0	Reddish Brown	Red Decoration	O	V	850-1050
Lem06 (B1)	High	16.3	Reddish Brown	Polished	O	IV+	800-900
Lem07 (B1)	High	15.3	Reddish Brown with a lighter core	Red Decoration	O	V	850-1050
Lem11 (A)	Medium	9.3	Reddish Brown	NT	O	NV	<800
Lem14 (B2)	Medium	10.3	Reddish Brown	Red Decoration	O	V	850-1050
Lem16 (A)	Medium	9.7	Reddish Brown	Black Decoration	O-R-O	IV+	800-900
Lem18 (C1)	High	12.7	Reddish Cream	NT	O	IV	800-850
Lem27 (A)	High	10.5	Reddish Brown	NT	O	V	850-1050
Lem28 (C1)	High	14.0	Light Brown (Greyish/Reddish)	NT	O	IV	800-850
Lem29 (C1)	High	11.2	Reddish Brown	NT	O	V	850-1050
Lem36 (A)	Medium	9.4	Reddish Brown	Red and Black Decoration	O-R-O	IV	800-850
Lem37 (A)	High	11.1	Reddish Brown	Black Decoration	O-R-O	IV+	800-900
Lem41 (A)	High	9.6	Reddish Brown	Red Decoration	O	IV+	800-900
Lem45 (C1)	High	11.0	Reddish Brown/Lighter core	NT	O	IV+	800-900
Lem53 (B1)	High	12.0	Light Reddish Brown	NT	O	V	850-1050
Lem55 (C1)	High	12.7	Reddish Brown/Cream	Red and Black Decoration	O-R-O	V+	>900-950
Lem58 (C3)	Low	1.8	Reddish Brown/lighter core	Red Decoration	O	V+	>900-950
Lem59 (C2)	Low	1.8	Reddish brown/light core	Red Decoration	O	IV	800-850
Lem61 (D)	Low	5.2	Reddish brown margins/ dark grey core	Red Decoration	O	CV	>950-1000
Lem62 (D)	Low	1.6	Reddish brown margins/ very light greyish brown core	Red Decoration	O	CV	>950-1000

*Table 7: Presentation of the samples according to CaO contents within the ceramic bodies, color of the bodies after firing, surface decorations, assigned firing atmospheres (O=Oxidation; O-R-O=Oxidation-Reduction-Oxidation), vitrification levels of the ceramic bodies (NV=No vitrification, IV=initial vitrification, V=extensive vitrification, CV= continues vitrification, IV+ = between initial and extensive vitrification, V+ = between extensive and continues vitrification) and possible maximum firing temperatures reached during firing.*

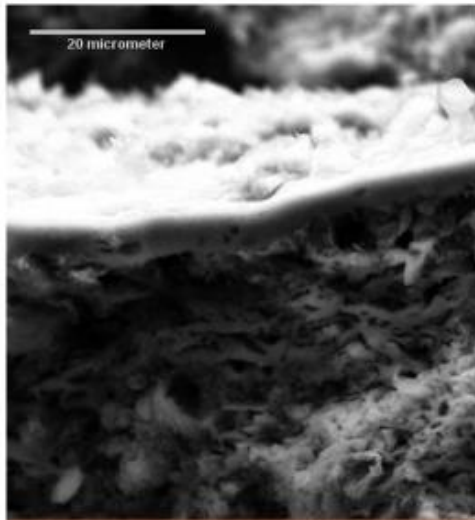


*Figure 66: Lem03 surface decoration 2000X, scale presents 20 micrometers a) 1<sup>st</sup> surface, slipped, red decoration b) 2<sup>nd</sup> surface, slipped, red decoration*

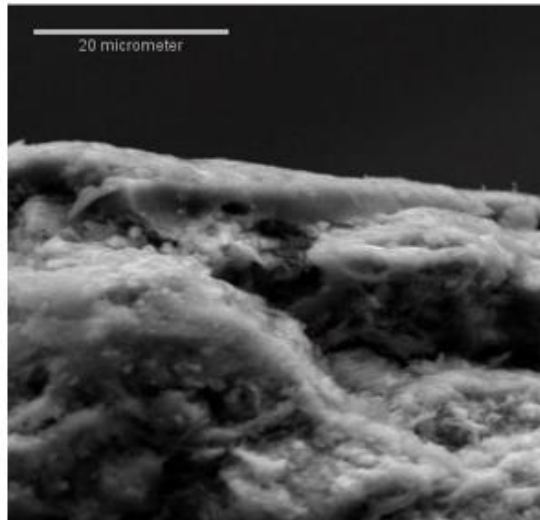


*Figure 67: Lem07 surface decoration 2000X, scale presents 20 micrometers, poorly bonded slip a) 1<sup>st</sup> surface, slipped, red decoration b) 2<sup>nd</sup> surface, slipped, red decoration*

a)

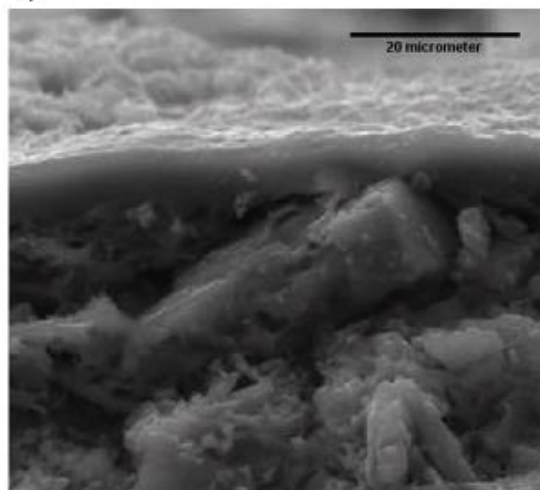


b)

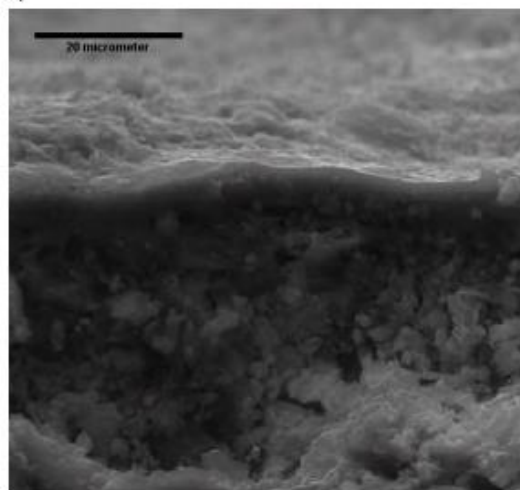


*Figure 68: a) Lem14 red surface decoration 2000X, scale presents 20 micrometers, slipped b) Lem16 black surface decoration 2000X, scale presents 20 micrometers, slipped.*

a)

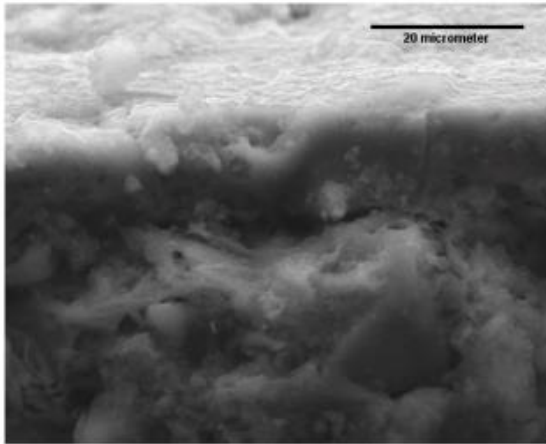


b)

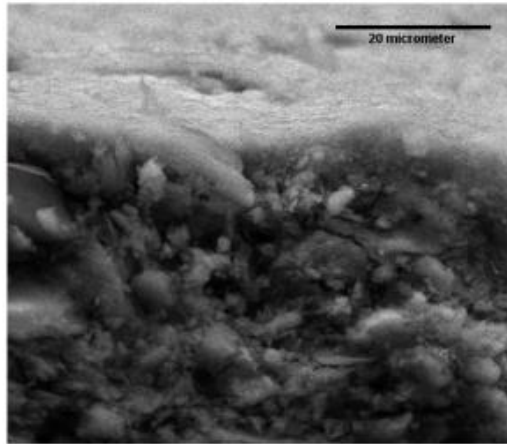


*Figure 69: Lem36 surface decoration 2000X, scale presents 20 micrometers a) 1<sup>st</sup> slipped surface, red decoration b) 2<sup>nd</sup> slipped surface, black decoration.*

a)

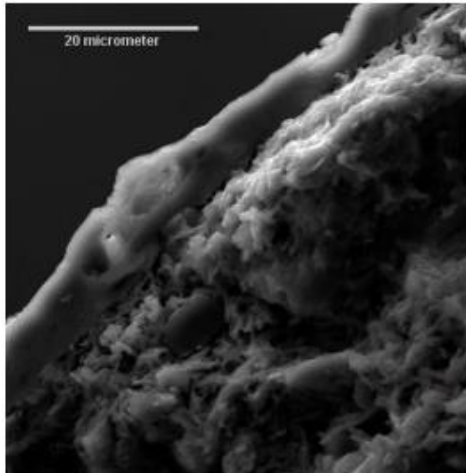


b)

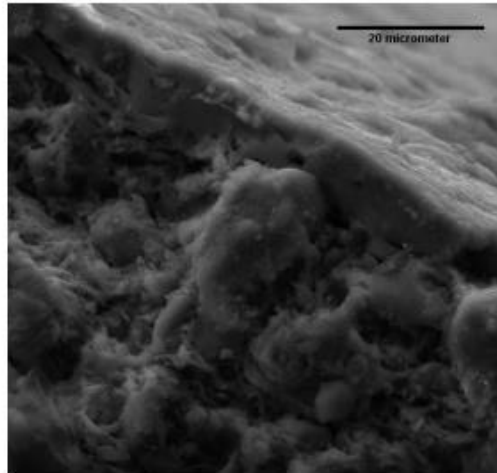


*Figure 70: a) Lem37 slipped, black surface decoration 2000X, scale presents 20 micrometers b) Lem41 slipped red surface decoration 2000X, scale presents 20 micrometers.*

a)

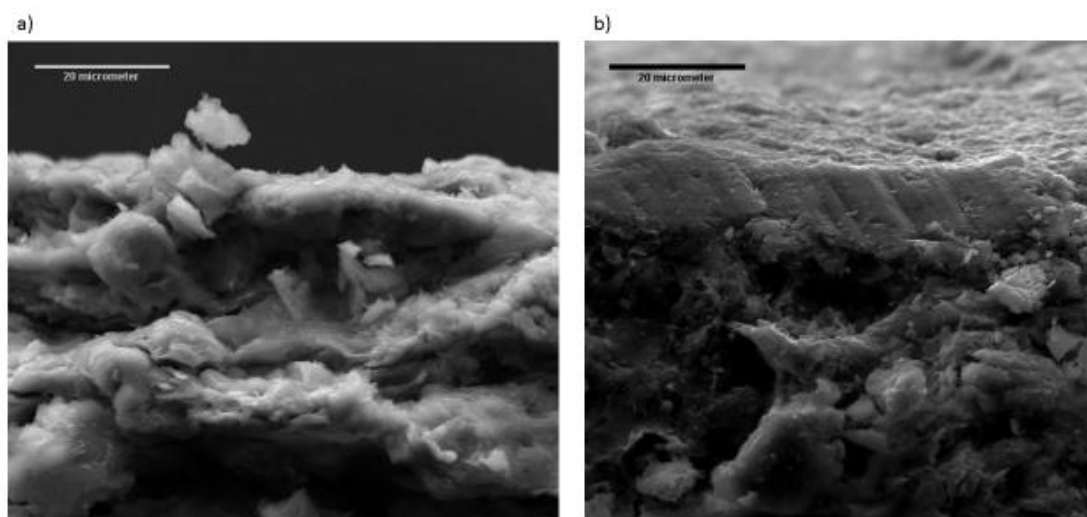


b)

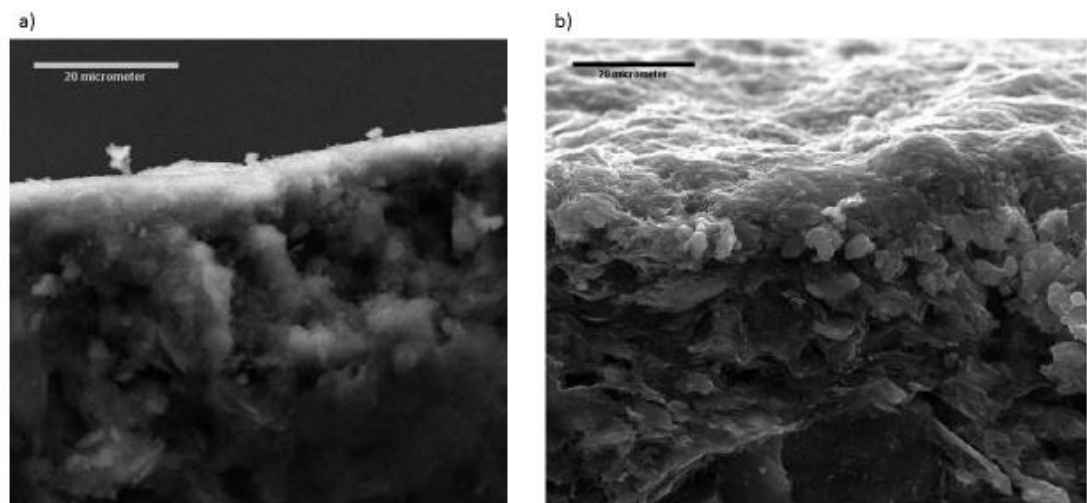


*Figure 71: Lem55 surface decoration 2000X, scale presents 20 micrometers a) internal slipped surface b) outer slipped surface.*





*Figure 72: Lem58 surface decoration 2000X, scale presents 20 micrometers a) 1<sup>st</sup> slipped surface, red decoration b) 2<sup>nd</sup> slipped surface, red decoration.*



*Figure 73: a) Lem59 slipped, red surface decoration 2000X, scale presents 20 micrometers b) Lem61 slipped, red surface decoration 2000X, scale presents 20 micrometers.*

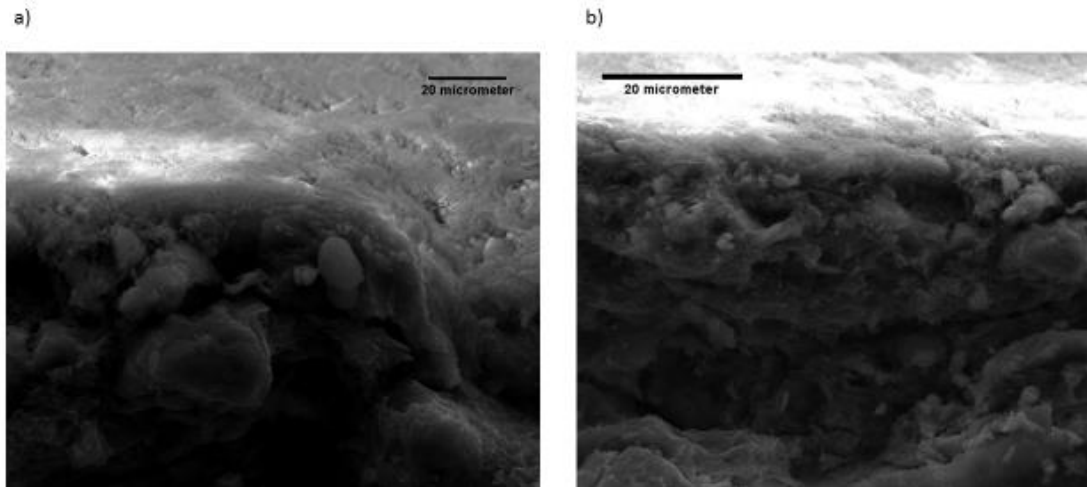


Figure 74: Lem62 surface decoration 2000X, scale presents 20 micrometers a) 1<sup>st</sup> slipped surface, red decoration b) 2<sup>nd</sup> slipped surface, red decoration.

Samples	Surface( $\mu\text{m}$ )	
Lem03	1st slipped surface	~15-8
	2nd slipped surface	~12-8
Lem07	1st slipped surface	~16-12
	2nd slipped surface	~10-8
Lem14	slipped on one side	~6-4
Lem16	slipped on one side	~8-6
Lem36	1st slipped surface	~6-4
	2nd slipped surface	~11-6
Lem37	slipped on one side	~20-15
Lem41	slipped on one side	~10-8
Lem55	1st slipped surface	~14-8
	2nd slipped surface	~18-13
Lem58	1st slipped surface	~8-5
	2nd slipped surface	~12-9
Lem59	slipped on one side	~8-5
Lem61	slipped on one side	~7-5
Lem62	1st slipped surface	~7-3
	2nd slipped surface	~8-4

Table 8: Approximate surface thicknesses of the decorated samples.

Samples	Body and Surface averages	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl <sub>2</sub> O	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>
Lem03	body average	0.3	3.0	14.9	50.3	0.4	0.3	0.2	3.4	16.0	1.0	0.2	0.2	0.4	9.4
	1st surface average	0.81	2.25	24.25	45.11	0.26	0.41	0.14	10.20	4.87	0.83	0.29	0.19	0.18	10.25
	2nd surface average	0.60	3.75	15.29	46.33	0.60	1.89	0.65	3.20	16.93	1.33	0.18	0.14	0.29	8.86
lem07	body average	0.2	4.4	17.0	48.5	0.2	0.2	0.1	2.5	15.3	1.2	0.1	0.1	0.3	9.7
	1st surface average	0.6	3.1	31.3	39.0	0.2	0.3	0.2	3.8	2.3	1.3	0.1	0.2	0.2	17.7
	2nd surface average	0.9	2.8	30.8	43.1	0.1	0.3	0.3	3.9	2.7	1.2	0.2	0.2	0.2	13.5
Lem14	body average	0.68	4.34	16.03	48.94	0.28	0.43	0.41	3.15	10.31	1.20	0.32	0.32	0.27	13.33
	surface average	1.0	2.3	25.8	48.2	0.5	0.2	0.2	6.7	3.3	1.1	0.3	0.3	0.3	10.0
Lem16	body average	1.19	3.01	16.23	53.63	0.29	0.41	0.32	3.90	9.67	1.21	0.25	0.24	0.33	9.34
	surface average	3.5	2.8	26.1	47.1	0.3	0.3	0.2	7.7	1.9	0.8	0.2	0.2	0.1	8.6
Lem36	body average	1.28	4.19	16.48	55.00	0.25	0.27	0.09	2.37	9.37	0.93	0.20	0.17	0.27	9.14
	1st surface average	1.5	3.1	28.5	46.0	0.2	0.0	0.0	4.7	2.6	1.1	0.2	0.2	0.2	11.8
	2nd surface average	2.43	3.25	24.57	47.45	0.75	0.47	0.06	2.73	7.69	0.73	0.08	0.10	0.14	9.56
Lem37	body average	1.20	3.13	16.05	52.10	0.37	0.13	0.10	3.15	11.13	1.20	0.24	0.18	0.32	10.70
	surface average	2.75	2.54	22.38	44.69	0.78	0.32	0.30	4.88	5.65	1.00	0.23	0.25	3.02	11.24
Lem41	body average	0.97	3.28	16.41	54.45	0.31	0.11	0.15	2.95	9.58	1.00	0.10	0.11	0.17	10.40
	slip average	0.5	3.4	24.2	45.9	0.4	0.5	0.6	4.5	3.8	1.7	0.2	0.2	0.2	14.0
Lem55	body average	1.1	2.7	15.0	55.5	0.3	0.3	0.2	2.3	12.7	1.0	0.2	0.2	0.3	8.2
	int. slip average	3.0	2.1	24.9	43.9	0.3	0.5	0.7	7.6	3.6	0.9	0.2	0.2	0.2	11.9
	out. slip average	3.1	1.9	23.5	44.2	0.2	0.7	0.4	6.2	6.5	1.1	0.3	0.3	0.3	11.2
Lem58	body average	1.50	2.74	17.45	62.33	0.14	0.24	0.10	2.80	1.77	1.04	0.00	0.26	0.21	9.45
	1st surface average	0.6	3.4	17.9	54.9	0.3	0.3	0.1	2.8	1.7	0.9	0.2	0.2	0.3	16.3
	2nd surface average	0.4	3.1	18.6	56.5	0.2	0.3	0.1	2.6	1.9	1.0	0.2	0.2	0.2	14.7
Lem59	body average	1.38	3.08	18.18	61.69	0.28	0.04	0.01	3.09	1.83	0.95	0.00	0.00	0.00	9.33
	slip average	1.2	2.6	19.4	57.0	0.3	0.4	0.4	4.5	3.7	0.7	0.2	0.1	0.1	9.3
Lem61	body average	1.1	2.9	15.7	61.2	0.2	0.2	0.1	2.8	5.2	1.1	0.2	0.2	0.3	8.8
	surface average	1.5	2.7	15.9	58.0	0.1	0.3	0.2	4.3	5.3	1.2	0.2	0.2	0.2	9.9
Lem62	body average	1.2	2.8	16.0	64.3	0.1	0.1	0.1	3.0	1.6	1.0	0.2	0.2	0.3	9.0
	1st surface average	1.2	3.1	18.5	54.7	0.9	0.3	0.2	2.6	1.8	1.5	0.1	0.0	0.2	14.7
	2nd surface average	0.8	2.8	19.3	58.3	0.5	0.4	0.3	3.7	2.1	0.9	0.3	0.3	0.2	10.0

Table.9: SEM-EDS Elemental composition comparisons of the ceramic bodies and surfaces for each decorated samples (in wt%) (Standard deviations are presented for ceramic bodies in Table 5 and Table 6 for surfaces in the thesis.

## 6. Conclusion:

Mycenaean pottery technology generally includes a paste prepared with refined calcareous clay, a potter's wheel as a shaping method, surface treatments such as smoothing or polishing and coloring usually with an iron-rich slip. The firing techniques applied for the production of Mycenaean pottery was oxidation, and/or an oxidizing-reducing-oxidizing alternating atmosphere, in updraft kilns that could have controlled atmosphere conditions.

The analysis conducted in this research revealed that all of the pottery samples except the local Koukonisi pottery (Lem58, Lem59, Lem61, Lem62) showed the same technological characteristics described above with fine, homogeneous fabrics. These samples are Lem03, Lem06, Lem11, Lem14, Lem16, Lem18, Lem27, Lem28, Lem29, Lem36, Lem37, Lem41, Lem45, Lem53, Lem55. From these samples, only Lem03, Lem07, Lem14, Lem16, Lem36, Lem37, Lem41 and Lem55 had surface coloring with iron rich calcareous slips. Local samples Lem58, Lem59, Lem61 and Lem62 had low to non-calcareous bodies and the surface coloring was made with iron-rich slips, although the clay used for the slips were non-calcareous and a possible ochre addition was identified. Considering the slipped samples, surface thicknesses did not show a unified picture and were not consistent (**Table 8**).

Observation of the microstructures and vitrification levels revealed six vitrification patterns as NV, IV, IV+, V, V+ and CV and possible maximum firing temperatures ranging from <800 °C to 1050 °C were assigned according to these characteristics and CaO concentrations within the ceramic bodies. According to the color of the ceramic bodies and surface decorations made with iron-rich slips, firing atmospheres were assigned as oxidation or three staged O-R-O technique (**Table 7**). An important result reached from these information is that apart from local pottery samples Lem58, Lem59, Lem61 and Lem62, all of the samples were fired in updraft kilns that would allow the control of the atmosphere conditions. However, Lem61 and Lem62 showed fast firing characteristics, darker core and red slipped surface. This could be an indication of a non-kiln firing.

In general, four different patterns were observed for the surface decorations (**Figure 65a and 65b**). Comparison of these patterns with the chemical groups indicates that some samples

belonging to different chemical groups also exhibited the same technological patterns and moreover, they revealed some relationship between Troia, the Argolid and Koukonisi.

For example, the results indicate that local pottery is produced with slightly differing surface technology patterns even though they all have red slipped surfaces. Moreover, according to the comparison of technological patterns with the chemical groupings identified with NAA, it was possible to say that Lem36 and Lem41 are similar to the A-Troy Argolid imports along with Lem07, or alternatively they could be more local Mycenaean imitations from Troy. These findings suggested that Koukonisi was subjected to Mycenaean influence and even though the local materials used for the pottery production was different than Mycenaean pastes, and the firing structure was not advanced like updraft kilns, iron-rich slipped surfaces with oxidized firing that made a red surface color indicated the Mycenaean influence in the area but without a local Mycenaean center of production.

Apart from the analytical results, this research showed that SEM-EDS analysis was useful for the identification of many characteristics of pottery production and was a beneficial supplementary method for the NAA analysis, with results that could not have been achieved from NAA alone. Identification of the technological characteristics for both local Koukonisi pottery and Mycenaean pottery imported from Argolid enables further discussions on agency and movement concepts. In the future these results, in collaboration with those obtained via petrographical and mineralogical analyses, can be interrogated using social theory to examine the reasons why pottery from Mycenae might be imitated in Troia and on Lemnos, areas on the periphery of the Mycenaean core cultural zone, and what that would mean in terms of the spread of technology, ideas, and people throughout the Late Helladic world.

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