MATERIAL CHARACTERIZATION OF THE LATE 12th-13th CENTURY BYZANTINE CERAMICS FROM KUŞADASI KADIKALESİ/ANAIA

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submitted by **BURCU KIRMIZI** in partial fulfillment of the requirements for the degree of **Doctor of Philosophy in Archaeometry Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Ümit Atalay
Head of Department, **Archaeometry**

Prof. Dr. E.Hale Göktürk
Supervisor, **Chemistry Dept., METU**

Prof. Dr. Asuman G.Türkmenoğlu
Co-supervisor, **Geological Engineering Dept., METU**

Examining Committee Members:

Prof. Dr. Emine Caner Saltık
Architecture Dept., METU

Prof. Dr. E.Hale Göktürk
Chemistry Dept., METU

Prof. Dr. Ömür Bakırer
Architecture Dept., METU

Prof. Dr. Mürvet Volkan
Chemistry Dept., METU

Assoc. Prof. Dr. Kenan Bilici
Art History Dept., Ankara University

Date: 24 January 2012

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Burcu Kırmızı

Signature :

ABSTRACT

MATERIAL CHARACTERIZATION OF THE LATE 12th-13th CENTURY BYZANTINE CERAMICS FROM KUŞADASI KADIKALESİ/ANAIA

KIRMIZI, Burcu

Ph.D., Department of Archaeometry
Supervisor: Prof. Dr. E. Hale GÖKTÜRK
Co-supervisor: Prof.Dr. Asuman G.TÜRKMENOĞLU
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This study investigates the petrographical and chemical characteristics of a group of *Zeuxippus Ware Related Ceramics* dating to the late 12th-13th centuries from Kuşadası Kadıkalesi/Anaia. Kadıkalesi was a Byzantine fortress at the coast of Aegean Sea. It was also a significant commercial port and an episcopacy center during the 13th century.

In this study, visual classifications of the ceramics were carried out based on their stylistic properties. Then, ceramic samples were investigated by several methods including mineralogical, micromorphological, chemical (SEM-EDX, ICP-OES, ICP-MS) and Raman Spectrometry techniques and further evaluated by statistical analyses. Bodies are found to be rich in SiO_2 and Al_2O_3 while relatively high amounts of Fe_2O_3 measured, agree well with their reddish bodies. These bodies mostly display micaceous matrix with a relatively low degree of vitrification. Cluster analysis performed among thirty selected samples, points out the presence of two main groups. Observed slip layers are also found to be rich in SiO_2 and Al_2O_3 contents and exhibit various types of crystalline and/or vitreous matrix. Glazes are found to be high lead glazes processed at or below. The glazes are found to be high lead glazes processed at or below 700°C as confirmed by SEM-EDX and Raman spectrometry investigations. Iron compounds are the major coloring agents for most of the glazes analyzed regardless of their observed colors. Presence of Raman peaks in some yellow glazes which may be assigned to a solid solution of *Naples yellow* type of pigment is significant since its use in the Byzantine period as a glaze pigment has been scarcely reported before.

Keywords: Kuşadası Kadıkalesi/Anaia, Byzantine ceramics, *Zeuxippus Ware*, Raman spectrometry, *Naples yellow*

ÖZ

KUŞADASI KADIKALESİ/ANAIA'DA BULUNAN GEÇ 12.-13.YÜZYIL BİZANS SERAMİKLERİNİN MALZEME KARAKTERİZASYONU

KIRMIZI, Burcu

Doktora, Arkeometri Bölümü
Tez Yöneticisi: Prof. Dr. E. Hale GÖKTÜRK
Ortak Tez Yöneticisi: Prof. Dr. Asuman G.TÜRKMENOĞLU
Ocak 2012, 215 sayfa

Bu çalışmada, Kuşadası Kadıkalesi/Anaia'da bulunan Geç 12. ile 13. yüzyıllara tarihlendirilen bir grup *Zeuxippus Seramiği* ile ilişkili seramiklerin petrografik ve kimyasal özellikleri araştırılmıştır. Kadıkalesi Ege Denizi kıyısında bulunan bir Bizans kalesidir. Ayrıca 13. yüzyılda önemli bir ticari liman ve piskoposluk merkeziydi.

Bu çalışmada, seramiklerin görsel sınıflandırmaları stilistik özelliklerine dayanarak gerçekleştirilmiştir. Sonra, seramik örnekleri mineralojik, mikromorfolojik, kimyasal (SEM-EDX, ICP-OES, ICP-MS) ve Raman spektrometri tekniklerini içeren çeşitli metodlarla incelenmiş ve istatistik analizlerle değerlendirilmiştir. Hamurlar SiO_2 ve Al_2O_3 açısından zengin olarak bulunmuştur. Görece yüksek olarak ölçülen Fe_2O_3 içerikleri de hamurların kırmızı renkli görünümüyle uyumludur. Bu hamurlar çoğunlukla görece düşük bir camlaşma derecesiyle birlikte mikalı bir matriks sergilemektedirler. Seçilmiş otuz örnek üzerinde yapılan kümeleme analizi iki temel grubun varlığını işaret etmektedir. Gözlenen astar tabakaları da SiO_2 ve Al_2O_3 içeriği açısından zengin bulunmuştur ve kristalen ve/veya camsı olarak çeşitli matriks tipleri sergilemektedirler. SEM-EDX ve Raman spektrometri incelemelerine dayanarak, sırlar 700°C veya altında pişirilmiş yüksek kurşunlu sırlardır. Demir bileşikleri gözlenen renkten bağımsız olarak, analizi yapılan birçok sır için ana renklendirme ajanlarıdır. Bazı sarı sırlarda *Nepal Sarısı* tipindeki pigmentin katı çözeltilerine atfedilebilecek Raman piklerine rastlanması önemlidir çünkü bu tip pigmentin sır pigmenti olarak Bizans dönemindeki kullanımı daha önce çok az bildirilmiştir.

Anahtar Sözcükler: Kuşadası Kadıkalesi/Anaia, Bizans seramikleri, *Zeuxippus Seramiği*, Raman spektrometri, *Nepal sarısı*

To my parents

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INTRODUCTION

1.1 Kuşadası Kadıkalesi/Anaia

1.1.1 Location and Historical Background

Kadıkalesi is a Byzantine fortress, located at about 8 km south of Kuşadası district of Aydın, in Western Anatolia region of Turkey. It is situated at the northwest of Davutlar locality, which is today a holiday resort, facing one of the longest beaches in the Aegean region. The geographical location of Kadıkalesi is significant as it could serve as a control point for the Sisam (Samos) Channel (Figure 1.1). Kadıkalesi was associated with the ancient city of Anaia which was a significant commercial port and an episcopacy center within the metropolite of Ephesos during the 13th century (Foss 1979, p.124; Mercangöz 2009).

Anaia had fertile lands in its environs which made this area suitable for agriculture. At the beginning of the 13th century, Anaia held the status of being an *emporion* and *kommerkion* which shows that it was a trade center and customs gate (Foss 1979, p.124; Mercangöz 2010). With the conclusion of the "Nymphaion treaty" in 1261, the Genoese merchants were granted privilege in the Byzantine territory where Anaia was also included (Jacoby 2010). As a result, they had settled down in Anaia, establishing small colonies and continued their commercial activities on a convenient basis.

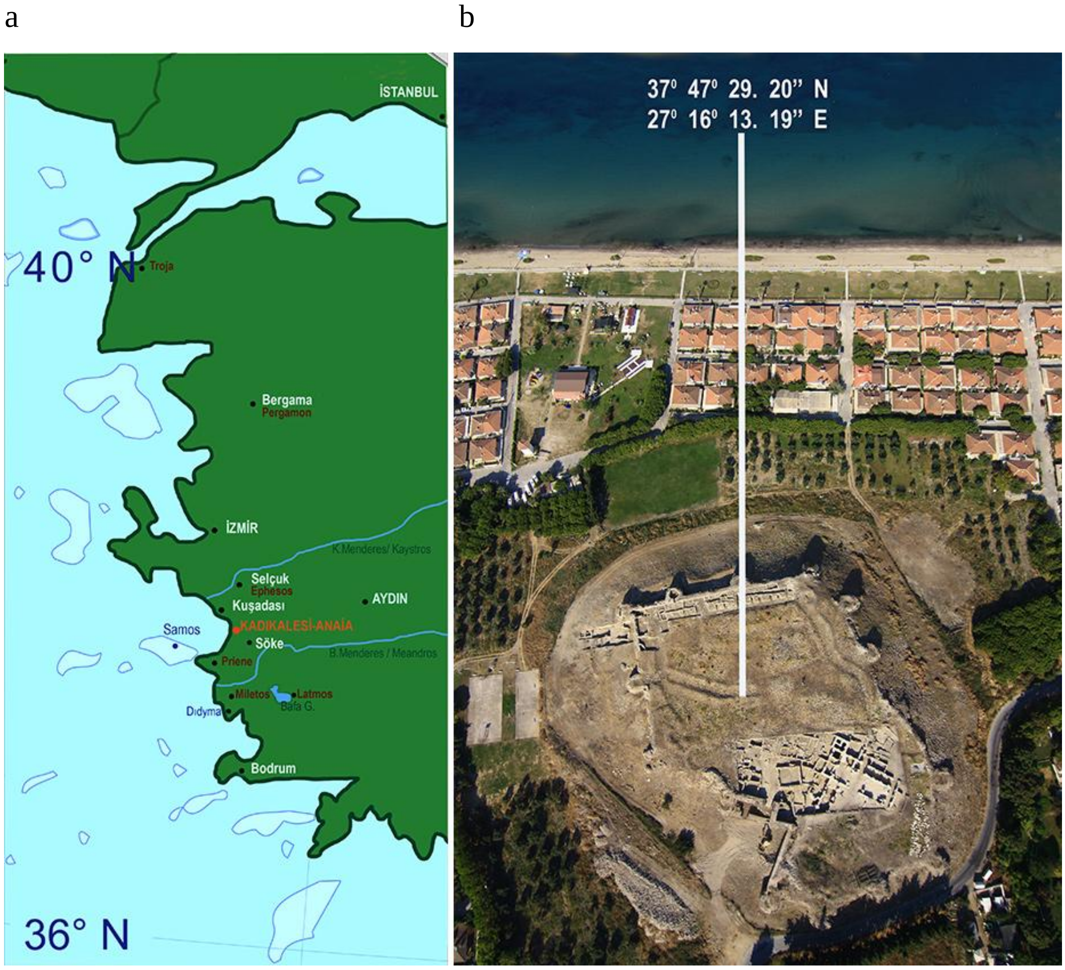


Figure 1.1: a) Geographical location of Kuşadası Kadıkalesi, b) Bird’s eye view of Kadıkalesi (http://www.kadikalesianaia.org/cogkonum.html, last accessed date: May 2011)

Kadıkalesi is located on a prehistoric mound dating back to the 2nd millenium B.C. (Akdeniz 2006) (Figure 1.2). It is now considered that the construction of Kadıkalesi was probably during the 13th century when the limited information about its history and architectural features are taken into account (Mercangöz 2010). It was most probably built for the defense of the ancient city of Anaia (Foss 1979, p. 125). Besides its defensive character, the rich variety of finds in the fortress showed that it also had incorporated several workshops of ceramics, glass, metal and bones. Additionally, the finds such as moulds for earrings and icons suggest the diversity of craftsmanship that existed in Kadıkalesi (Mercangöz 2007, 2010).

Kadıkalesi was captured by the Turks in the early 1300s and then passed onto the Aydınoğulları Principality during the 14th century. It was then taken under the rule of the Ottomans in the beginning of the 15th century (Doğer 2004).

a

b

c

Figure 1.2: Photos of Kuşadası Kadıkalesi/ Anaia

a. General view of Kadıkalesi fortress situated on a prehistoric mound (http://www.kadikalesianaia.org/fotogaleri.html, last accessed date: December 2011).

b-c. General views of Kadıkalesi/Anaia at the excavation campaign in 2008.

1.1.2 The Surveys and Excavation in Kuşadası Kadıkalesi/Anaia

The earliest survey in Kadıkalesi was carried out by T.Wiegand and H.Schrader in 1904. In the later years, several publications about the archaeology of Western Anatolia region done by Müller-Wiener (1961) and Foss (1979), also give information about Kadıkalesi.

The present excavations in Kadıkalesi were initiated in 2001 by Prof. Dr. Zeynep Mercangöz from Ege University together with Emin Yener, the director of Aydın Museum (Mercangöz 2003). The campaigns directed by Z. Mercangöz since then have led to significant finds from the Late Byzantine period which made great contribution to Byzantine archaeology in Western Anatolia and in the Aegean regions. At present, there are two main excavation areas in Kadıkalesi, the first one is mainly located at the entrance gate in the east within the walls (Sector I) and the second area is located outside the walls in the south (Sector II) and in the west (Sector III) (Figure 1.3). The first excavation area embraces an outer gate and an entrance courtyard, advancing towards the inside of the fortress. Structures such as a small mosque (mescit) and a complex of church-monastery were also revealed in this area. This complex is considered to have been occupied during the 11th century and beyond. Within the grid squares located in the south and west of the fortress entrance, rich finds revealed suggest the presence of workshops producing pottery, glass and metal objects (Mercangöz 2009, 2010).

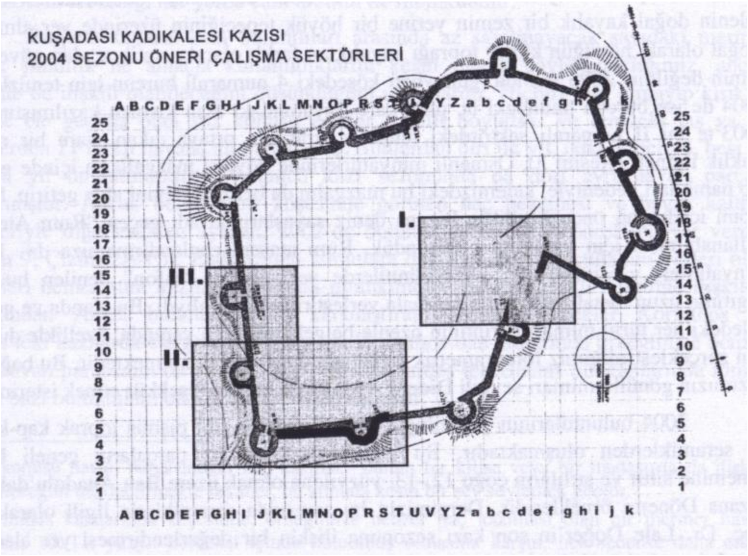


Figure 1.3: Map of Kuşadası Kadıkalesi/Anaia excavation sectors (I, II and III) (Mercangöz 2005).

1.2 An Introduction to Ceramics and Ceramic Making

The term “ceramic” derives from the Greek “keramos” that can be translated as “burned material” or “earthenware”. Ceramic production is the earliest technology of the mankind with its origins going back as early as 30000 B.C. (Zimmermann and Huxtable 1971). However, the Neolithic period was the period when an increase and dissemination in ceramic making throughout the world had occurred, with the nomadic societies transforming into the sedentary communities (Arnold 1985).

Classification of Ceramics

From the archaeological point of view, ceramics encompass cooking, serving and storage utensils or tiles used for architectural purposes. The term “pottery” very broadly refers to the cooking and storage vessels, tableware of terracotta, earthenware (glazed and unglazed), stoneware and porcelain (Rice 1987, p.5) whereas the term “ceramics” might also be used for the same purpose (especially for the fine glazed ware).

Prehistorical, historical and modern pottery and ceramics are classified according to their composition, firing conditions and surface treatments (Norton 1970). The first group is the terracottas. They are porous, low fired and unvitrified ceramics fired usually less than 900°C, with no glazes. But, they may display various surface treatments such as roughening and slipping. Earthenwares are also porous and unvitrified bodies but they may be fired at higher temperatures than those of terracottas at about 900°C. They may be glazed or unglazed (Rice 1987, p.5). The type of clay used in the manufacture of earthenware is generally coarse, plastic clay which gets red due to firing. Earthenwares consist of a wide range of products, ranging from coarse types such as bricks and tiles, to fine types such as wall tiles and maiolica vessels with tin glazes (Herz and Garrison 1998, p.249). Stonewares are fired at high temperatures of 1200-1350°C, causing the partial fusion and vitrification of the clay body. The body is gray or light brown, has medium to coarse grains and shows opacity. Modern stonewares are manufactured from sedimentary clays like ball clays which are highly plastic and low in iron content. Archaeological stonewares can be either glazed or unglazed (Rhodes 1973, p.20-21; Herz and Garrison 1998, p.249). Porcelains exhibit the most advanced technique of fine pottery, with the firing temperatures of 1300-1400°C or even higher. Kaolin which is a highly refractory clay, used in their preparation gives the product its translucency, vitreous characteristics, hardness and characteristic sound of knocking (Rice 1987, p.6).

General Techniques in Pottery Making

Pottery making is basically carried out by several techniques like pinching and/or drawing, slab modeling, molding, coiling and throwing. Sometimes, more than one technique can be used for the making of a single vessel (Rice 1987, p.124). The pinching method is a hand-building technique, which is suitable for small vessels. It involves pinching the clay ball all around with the fingers of one hand while it is being revolved in the palm of the other. The slab method is also a hand-building technique, which suits well to the making of geometric shapes. The rolled slabs of clay are joined together to form the vessel (Rice 1987, p.124-125).

In molding, the clay is pressed into a form using concave or convex molds. It has the advantage of speeding up the production (Shepard 1971, p.63). The molds may form the entire body or parts of the body. They are usually made from plaster of paris or fired clay. Parting agents such as powdered clay, ash, manure, pumice or fine sand are applied to seperate the ceramic from the mold more easily (Rice 1987, p.125).

Coiling is a common hand-building method of forming the vessel with superimposed rolls of clay. It is also a suitable method for the construction of very large vessels (Shepard 1971, p.57).

Throwing on the potter’s wheel is a common method, which has been developed since prehistoric times. The so-called kick wheel is a heavy and complex mechanism which is usually involved in large-scale workshop production. Clay which is softer and wetter than that used in hand-building, for facilitating the shaping process and coping with the drying caused by the air circulation during rotation is placed in the centre of the wheel. It also has usually finer texture to prevent the additional abrasion caused by hands. The clay paste first is opened, by inserting the thumbs into the centre while it is being rotated. The shape is given by pressing the paste upward with one hand and drawing the exterior upward and outward with the other. When the vessel is finished, it is cut from the wheel with a wire or thread. Wheel-thrown pottery exhibits rilling marks which are rhythmic lines, spiraling around the walls of the vessels (Rice 1987, p.128-129).

Raw Materials Used in Ceramic Production

Ceramics in general consist of three layers: body, slip and glaze.

Body: Raw materials used in ceramic bodies are mainly clays and fillers or tempers such as silica and fluxes (Table 1.1). Clays are hydrous alumino-silicates having a fine particle size, constituting the backbone of the ceramics. Silica (SiO_2) in the form of sand or flint, is very abundant on the earth while it is also common in the form of quartz crystals in all types of rocks. Silica is added to ceramic bodies to reduce the drying shrinkage, thus to prevent cracking of the body, to reduce the firing shrinkage and to constitute the skeleton of the ceramic body. Another important constituent of the ceramic bodies is fluxes. Fluxes allow the vitrification process by decreasing the melting point. This vitrification gives strength and hardness to the ceramic body. One of the fluxing materials (agent) is feldspars which are anhydrous alumino-silicates mostly containing potassium, sodium and calcium. Other fluxes such as nepheline-syenite, limestone and magnesite are also used in ceramic bodies (Norton 1956, p.142).

Slip: Properties of ceramics may be enhanced either by roughening the surfaces by beating with a cord or smoothing them by covering with slips. Roughening provides the surface the ability to absorb heat and decreases the sliding when wet. Slips which are solutions of fine-grained clay and water are applied to the surface to reduce the porosity and prevent the leaking, before the firing process. They have generally a different colour than the body. A slip consists of fine-grained clays, fluxes, fillers such as silica, hardeners like borax, as well as opacifiers and colorants (Rhodes 1973, p.251). A slip should adhere well to the body. The coefficients of expansion of the body and slip should be the same for preventing the defects such as peeling or crazing. A slip should also get hardened within the same temperature range as the body. Finally, a slip should have enough consistency to cover the entire surface of the body. The consistency of the slip is related to the type of clay mineral used, its particle-size range, adsorbed ions and degree of dispersion (Shepard 1971, p.67-68). They are applied to the leather hard bodies of ceramics by one of the following techniques: dipping in the slip, pouring the slip, wiping the pottery with slip and applying with a brush (Rice 1987, p.150).

Glaze: A glaze is a thin coating of glassy substance, applied directly on the body or the slip of vessels. It is applied for similar reasons as the slips, for giving texture, decorating and providing the impermeability. The main constituents of a glaze are acidic oxides which are the glass forming materials like silica, the stabilizing materials which make up the body of the glaze and fluxes which make the glaze melt (Cooper 2004, p.11) (Table 1.1). Stabilizing materials have the functions of increasing the viscosity of the glaze and giving strength by reducing the defects during the firing process. The main stabilizing materials are aluminum oxide, lead oxide, calcium oxide, zinc oxide, zirconium oxide and cadmium oxide. Fluxes include potassium oxide, sodium oxide, lead oxide, magnesium oxide and boric oxide (borax) which lower the very high melting point of silica (1710°C). Some of these oxides may serve both as stabilisers and as fluxes (Parmelee 1973; Rice 1987, p.99).

The glaze materials are usually applied in the form of finely ground powders (Cooper 2004, p.11). They are made either from raw materials or from frits. Frits are actually pre-melted glazes of silica and a flux melted together, cooled and then ground into a powder before adding to the glaze mixture. They may be applied directly by various techniques such as dipping, pouring, splashing, painting and spraying (Parmelee 1973, p.139; Rice 1987, p.100) on the unfired body of the vessel or after the first firing, so-called “biscuit firing” of the body. After the application of glaze, the vessel is subjected to a second firing.

Temperature of this firing may be the same with the biscuit firing, higher or lower (Rice 1987, p.99).

Various metallic oxides such as the oxides of iron, copper, manganese, cobalt and chromium are added as colorants to the glaze. They can also be used for underglaze painting. The combinations of these oxides are made to obtain the full range of colours. The metallic oxides are mixed with a flux to make them sinter and a refractory material such as flint to prevent running under the glaze. The very fine powder of this material mixed with water or other type of media to provide the desired consistency is applied thinly either by brushing or spraying on the raw or fired body of the vessel or on the slip of the vessel. Then, they are covered with a transparent glaze. The kind of glaze applied over the underglaze pigments, the firing temperature and the atmospheric conditions influence the final colour (Rhodes 1973, p.255-256).

Organic materials can also be added as binders to strengthen the raw glaze (Parmelee 1973, p.589). Knapp (1954) classifies them in four groups: a) alcohols and cellulose derivatives, b) sugars, starches and flours, c) gums, d) wax emulsions.

Table 1.1: Raw materials used in ceramic production (Norton 1956; Parmelee 1973; Kerr 1977, p.285; Rice 1987; Moore and Reynolds 1989, p.131).

Body and Slip Materials	**Glaze Materials**
Clays: 1-Serpentine-kaolin 2- Talc-pyrophyllite 3- Smectite 4-Vermiculite 5- İllite 6- Mica 7- Brittle mica 8- Chlorite 9- Sepiolite-palygorskite	**Stabilising materials:** a.Aluminum oxide b.Lead oxide c.Calcium oxide d.Zinc oxide e.Zirconium oxide f.Cadmium oxide
Silica: Macrocrystalline forms: sandstone, ganister, quartzite Cryptocrystalline forms: chert, flint, chalcedony Hydrated forms: opal	
Fluxes: 1-Feldspars a.Alkali-feldspars: microcline, orthoclase, sanidine b. Plagioclases: albite, anorthite, andesine 2- Nepheline-syenite 3-Limestone, calcite, sea-shells, gypsum, magnesite	**Fluxes:** a.Potassium oxide b.Sodium oxide c. Lead oxide d. Magnesium oxide e. Borax
	Colorants: a.Iron oxide b.Copper oxide c.Manganese oxide d.Cobalt oxide e.Chromium oxide

1.3 An Overview of Byzantine Pottery Production

1.3.1 Ceramic Types in the Byzantine Empire

Byzantine Empire (330-1453) had an influential control on many aspects throughout Asia Minor and the whole Mediterranean under the reign of Justinian I (527-565) as a continuum of the long-lasting Roman Empire (Figure 1.4). The Byzantines produced ceramics in large scales, including a great variety of pottery both glazed and unglazed as well as glazed tiles for architectural purpose.

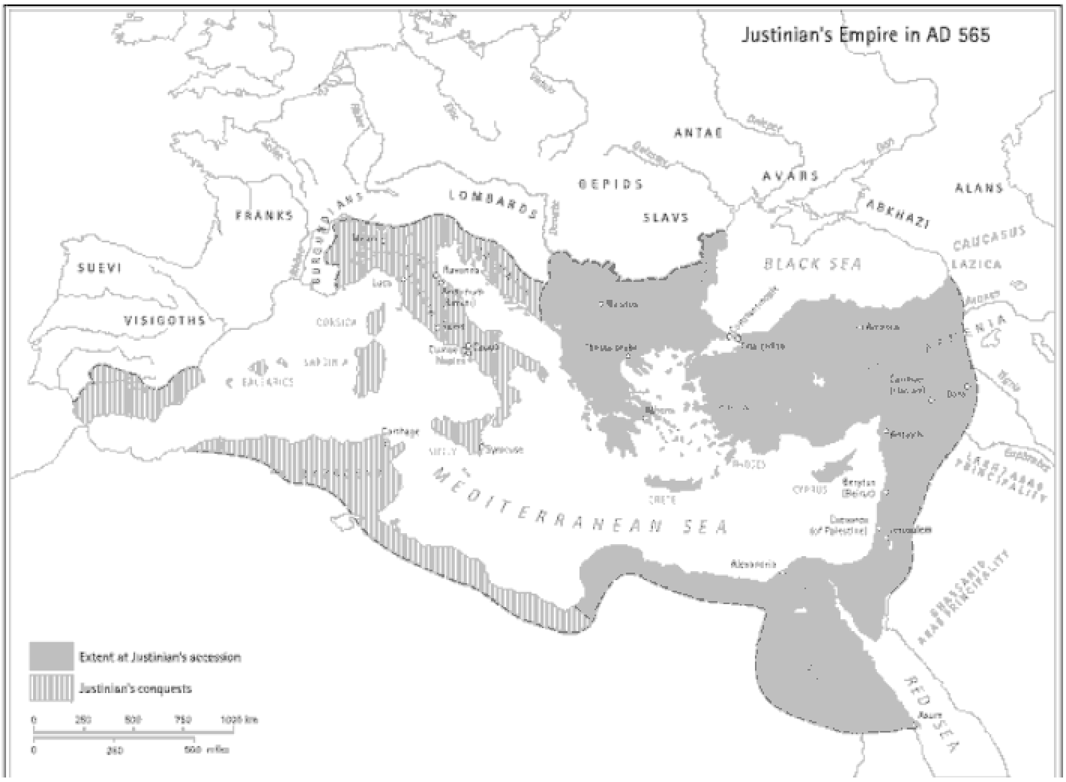


Figure 1.4: Map of the Byzantine Empire in the 6th century (Haldon 2008, p.251).

Byzantine pottery can be roughly classified into five categories on the basis of functional purpose: 1-cooking pots, 2-storage vessels, 3-amphorae, 4-tableware, 5-architectural bowls. The first three classes are the unglazed pottery types. Cooking pots displayed open or closed forms and had a highly durable body in order to resist the high temperature while cooking and to conduct heat to their contents evenly. Storage vessels which had both open and closed forms, were used in households mainly for the storage of wheat, flour, wine and oil. The closed ones are given a particular name “pithoi” (Armstrong 2008). Production of amphorae was a well-established industry during the Roman period, used in long distance trade and this tradition had also continued throughout the Byzantine period (Dark 2001, p.37). They were mainly used for the transportation of materials such as wine and olive oil. Tableware whether glazed or unglazed had also open and closed forms. Open forms included plates, dishes (chafing) and bowls which were mostly glazed. Closed forms included jugs and cups etc. which were either glazed or unglazed. Tableware type of pottery has attracted more attention of the researchers due to their colorful glaze decorations. The last group of pottery is the least encountered one, in the form of bowls being placed into the masonry on the exterior facades of churches (Maguire and Maguire 1992). These bowls are called as *bacini* which are mainly found in religious buildings located in Greece and Italy (Berti and Gelichi 1997; Vroom 2007).

Glazes used by the Byzantine potters were mostly high lead glazes which had been widely used throughout Europe and the Near East (Tite et al. 1998) since the Hellenistic period (Greene 2007) (for a detailed discussion see section 1.3.2).

Red Slip Ware

Between the 4th and 7th centuries, the Roman ceramic tradition had continued throughout the Byzantine Empire in the form of *Red Slip Ware* with impressed (stamped) decoration and additional motifs in the decoration repertoire other than those of the Roman types, which are related to Christian symbolism (Doğer 2007).

Glazed White Ware

During the 7th century, glazed wares emerged in the capital Constantinople (İstanbul) and started to be distributed to Anatolia and Greece (Dark 2001, p.63; Doğer 2010). Well stratified data for the earliest Byzantine glazed pottery comes from the Saraçhane excavations in İstanbul (Hayes 1992, p.12-34). The most characteristic production of this earlier phase of Byzantine glazed pottery is the *Glazed White Ware* which had white or pink-colored fabric decorated with painted, incised or impressed designs and covered with green, yellow and brown-colored glazes. Constantinople is assumed to be the main production center for the *Glazed White Ware* from the 8th to 12th centuries. The distribution area of this ware covers Western Anatolia, Greece, the Balkans, Cyprus as well as Crimea (Dark 2001, p.121). However, there were other production centers for this type of ware such as Corinth (Southern Greece) (Sanders 2003) and Nicaea (İznik) (François 1997a).

Polychrome White Ware

Dating from the late 9th century onwards, *Polychrome White Ware* was being produced in Constantinople as the most elaborate and finest type of white ware. This ware is characterized mainly by geometric or floral designs painted underglaze in various colors and covered with transparent, yellow or green glazes. It also had a distinctive and studious character as being the only gilded type of Byzantine pottery where powders or leafs of gold were applied to the surface before glazing. It was distributed through the Byzantine Empire to a great extent. Other production centers include Sparta, Corinth and Bulgaria after the 11th century (Morgan 1942; Dark 2001, p. 64,123-124; Doğer 2010). Besides the production of tablewares, tiles were also produced in the same manner as *Polychrome White Ware* from the second half of the 9th century to the 11th century (Talbot Rice 1954; Mason and Mango 1995). The production centers for polychrome tiles are not well confirmed since there is not enough direct evidence for the location of tile workshops. However, factories of polychrome ware were found at Preslav in Bulgaria which might also have been served for the production of tiles in the same region (Akrabova-Zhandova 1955) and there is also some evidence like the wasters found at Kalenderhane Camii in İstanbul (Megaw and Jones 1983).

Sgraffito Ware

Towards the end of the 11th century, red fabrics had started to take place of white fabrics for the production of glazed pottery through the whole Empire and had dominated till the end of the Byzantine period (Doğer 2010). The emergence of "sgraffito" decoration, that is the scraping of the slip layer over the body by the use of a fine tool, was a significant innovation in the development of later Byzantine pottery (Dark 2001, p.65). The term of "sgraffito" refers to all applications of removing the slip such as scratching, incision and deep-carving *(champlevé)* (Doğer 2010).

The earlier phase of sgraffito-decorated pottery implies *Duochrome Sgraffito Ware* which had different colored glazes on two sides of the same vessel as yellow, green or brown and was characteristic of the 11th century productions. From the 12th century onwards, *Fine Sgraffito Ware* had appeared with the use of a single glaze either with tones of yellow and green and decorations of geometric, animal and pseudo-Kufic motifs (Kufic: angular type of Arabic script) (Figure 1.5a). In fact, *Duochrome Sgraffito Ware* and *Fine Sgraffito Ware* are considered as identical productions with the difference of the use of a single-colored glaze for the latter. The distribution area of *Fine Sgraffito Ware* covers Constantinople, Anatolia, the Black Sea coast of the Balkans, Crimea, Cyprus, Greece, Italy as well as the Crusader sites of the Palestine. Another type of sgraffito pottery during the 12th century is *Incised Sgraffito Ware* where broader removal of the slip was carried out with the use of a gouge. It also displays different types of designs than *Fine Sgraffito Ware.* The distribution area includes Constantinople region, Anatolia, the Balkans, Crimea, Cyprus and Greece (Dark 2001, p.65-67, 130-132). A distinctive class of *Incised Sgraffito Ware* is named as *Aegean Ware* by A.H.S. Megaw (1975) according to the excavations of Saranda Kolonnes at Paphos in Cyprus. *Aegean Ware* is characterized by a pale yellow or a green glaze and sometimes green splashes on the yellow glaze with bowl shapes and some specific designs, dating to the late 12th century and the early 13th century (Figure 1.5b). Another variant of *Incised Sgraffito Ware* is *Elaborate Incised Ware* which displays incised intricate designs covered with a green or yellow glaze, later painted with another darker tone of glaze. This ware was not very common and found only in Constantinople (İstanbul) and Thessaloniki (Selanik). *Champlevé Ware* was another 12th century innovation displaying larger portions of slip removal and may be linked to again *Incised Sgraffito Ware.* During the 12th century, another distinctive group of glazed pottery named as *Measles Ware* with red-slip painted dots outlined in sgraffito was possibly produced in Corinth (Dark 2001, p.67-70, 126, 134).

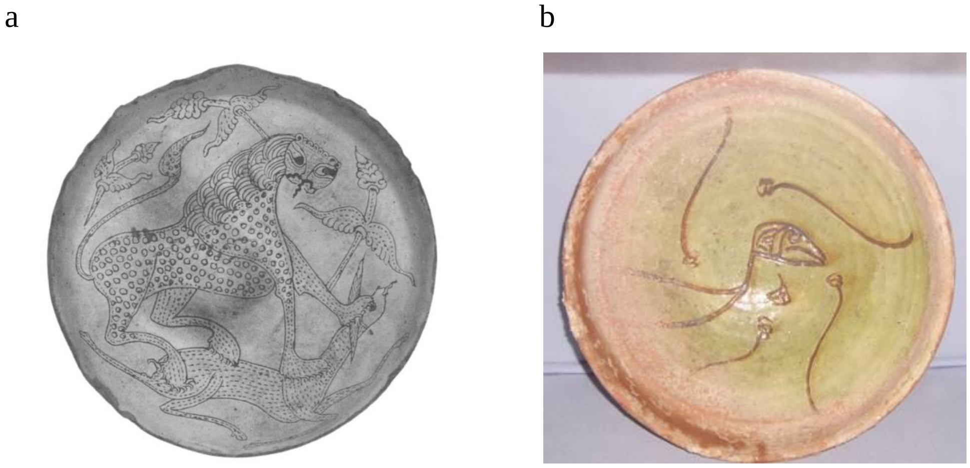


Figure 1.5: Types of *Sgraffito Ware*, a) *Fine Sgraffito Ware* (mid 12th century) (François 2004, p.243), b) *Aegean Ware* (beginning of the 13th century) (İzmir Archaeological Museum).

Green and Brown Painted Ware

Green and Brown Painted Ware, which dates to the 11th century at the earliest, was also in fashion throughout the empire till the end of the Byzantine period. During the 11th and 12th centuries, the white slip was painted with green and brown paints and then covered with a clear glaze, which resulted in the formation of a matt effect. However, in the late 12th century the green and brown pigments were mixed with the glaze. As a result, the appearance was glossy with the effect of mixed brown and green colors. The production center was mainly Greece and the distribution area covered Constantinople region, Anatolia, the Balkans, Cyprus and Greece (Dark 2001, p.70, 129-130).

Slip Painted Ware

Slip Painted Ware is also a common group of pottery where the designs were painted as slip to the surface with the earliest examples dating to the 11th century (Dark 2001, p.70) (Figure 1.6a). This technique was mostly being used since the 9th century in the Islamic world (Öney 1989, p.109).

Zeuxippus Ware

One of the most widespread 13th century productions was *Zeuxippus Ware* and *Zeuxippus Ware Related Ceramics* (for the discussion of this topic see section 1.4) (Figure 1.6b). Besides *Zeuxippus Ware* and *Zeuxippus Ware Related Ceramics*, other categories of fine ware such as *Incised Sgraffito Ware* and *Slip Painted Ware* were continued to be produced throughout the Late Byzantine period (Doğer 2010).

a b

Figure 1.6: Images of a) *Slip Painted Ware* (1100-1300) (http://www.metmuseum.org/works_of_art/collection_database/all/bowl_with_three_animals, last accessed date: May 2011)
b) *Zeuxippus Ware* (13th century) (Megaw 1968)

1.3.2 The Historical Background and General Characteristics of Byzantine Ceramic Production

The diversity of Byzantine glazed pottery types certainly came out as a consequence of diverse cultural influences both inherently within a very extensive political geography and externally within a time period of about ten centuries. The influences from the Islamic Near East were the most dominant ones while Chinese effects may also be considered to a lesser extent (Maguire and Maguire 1992).

The glazed pottery of Byzantine cultural sphere was of lead-glazed type, a tradition already well-established by the Romans. The reasons for the use of lead glazes usually depend on two factors which are the accessibility of the raw material and its technological advantages. The lead glazes are easier to apply since they do not need to be fritted as in the case of alkali glazes. Lead also lowers the melting point of the glaze mixture, making the glass formation possible at relatively lower temperatures. Lead glazes also adhere well to the clay bodies (Tite et al.1998). The technology of lead glazing has been evidenced as early as the 5th century B.C. in China, which was later enhanced during the Han Dynasty (206-200 A.D.) (Carter and Norton 2007, p.20). Lead glazes were also present in the Near East about the 1st century B.C. (Rice 1987, p.12). Regarding the western cultural sphere, it was also not before the Late Hellenistic period (i.e. about the 1st century B.C.) that lead glazing technology was being used in several sites of Anatolia like Tarsus in Southern Anatolia (Goldman 1950, p.191-196) and Smyrna (İzmir) in Western Anatolia (Hatcher et al.1994). This technology had then evolved into the Roman period where lead-glazed pottery was most probably being produced as imitations of metal vessels that were in fashion during those times (Vickers 1995). During the late 1st century B.C., lead glazing technology had been transferred to Italy and the Rhone valley from Anatolia (Desbat 1986). However, it was only during the late 1st century A.D. that production of lead-glazed pottery was taking place in Italy and the Rhone valley in the true sense. It was also during these times that lead glazing technology had advanced into

Northern and Southwestern Europe, as well as the Balkans (Walton and Tite 2010). On the other hand, the production of lead-glazed pottery had decreased in Asia Minor and the Mediterranean until the Early Medieval period (Greene 2007). However, the method of lead glazing was not forgotten and had reached to the Byzantine period by the time. The Byzantines established the industry of lead–glazed pottery, emerging in various styles for many centuries which were distributed within the borders of the Empire and beyond.

There were mainly two types of ceramic bodies used by the Byzantine potters as the white and red bodies. The white body showed variations from a coarse gritty grey white and shades of pale pink to a fine pure white body. The coarser body was mostly used for the production of utilitarian vessels such as lamps, candlesticks, chafing dishes, bowls and jugs while the finer one was mostly used for tiles and icons as well as for finer versions of bowls and cups, so-called *Polychrome White Ware*. The white bodied ceramics did not include any slips while the red bodied ones were generally covered with white slips for decoration purposes (Armstrong et al. 1997).

During the 9th and 10th centuries, the glazed ceramic finds at Byzantine sites showed a general trend in constituting a small quantity of the total ceramics found in contrast to unglazed pottery (Armstrong 2002). However, after the red bodies had emerged in production during the 11th century, the quantity of glazed ceramics increased tremendously when compared to unglazed pottery (Armstrong et al. 1997). Especially, tablewares with red bodies are often encountered in greater numbers at the rural sites than the glazed white pottery types found in similar sites (Armstrong 1989).

François and Spieser (2002) noted that there happened to be an increase in the circulation of people throughout the whole Mediterranean during the 12th century and in turn, a general increase in ceramic production in the same region. The increase in the number of ceramic production sites during this period thus led to a great variation of body properties in the case of red type since a variety of raw materials had been exploited.

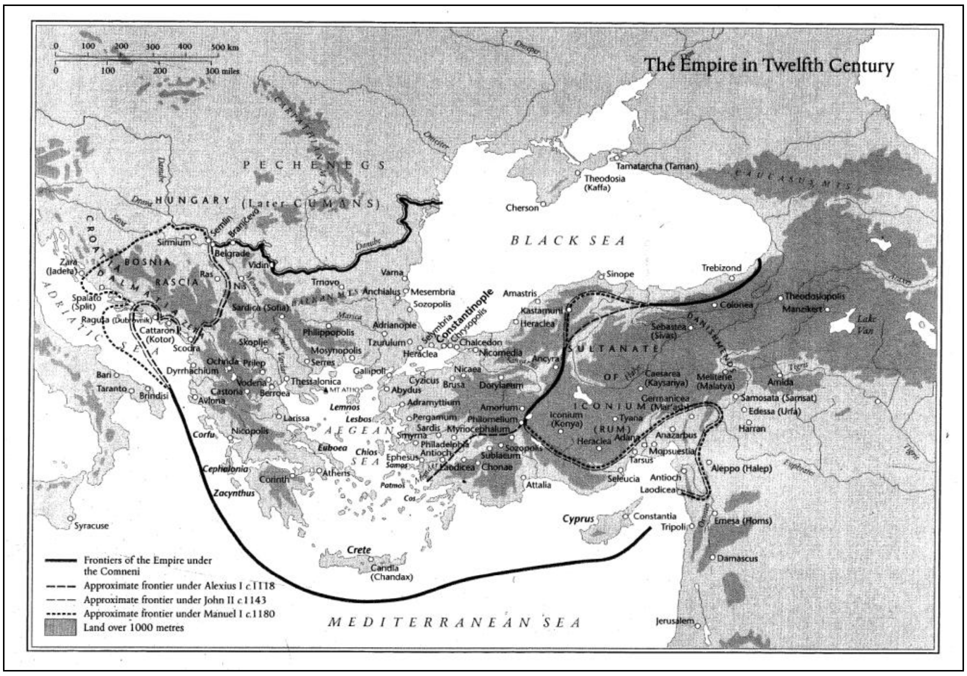


Figure 1.7: Map of the Byzantine Empire during the 12th century (Laiou 2008).

Another significant reason for this increase in pottery production was the use of specific kiln-furniture as tripods, a significant improvement in ceramic production technology. These devices were used to separate the pots stacked on top of each other in order to prevent the flow of the glazes. Consequently, this had enabled the potters to fill up the kilns more easily and also increased the quantity of the production (Papanikola-Bakirtzis 1999). The use of tripods dates as early as the period of Three Kingdoms (A.D. 220-265) in China (Papadopoulos 1992). Islamic merchants brought these devices to the Near East as early as the 9th century. The Byzantine craftsmen started to use these tripods which led to productions of higher quality in the late 12th century and the early 13th century (François and Spieser 2002). Also, sizes of the pots had decreased as the use of tripods was more convenient with the smaller size and thinner walled vessels.

Consequently, ceramic production increased in Greece, Western Thrace, Northern Italy and the Eastern Mediterranean (Doğer 2010).

13th century and beyond as the Late Byzantine period witnessed drastic political changes as the Frankish and Venetian Crusaders in 1204 captured the capital Constantinople and established a Latin Kingdom there. The Byzantine Empire was fragmented and Frankish states were established across the Aegean. Soon after, Theodoros Laskaris I had established a new Byzantine state in Nicaea (İznik) (Eyice 1991, p.14) (Figure 1.8). Frankish invasions had resulted in the economic collapse of the Byzantine Empire and had forced the people for a poor diet based on soup and meat broth (Doğer 2010). At the same time, a new demand rose for food stuffs, raw materials and industrial products by these outsiders coming from the West (Jacoby 2010). Depending on this, 12th century pottery forms with low ring bases had been replaced by deep bowls displaying higher bases. Chafing dishes which were common after the 9th century had also disappeared by this time (Armstrong 2008).

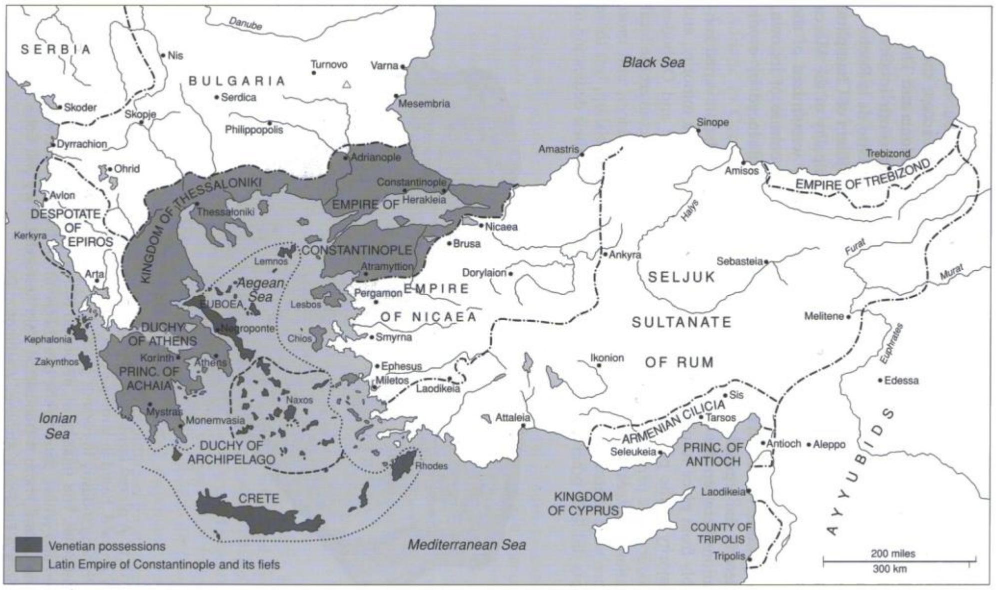


Figure 1.8: Map of the Byzantine Empire after 1204 (Gregory 2010, p.331).

Another consequence of these border changes in the Byzantine Empire was the establishment of new pottery production centers in Western Anatolia. These centers mainly include Nicaea (İznik) (François 1997a), Alexandria – Troas (Çanakkale) (Japp 2007), Pergamon (İzmir) (Spieser 1996), Sardis (Manisa) (Scott and Kamilli 1981), Metropolis, Ephesos (İzmir), Magnesia, Miletos (Aydın) (Böhlendorf-Arslan 2004, p.324) as well as Kuşadası Kadıkalesi/Anaia (Aydın) (Doğer 2009). Furthermore, the increase of potter's marks on the bases of ceramics after the middle of the 12th century may indicate the raised status of the craftsman as an individual in the Empire (Dimopoulos 2007).

General characteristics of 13th century Byzantine ceramics are observed to be reflected in the different aspects of the slip and glaze layers. Slip application had increased with the application of pink-colored slips by some workshops together with the white to cream-colored ones. The glaze colors tended to be dark yellow, ochre yellow, orange and dark green instead of pale yellows and apple greens of the Middle Byzantine period. Monochrome glazes were enriched with the application of green, dark yellow, brown and purple colored stains/paints, which was a novelty of Byzantine ceramics (Dark 2001, p.73; Doğer 2010).

Commercial activities with the Islamic Lands had also influenced the ceramic production especially starting from the second half of the 11th century to the beginning of the 13th century in the Byzantine Empire, in terms of technique and design schemes (Doğer 1997, 1999, 2010).

1.3.3 Trade of Ceramics throughout the Byzantine Empire

Since the classical times, trade activities in general had been carried out by sea to certain centers and then by land to the regions surrounding them (François 1997b). Sea-borne trade especially throughout the Mediterranean had been intensive with abundant cargoes of amphorae supplemented by glazed ceramics since the Early Byzantine period (5th- 7th centuries). Most of the main settlements of the Byzantine Empire including Constantinople had appropriate harbours for the handling and distribution of these amphorae which contained wine, oil and other goods. Glazed ceramics of this period had been widely distributed to Spain, France, England and Ireland in the West, as well as North African coast and Crimea (Dark 2001, p.90).

However, in the following period of Middle Byzantine (8th-10th centuries), sea-borne trade seems to have decreased mainly due to the utilization of land routes. Distribution of ceramics was mostly throughout the Empire rather than the West (Dark 2001, p.92). During the 11th century, seaborne trade once more increased and was extended beyond the Empire as revealed by the shipwrecks discovered. The most significant shipwreck from this period is Serçe Limanı (Marmaris) which was found in the Aegean Sea (Dark 2001, p.92; Bass et al. 2009). The following centuries as the 12th century and the 13th century also witnessed large scale of trade activities with the surrounding regions, again confirmed by the findings of a great deal of shipwrecks. These shipwrecks were revealed in a wide area including Castellorizo (Kaş - the Mediterranean Sea), Pelagonnesos-Alonnesos, Skopelos (the northern Sporades- the Aegean Sea) (Doorninck 2002; François and Spieser 2002), Çamaltı Burnu (Marmara Island - the Marmara Sea) (Günsenin 2005) and Novy Svet (Crimea, Ukraine- The Black Sea) (Waksman and Teslenko 2010) dating to the mentioned periods. Some of these ships contained mainly *Sgraffito Ware* including *Fine Sgraffito Ware* (e.g. Pelagonnesos-Alonnesos) or *Aegean Ware* (e.g. Castellorizo and Skopelos) as their cargoe (Waksman and Von Wartburg 2006). These ceramic types essentially constituted a large distribution throughout the Empire mainly on coastal sites than inland ones as a result of sea-borne trade (Dimopoulos 2007). Besides *Sgraffitto Ware*, *Zeuxippus Ware Related Ceramics* which constituted the broadest dissemination in the 13th century, were also carried by these ships as in the case of Novy Svet shipwreck (Waksman and Françoise 2004-2005; Waksman and Teslenko 2010). The increased pottery production during these periods had probably given rise to this large scale distribution of products.

However it should be noted that this large scale distribution of Byzantine ceramics was not only carried out by the Byzantine merchants but the Italians who started to become more active in trade from the early 13th century onwards. This was especially the situation for *Zeuxippus Ware Related Ceramics* as their distribution was shared between the Byzantine and Italian merchants (Megaw 1968).

After the fall of Constantinople in 1204 by the Fourth Crusaders, there was a turning point in the Byzantine trade system. The Venetians took hold of some ports and islands in the Aegean Sea which led to the development of their trade (Harvey 2008). In fact, the appropriate medium for the changing pattern of trade in the Byzantine Empire had been initiated during the 12th century. The decreasing in the sea power of Byzantines during this period led to the reliance upon the Venetians which were granted commercial concessions. Besides Venice, the rise of other Italian maritime cities as Pisa and Genoa also played a key role in the development of Italian dominance in trade during the 13th century (Haldon 2005, p.137; Jacoby 2009).

After the 13th century, Byzantine Empire had lost a great deal of effectiveness over trade activities which were directed by the Italians then. Accordingly, the trade of Byzantine ceramics had decreased to a certain extent. This phenomenon was also partially due to the growing ceramic production in Italy from the 13th century onwards with specific types such as *Roulette and Protomaiolica Wares*. It may also result from the decline of former large well-organized production centers. The trade of Byzantine ceramics in the last times of the Empire mostly waned to a more limited regional basis (Laiou and Morrisson 2007, p.186).

1.4 *Zeuxippus Ware* and *Zeuxippus Ware Related Ceramics*

Being the most significant type of production of the Late Byzantine period, *Zeuxippus Ware* gets its name from the Zeuxippus Baths in the Hippodrome area of İstanbul which was excavated by the British Academy in 1927. A special type of pottery was found in great quantities during these excavations and was then described to a certain extent by David Talbot Rice as *Shiny Olive Incised Ware* (1928). The precise archaeological context of this particular ceramic type was not so clear, thanks to the datable contexts with coins from the later Saraçhane excavations (Hayes 1992). The evidences from the stratified deposits of Kalenderhane Camii (İstanbul) made it possible to date *Zeuxippus Ware* to the end of 12th and the early 13th centuries (Megaw 1989). The main characteristics of *Zeuxippus Ware* are their fine dense red fabric, thin walled forms and a superior type of glaze quality comparing to other Byzantine glazed ceramics of the same period. It also displayed a flaring profile of the inner face of its ring feet. The characteristic finds are the small bowls whereas closed shapes such as flasks with quatrefoil mouths have also been revealed. The inner sides of the bowls were covered with thick white slips. In most cases, the same white slip was used to decorate the outer sides of the bowls in the form of circle patterns (Megaw et al. 2003). The glaze colors varied from tones of yellow, orange, brown to green and the decorations included *sgraffito*, incision and *champlevé* as well as impression techniques.

Based on the finds from Saranda Kolones (Cyprus), *Zeuxippus Ware* is categorized into two main classes as *Zeuxippus I (A-B-C)* and *Zeuxippus II* using their glaze colors by A.H.S. Megaw in 1968 (Table 1.2).

Table 1.2: The classification of *Zeuxippus Ware* by A.H.S Megaw (1968).

Zeuxippus Ware **classification**	**Added colors**	**Glaze color**	**Decoration Scheme**	**Additional Remarks**
Class IA	–	Cream, yellow, colorless or greenish	Concentric circles, rouletting*	No mark of the use of a tripod stilt
Class IB		Orange-brown		Tripod stilt used
Class IC		Dark green	-	Rare occurrence
Class II	Yellow-brown, green and purple	Cream, yellow	Concentric circles, central medallions, oval or triangular motifs on the rims	Systematic use of tripod stilt

*: decorating with a wheel-like tool to create a continuous pattern impressed into the surface of the ceramic (Dark 2001, p. 143).

According to this classification, Class I is generally characterized without any added colors on the monochrome type of glaze. Class IA includes small vessels with spherical bellies with slips and colorless, cream, yellow and greenish glazes. The interior of the vessels usually displays incised concentric circles, sometimes together with removal of the slip in broader bands which is associated with *champlevé* technique. There are no marks visible on the interior of the vessels, indicating the use of a tripod stilt during production. Class IA is mainly dated to the end of 12th century. Class IB has similar characteristics with those of Class IA, with the exception of having an orange-brown glaze and marks indicating the use of a tripod stilt while Class IC can be characterized with a dark green glaze. Finally, Class II displays the added colors of yellow-brown, green and sometimes purple on the monochrome glazes of cream and yellow at the forefront. It consists of larger vessels covered with slips. The use of a tripod-stilt is well-confirmed in this class. Regarding the schemes of decoration, the concentric circles stand out expectedly which may constitute central medallion motives of palmettes, clovers and small flowers while on the edges, oval or triangular motives, parentheses and overlapping stripes are encountered.

Constituting the most common occurrence during the 13th century Byzantine cultural sphere, *Zeuxippus Ware* and *Zeuxippus Ware Related Ceramics* have a large distribution area, rising from the heart of the Empire, mainly from the capital Constantinople (Istanbul) (Megaw 1968) as well as Nicaea (İznik), extending from Southern France (Vallauri and Demians d'Archimbaud 1999) in the west to the Levant as Acre (Waksman et al. 2008), Alexandria and Cairo (Françoise 1999) in the south to Chersonesos in the north (Waksman and Romanchuk 2007). The four groups of *Zeuxippus Ware* which were described by Megaw in 1968 (Table 1.2) are also considered as "prototypes" for these *Zeuxippus Ware Related Ceramics* later on (Megaw et al. 2003). After the numerous findings of these ceramics around the Mediterranean and the Black Sea, Megaw later proposed to extend his definition of *Zeuxippus Ware* to *Zeuxippus Ware Family* (Megaw 1989) since these wares do not represent a homogeneous category but diverse productions. However, different authors used different specific namings rather than *Zeuxippus Ware Family* to describe this type of ware such as *Zeuxippus Ware Derivatives* (Armstrong 1992), *Imitation Zeuxippus* (Spieser 1991), *Zeuxippus-Influenced Ware* (Stern and Waksman 2003), *Late Sgraffito* (Sanders 1993) and *Zeuxippus Subtype* (Vroom 2005, p.111). The use of different namings has made the situation subjective to some extent, misleading and very intricate. Additionally, the naming of a non-Byzantine ceramic type called *Graffita Arcaica* as *Zeuxippus Ware Derivative* which was produced in Southern Italy, Liguria and Venice further complicates the descriptions (Laiou and Morrisson 2007, p.185).

Due to the complicated nature of the terminology used for describing *Zeuxippus Ware Related Ceramics* and in search of unity in the literature, Waksman and François proposed a new terminology based on grouping by chemical compositions of *Zeuxippus Ware Related Ceramics* found at sites scattered through a very large geographical region (2004-2005). They proposed alternative names as *Zeuxippus Ware stricto sensu* and *Zeuxippus related wares of Novy Svet type* in relation to the findings from a shipwreck near Crimea (Section 1.3.3). Yet at present, the terminology used for defining *Zeuxippus Ware Related Ceramics* has not been established on a firm basis.

Regarding Anatolia, *Zeuxippus Ware Related Ceramics* were revealed in several sites such as Nicaea - İznik (Bursa) (Böhlendorf-Arslan 2004, p.180-182), Gülpınar (Çanakkale) (Yenişehirlioğlu 1989), Karacahisar Castle (Eskişehir) (Bursalı 2007), Adramyttion (Balıkesir) (Çoruhlu 2002), Pergamon (İzmir) (Waksman and Spieser 1997), Selçuk-Ayasuluk (İzmir) (Parman 1989), Alanya (Antalya) (Bilici 2008), Miletos (Aydın) and Yumuktepe (Mersin) (İnanan 2010a).

Since its discovery occurred in the Hippodrome area at İstanbul in large quantities in 1927, it is generally presumed that *Zeuxippus Ware* was being produced in the workshops of Constantinople. However, there is not enough evidence to prove this assumption as far as the locations of pottery workshops in the city are concerned. Yet still, the finds in Constantinople are called as *Genuine Zeuxippus Ware*. Besides, the high probability of several workshops in other places which could have been involved in these productions is now being taken into account. Furthermore, the evidences of production for *Zeuxippus Ware Related Ceramics* come from several sites, such as Pergamon in Western Anatolia (Waksman and Spieser 1997), Lemba in Cyprus (Megaw and Jones 1983), Venice in Italy (Berti and Gelichi 1997), Nicaea (İznik) (François 1997a) as well as Kuşadası Kadıkalesi/ Anaia (Doğer 2009).

Further scientific investigations are expected to clarify the production sites of *Zeuxippus Ware Related Ceramics* which constitutes a significant research domain regarding Byzantine ceramics at present.

1.5 12th-13th Century Glazed Ceramics Found in Kuşadası Kadıkalesi/ Anaia

The excavations in Kuşadası Kadıkalesi/Anaia have yielded a rich variety and good quality of Byzantine glazed and unglazed ceramics which are mostly dated to the 12th and 13th centuries. Most of these ceramics have been found on the surface, on the south and southeast of the fortress. Besides Late Byzantine ceramics, a variety of pottery groups was also recovered dating back to as early as Middle Bronze Age. *Grey Minyas Ware* and *Gold Wash Ware* (the most characteristic production of Middle and Late Bronze Ages), Mycenaean pottery, *Protogeometric*, *Subprotogeometric* and *Geometric* pottery types (the 8th and 10th centuries B.C.) were all encountered in Kuşadası Kadıkalesi/Anaia excavations. The uninterrupted sequence of pottery can be followed until the end of Hellenistic period. Late Roman and Early Byzantine red slip pottery was also found dating to the 3rd to 7th century A.D. in Kuşadası Kadıkalesi/Anaia (Doğer 2003, 2009).

There are strong evidences that local ceramic production had existed in Kadıkalesi/Anaia although not even a single ceramic kiln could have been located up to now. During the first excavation season in 2001, a stack of clay was found outside the fortress in the south, which was then followed by the uncovering of a semicircular clay pool adjacent to a wall during the 2004 excavation. A dump area having burnt pieces and ash wastes which may be associated to a ceramic workshop was also found in Sector I (Figure 1.3) (Mercangöz 2009). The consistency of the finds such as tripods and defective production wastes strongly suggests the presence of ceramic workshops in the north and west sides of Sector I. Additionally, the recovery of pithos in-situ adjacent to the west wall and on the south of the entrance to the fortress also support the existence of ceramic workshops in the area. Among the Byzantine pottery finds, most of them are defective production wastes while a limited number of them are actual vessels (Mercangöz 2010). Consequently, all of the evidences indicated strongly support the state of Kadıkalesi as one of the important ceramic production sites which had started to develop in the Aegean sphere after the establishment of the Latin Kingdom in Constantinople by the Fourth Crusaders in the early 13th century. The rich variety of ceramics recovered may also be associated with the position of Kadıkalesi/Anaia as an active harbour within the context of Mediterranean trade. Some groups of ceramics might have been imports from other places while a part of them were also presumably being produced in the Kadıkalesi/Anaia workshops as export goods to other cities (Doğer 2009; Mercangöz 2010).

Ceramic Typology of Kuşadası Kadıkalesi/Anaia

Most of the 12th-13th century Byzantine ceramics found in Kuşadası Kadıkalesi/Anaia are *Fine Sgraffito Ware, Incised Sgraffito Ware, Painted-Incised Ware, Aegean Ware* and *Champlevé Ware* types (Doğer 2004, 2009). Besides these most frequent groups; the 12th century productions of *Painted-Sgraffito Ware, Green/Green and Brown Painted Ware, Aegean Type Slip Painted Ware* were also recovered during Kuşadası Kadıkalesi/Anaia excavations. Among these 12th-13th century pottery groups, the most common type belongs to *Zeuxippus Ware Family* having similar features to those of *Zeuxippus Ware I* and *II* classes (Megaw 1968). *Zeuxippus Ware Family* ceramics are the most commonly encountered ones in the state of unfinished pieces and defective productions during the excavations. Thus, a group of *Zeuxippus Ware Family* ceramics with a good quality of paste is considered as local productions of Kadıkalesi/Anaia (Doğer 2004, 2009). These ceramics are subdivided into groups according to their body characteristics and the quality of the decorations. The main forms are simple outrolled large or narrow, flat and small deep bowls. The glaze colors used are the tones of yellow, green, orange and brown which were applied on light pink or white slips. *Sgraffito,* incision, *champlevé* and slip techniques were used in the decoration schemes. A detailed classification of *Zeuxippus Ware Type* ceramics from Kuşadası Kadıkalesi/Anaia was carried out by Filiz İnanan in her Ph.D. thesis (2010b).

Other groups of pottery which may be related to *Zeuxippus Ware Family* are *Green and Orange Stained Ware*, *Manganese-brown Stained Ware, Incised-manganese Ware* and *Green Stained Ware* coming from the contexts belonging to the mid-12th century and the early 14th century in Kuşadası Kadıkalesi/Anaia. The terminology used for these groups of ceramics is not well-established at present. Similar groups of pottery were also found in some other Western Anatolia sites like Ilion (Çanakkale), Pergamon, Metropolis (İzmir), Sardis (Manisa), Magnesia and Priene (Aydın) within the 13th-14th century contexts (Doğer 2009).

During the 13th century after the capture of Constantinople by Frankish and Venetian crusaders in 1204, Italian merchants settled in Anaia. It is suggested that they influenced the ceramic making in the workshops of Kadıkalesi which can be predicted from the decorations on some pottery finds such as several monograms, crosses and emblems. This type of ceramics, named as *Frankish Style Ceramics,* refers to local productions of Kadıkalesi using the Byzantine tradition but in the taste of Frankish culture (Mercangöz 2009). In fact, Frankish is the name given to Western European people coming from the north of the Alpine region. However, in Byzantine archaeology the term “Frankish” implies all groups of people coming from Europe with a Crusader identity, regardless of their ethnic origin (Boas 1999, p.7). The phenomenon of *Frankish Style Ceramics* is also valid for other sites across the Aegean where the Frankish people settled down after 1204 and gave rise to new styles of pottery, such as in Corinth (Joyner 2007) and Boeotia (Central Greece) (Vroom 2003).

1.6 Archaeometric Studies on Byzantine Ceramics

Historians and art historians have mostly taken part in the research of Byzantine remains to what we can refer as architecture and written documents and they have constructed the history of Byzantine civilization based on these aspects. These studies have been the main basis for shaping our present understanding of the Byzantine Empire where the evidence of material culture has been investigated to a lesser extent. Reconstruction of a society's culture is incomplete without the study of the artifacts which refer to objects of daily life, like ceramics. Ceramics have been a prevailing example of material culture since the early periods of human history. In each settlement, even the ones being in the same geographical area like Anatolia, different ceramic types were produced according to the special needs, the technological competence of the period, the culture and the influences from nearby cultures. The investigation of ceramic production technologies is important as it provides insights for understanding the degree of social, commercial and cultural contacts between different societies as well as the technological level reached by them. Yet at present, we have not understood completely some aspects of the technology used in the making of materials as ceramics, glass and enamels etc. by ancient civilisations since the documentary sources are usually scarce. Consequently, studies based on scientific techniques have been increased in the last decades for the study of historical and archaeological ceramics by various research groups around the world.

In the last decades, an interest has particularly risen for the investigation of Byzantine ceramics resulting in an increased number of publications, especially from the archaeometrical point of view. There are two aspects of these archaeometric studies as the identification of ceramic production centers based on raw material sources (provenance analysis) and the technology used in the production of these ceramics. Determination of ceramic production centers in the Byzantine Empire has been the primary focus of archaeometric research until now since these centers are yet ill-defined due to the absence of the literary sources and incomplete archaeological evidence. Ceramics with similar technical and decoration characteristics were evidently being produced in more than one place during the Byzantine period. Localization of these production centers is important to reveal the patterns of ceramic production and trade activities throughout the Empire. The first step in defining production centers is to make chemical classifications of ceramic groups by analyzing their major, minor and trace elements using techniques such as ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry), ICP-MS (Inductively Coupled Plasma-Mass Spectrometry), AAS (Atomic Absorption Spectrometry), XRF (X-Ray Fluorescence Spectrometry) and NAA (Neutron Activation Analysis) etc. In this case, trace elements are the key ones for differentiating the raw materials used. This approach excludes the possible biases based on the visual aspects of ceramics which seem most of the time similar. The second step is to correlate these chemical fingerprints with the surrounding geological formations such as the clay sources. Petrographic properties of the ceramics should also be taken into account in defining the raw material sources. Technological elements can also be leading in provenance analysis when a technological feature is confidently defined for a particular region.

The production technology of Byzantine ceramics including the raw materials processing, firing conditions of the body, slip and glaze parts and particularly the glaze compositions and their coloring mechanisms has been studied to a lesser extent when compared to provenance studies. The most common techniques used for this type of studies are XRD (X-Ray Powder Diffraction), SEM-EDX (Scanning Electron Microscopy coupled with Energy Dispersive Analyzer), Electron Microprobe, Raman Spectrometry and so on.

Provenance Studies

The pioneering study in the analysis of Byzantine ceramics was conducted by Megaw and Jones in 1983. This study is very significant both as being of the first application of scientific techniques to Byzantine ceramics and initiating the research domain for the localization of production centers. In this study, several groups of ceramics taken from the defined production sites of Corinth, Cyprus (Lapithos and Lemba) and Thessaloniki etc. and sites like İstanbul and Athens etc. as not yet ascertained for production, were analysed by OES for chemical characterization. Other groups including related waster material, modern bricks, clays and ceramic types dating to the earlier time periods were also analyzed for comparison. Additionally in regard to *Zeuxippus Ware,* the authors propose an Aegean origin for its production as the composition of this ware coming from Paphos (Cyprus) differed from their other main composition batches and also from the common 12th century Byzantine ceramics found at Constantinople. Outcomes of this study proved to be useful as a first step in creating the chemical database for different types of Byzantine ceramics. It can also be considered as an introductory step for identifying the locations of *Zeuxippus Ware* production.

An earlier study was published in 1981 based on the petrographical and mineralogical caharacterization of Late Byzantine ceramics from Sardis (Manisa) (Scott and Kamilli 1981). It was suggested that most of these ceramics were locally produced in Sardis.

A petrographical study about a group of 12th century Byzantine ceramics with monochrome glaze and *sgraffitto* decoration found in Liguria (coastal region of Northwestern Italy) and Pisa (North Italy) was published by Mannoni in 1993. Differences were observed among the groups although the geolithic characteristics of all seemed to be consistent with Greece and the Western Aegean. Consequently, it was concluded that these ceramics had been imported to Italy from Greece.

In the course of time, the onset of research on Pergamon was significant in terms of restarting the discussions on Byzantine ceramic production sites (Waksman et al. 1994; Waksman et al. 1996). In Pergamon, kiln wasters and unfinished ceramic pieces were revealed. In the primary publication, it was suggested that *Zeuxippus Ware Imitation* ceramics from Pergamon were local productions as correlated with the kiln furniture by the statistical treatment of chemical data obtained by PIXE (Particle Induced X-Ray Emission Spectrometry) (Waksman et al. 1994). In the other publication, a more detailed classification of Pergamon ceramics was given on the basis of chemical analysis by PIXE and INAA (Instrumental Neutron Activation Analysis) and petrographic examination where an unglazed group of ware was additionally differentiated as a local group

(Waksman et al. 1996). Regarding the function of ceramic groups, the use of different clay deposits around the region was suggested, on the basis of mainly petrographical data. Overall results of the investigations on Pergamon ceramics were published in the book called “Materials Analysis of Byzantine Pottery” (Waksman and Spieser 1997) which is a compilation of analytical studies on different types of Byzantine ceramics by various researcher groups. Among the origin studies to be mentioned in this volume is the one written by Wisseman et al. (1997) about the characterization of Serres and Thessaloniki (Northern Greece) ceramics. In this study, two different clay sources were proposed regarding the two sites which are not far away from each other. So-called *Serres Ware*, that is *Colored Sgraffitto Ware* from the city of Serres (Papanikola-Bakirtzis 1997), which had also been found in Thessaloniki was found to be produced from Thessaloniki clay. Consequently, it was suggested that the two sites had shared the technology of this type of ware.

Another study also came in 1994 by A.J. Boas about the 12th-13th century Byzantine ceramics which had been imported to the Latin Kingdom of Jerusalem. Samples found in several sites in the Kingdom of Jerusalem and three sites in Cyprus were analysed by NAA. Most of the ceramic groups analysed were suggested to have a Cypriote origin, as the author marked the significance of Cyprus as an export center where various ceramic groups with different technical and stylistical properties had been produced. In addition, for *Zeuxippus Ware*, Boas claimed two different compositional groups with one of them belonging to Cyprus and the other belonging to an undefined place.

A small scale study was also undertaken regarding the body characterization of Byzantine *White Wares* from the collections of Ashmolean Museum (Oxford), based on petrography and chemical data (Mason and Mango 1995).

The big problem of identifying local and imported ceramic groups in the Byzantine cultural sphere had brought researchers together from disciplines of art history and chemistry in order to develop a project titled “Byzantine and Allied

Pottery" in Oxford University (Armstrong and Hatcher 1997). Yet, there are not any recent publications relating to the overall results of this project.

A significant analysis programme covered the 12th – 13th century ceramics from Acre, a significant port town in the Crusader Kingdom of Jerusalem during that period (Waksman et al. 1999; Stern and Waksman 2003). Besides *Frankish Style* ceramic types found at Acre (referred to as Levantine wares), imported Byzantine ceramic types, especially *Zeuxippus Ware Related Ceramics* were also characterized by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), ICP-MS, INAA and petrography. Different compositional groups among *Zeuxippus Ware Related Ceramics* were identified by chemical analysis, as also foreseen by typological varieties. Among these, the imported status of the first group which has similar characteristics with those of *Zeuxippus Ware* Class II (Megaw 1968) was confirmed as it diverged chemically and petrographically from the local productions of Acre. The second group with samples resembling *Cypriot Sgrafitto Ware* was found to differ chemically from Lemba (Cyprus) productions while the last one was found to correlate with productions of Venice.

Another publication about the local and imported ceramics from Crusader Acre was also released later in 2008 (Waksman et al. 2008).

Regarding *Zeuxippus Ware*, another study was published using ICP-OES in 2003 (Megaw et al. 2003). The two dimensions of this study were to compare chemically the two subgroups of *Zeuxippus Ware* (Class Ia and II) from Saranda Kolones castle in Cyprus defined by Megaw (1968) and to test these against similar productions of attested centers as Thessaloniki - Serres (Northern Greece) and Kaffa (Crimea). The two subgroups of *Zeuxippus Ware* were found to form a coherent group among all the other groups of ceramics analysed. Even the ceramics from one particular group such as Thessaloniki were found to be not homogeneous in composition. So, it was suggested that this ware did not originate from any of these sites. However, the number of samples used in this study was not sufficient for definite conclusions.

Another significant study involved the characterization of medieval ceramics from Ephesus by petrographical and chemical analyses using Wavelength Dispersive X-Ray Fluorescence Spectrometry (WD-XRF) (Sauer and Waksman 2005). According to the results, the use of different clay sources available in the vicinity for Late Byzantine ceramic types, as well as other medieval ceramics, was proposed. However, a larger number of samples should be studied to clarify the situation.

Another publication came up in 2006 about the characterization of *Slip Painted Ware, Green and/or Brown Painted Ware, Fine Sgraffito Ware* and *Aegean Ware* etc. mainly from Cyprus by chemical analysis (WD-XRF) (Waksman and von Wartburg 2006). A possible common origin was proposed for the different types of Byzantine ceramics analyzed, suggesting the use of a main workshop or a group of workshops located in the same region using very similar raw materials.

Other studies include the petrographical characterization of white bodied tiles (Vogt et al. 1997) and the chemical characterization by NAA of similar ones from the 9th-11th centuries (Lauffenburger and Williams 1997). In the latter study, the chemical compositions of the tiles were compared to those of ceramic vessels from the 10th-11th centuries.

A recent publication came in 2009 about the chemical characterization of Byzantine ceramics recovered during the excavations in Sirkeci (İstanbul). Mainly the finds such as tripods and fragments of *Elaborate Incised Ware* were analyzed by WD-XRF (Waksman et al. 2009).

Technology Studies

Studies about the technology used in the production of Byzantine ceramics are relatively few when compared to their provenance studies. A preliminary study was published in 1981 by J.A. Scott and D.C. Kamilli, which can be considered as a first step to initiate research on the technological characteristics of

Byzantine ceramics. In this study, the glazing technology of Late Byzantine ceramics from Sardis was investigated through compositional analysis of the main glaze constituents and coloring agents in the glaze by using Electron Microprobe Analysis.

Another preliminary study should also be mentioned as an attempt to understand the glazing technology of Byzantine ceramics through the samples from Serres (Northern Greece) (Wisseman 1992; Wisseman et al. 1997).

Another study covered the analyses of glasses and glazes applied on white bodies from the 10th-11th centuries by Electron Microprobe Analysis (Henderson and Mango 1995).

In fact, the first more detailed study came from Middle East Technical University Archaeometry Group in 1996 (Demirci et al. 1996). In this study, the body, slip and glaze parts of Byzantine and Seljuk *sgraffito* ceramic samples from Ephesus, İznik and Korucutepe (Elazığ - Eastern Turkey) were characterized by using optical microscopy, XRD, SEM-EDX and Fourier Transform Infrared Spectrometry (FTIR). These results provided a preliminary insight into the technology of medieval ceramics produced in Anatolia.

Another significant study was carried out by Armstrong et al. (1997) about the analyses of glaze compositions on white and red bodied ceramics, dating between the 9th to 13th centuries found in several sites such as Lakedaimon (ancient Sparta), Constantinople and Al-Mina (the port of St Symeon-the Eastern Mediterranean). According to these glaze compositions which seemed to be consistent throughout this time period, it was suggested that technological sources had not initiated the change from centralized to dispersed production of glazed ceramics in the Byzantine Empire.

The close technological relationship between tile and pottery making is evident since the same craftsmen who were travelling throughout the Empire, used to produce these ceramics (Lauffenburger et al. 2001). The glazes of Byzantine architectural tiles found in the collections of Walters Art Museum (the U.S.A.), Louvre and Sévres Museums (France) were also investigated by SEM-

EDX and WDX (Lauffenburger and Williams 1997; Vogt et al. 1997; Lauffenburger et al. 2001). In the first study, the lead content was found to be similar for the clear and amber colored glazes on the same tile (Lauffenburger and Williams 1997). In the other study (Lauffenburger et al. 2001), the glaze compositions were found to show differences in relation to the sizes, indicating the productions of different workshops.

Two other publications on the production technology of Byzantine ceramics by the Archaeometry Group in Middle East Technical University were released in 2002 and 2004 (Demirci et al. 2002; Demirci et al. 2004). The body, slip and glaze parts of the *sgraffito* ceramics from Ephesus, İznik and Korucutepe were again investigated by SEM-EDX, XRD and FTIR. The coloring mechanisms and firing temperatures of the bodies were discussed on the basis of their CaO and Fe_2O_3 contents and the compositions of slips and glazes were also figured out.

Other significant studies include the Raman spectrometry analyses of Byzantine ceramics from the Republic of Macedonia (Tanevska et al. 2009; Raskovska et al. 2010). The glazes of 12th – 14th century ceramics from the citadel of Markovi Kuli in Prilep, the central citadel Kale and Skopsko Kale in Skopje were characterized by means of Raman spectrometry, Infrared spectrometry and SEM-EDX.

The latest study for the technology of Byzantine ceramics is by Charalambous et al. (2010) who investigated the 12th-14th century Byzantine ceramics from sites between Limassol and Paphos in Cyprus. The compositions of glaze parts were analysed by micro-XRF as well as SEM-EDX and the firing temperatures of the bodies were discussed according to the results of XRD analysis.

1.7 Use of Raman Spectrometry in Glaze Characterization

Ceramic glazes are glassy materials which have the structure of SiO_4 tetrahedra (network formers) connected with bridging oxygen atoms located at the corners. As far as the Raman scattering is concerned, the SiO_4 tetrahedron is a covalent entity which has a well defined vibrational signature. If aluminium, magnesium, iron and other alkali-alkaline earth metal ions are also incorporated within this SiO_4 tetrahedral network, different types of Si-O arrangements are induced which modify the properties of glass such as its melting temperature, viscosity and color (Figure 1.9). These ions are called as “network modifiers” (Colomban 2005).

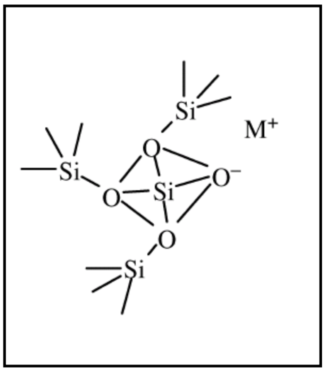


Figure 1.9: The illusration of SiO_4 vibrational unit, M^{n+}: Modifier cation.

In the glass structure, five different types of Si-O arrangements can be present at the same time due to the incorporation of these network modifier species. This phenomenon is indicated by the Q^n notation where n is the number of bridging oxygens varying from 0 to 4 (Figure 1.10). Structures with Q^o, Q^1, Q^2,

Q^3 and Q^4 coordinations correspond to the different classes of crystalline silicates, as follows:

- nesosilicates, formed by isolated SiO_4 tetrahedra (coordination Q^o),
- sorosilicates, formed by couples of tetrahedra $(Si_2O_7)^{6-}$ (coordination Q^1),
- cyclosilicates, formed by rings of 3, 4 or 6 tetrahedra, e.g. $(Si_6O_{18})^{12-}$ (coordination Q^2),
- inosilicates, formed by simple or double chains of tetrahedra, as in $(SiO_3)^{2-}$, $(Si_4O_{12})^{8-}$, and $(Si_4O_{11})^{6-}$ groups (coordination Q^2),
- phyllosilicates, formed by sheets of tetrahedra in hexagonal groups $(Si_4O_{10})^{4-}$ (coordinations Q^2 and Q^3, depending on the degree of substitution),
- tectosilicates, formed by a three-dimensional network of interconnecting SiO_4 tetrahedra (coordinations Q^3 and Q^4, depending on the degree of substitution).

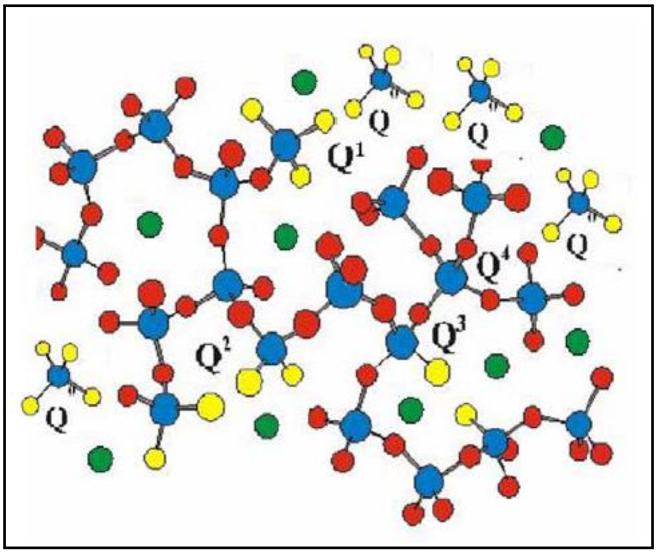


Figure 1.10: Schematic representation of SiO_4 network with different Si-O coordinations (Si^{4+}: blue circles, O^{2-}: red and yellow circles, modifier cations are represented as green circles) (Colomban and Prinsloo 2009)

The characteristic Raman spectrum of a glassy material consists of two broad peaks localized at around 500 cm^{-1} and 1000 cm^{-1}, respectively. These peaks (massifs) mainly result from the two most intense vibrational modes of the SiO$_4$ unit. The ~ 500 cm^{-1} massif results from the bending mode and therefore is called as the “bending massif” (δ Si-O) while the ~1000 cm^{-1} massif is due to the symmetric stretching mode and is called as “the stretching massif” (ν Si-O). The stretching massif is postulated to comprise five different spectral components as Q^0, Q^1, Q^2, Q^3 and Q^4 which are related to the five different Si-O tetrahedral arrangements as described above (Figure 1.10): Q^0 at ca. 800 - 850 cm^{-1}, Q^1 at ca. 950 cm^{-1} , Q^2 at ca. 1050 -1100 cm^{-1} , Q^3 at ca. 1100 cm^{-1} and Q^4 at ca. 1150 -1250 cm^{-1}. The bending massif is also considered to have at least four spectral components although the exact structure has not been understood yet (Colomban 2003 and 2004; Colomban and Paulsen 2005) (Figure 1.11).

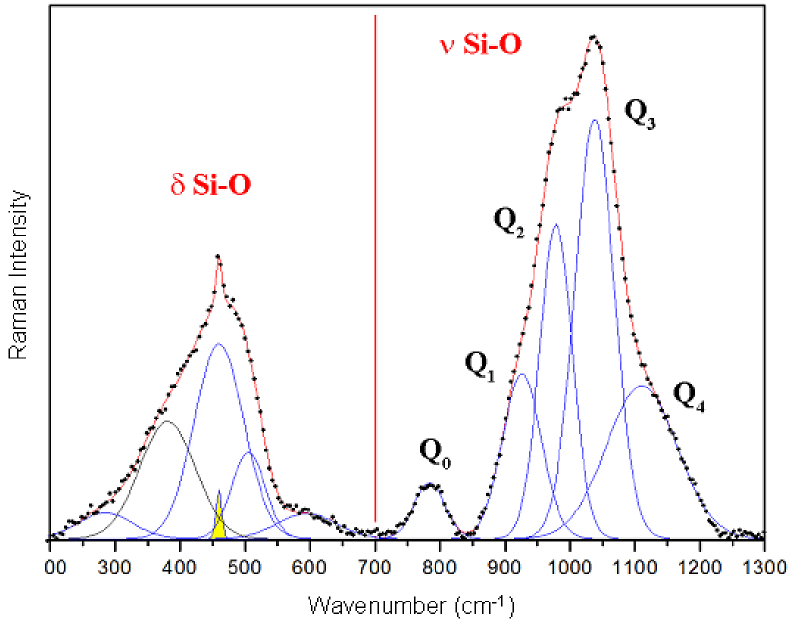


Figure 1.11: The spectral components differentiated in the Si-O stretching massif (ν Si-O) of a typical Raman spectrum of glass as Q^0, Q^1, Q^2, Q^3 and Q^4

The Raman intensity, bandwidth and spectral position of these Si-O bending and stretching massifs vary with the modifications in the glass structure. Thus, the investigation of these Raman parameters can be used to understand the composition of glass (Colomban and Paulsen 2005). In more detailed terms, wavenumber positions of Q^n bands, maxima of the bending and stretching massifs and the area ratio of these massifs, the so-called polymerization index (Ip= A_{500}/ A_{1000}) are directly related to the glass composition. High values of I_P correspond to silica rich and calcium, potassium poor compositions subjected to relatively higher firing temperatures while low Ip values correspond to modifier-rich and silica-poor compositions treated at relatively lower firing temperatures (Colomban and Paulsen 2005; Colomban et al. 2006)

Another type of information that can be extracted from Raman spectra is the nature of color development in the glassy matrices. Factors such as glass composition, firing temperature, atmospheric conditions, nature and size of the crystalline particles affect the final colour observed which directly corresponds to the technology used. Four different occasions of color development in glassy matrices are possible which produce different Raman features (Colomban 2004, 2005) as follows:

1- Transitional metal ions like Cu^{2+}, $Co^{2+ \text{ or } 3+}$, $Mn^{2+ \text{ or } 3+}$ etc. are dispersed in the glassy matrix. In this case, only the spectrum of glass is observed.
2- Small coloured crystals are precipitated in the glassy matrix. The small size of the crystals produces a characteristic band broadening in the Raman spectrum.
3- An insoluble coloured crystal (a pigment) is dispersed in the glassy matrix, leading to a characteristic Raman spectrum.
4- Metal nanoparticles (gold and silver etc.) are dispersed in the glassy matrix, inducing very low wavenumber Raman fingerprints

Subsequently, Raman spectrometry is a powerful technique in the study of glassy materials, enabling us to collect information about the glass composition, firing temperature and the factors affecting color formation in the glassy matrices.

1.8 Aim of the Study

Characterization of archaeological and historical pottery types on the basis of stylistic analysis and visual appearance can be regarded as subjective to some extent due to the distinct perceptions of the individuals. In this case, scientific investigations on more objective grounds are required for the characterization of pottery. The outcomes of archaeometric investigations with the study of morphological aspects as form should be used together for the classification of different pottery groups.

The aim of this particular study is to investigate the material specifications and technological characteristics of a collection of Byzantine glazed ceramics which are mainly *Zeuxippus Ware Related* productions dating to the late 12th -13th centuries from Kuşadası-Kadıkalesi/Anaia by scientific methods listed below:

1- Thin section analysis by optical microscopy
2- X-Ray powder diffraction analysis (XRD)
3- Scanning electron microscopy coupled with energy dispersive X-Ray analysis (SEM-EDX)
4- Inductively coupled plasma-optical emission spectrometry (ICP-OES) and Inductively coupled plasma- mass spectrometry (ICP-MS)
5- Raman spectrometry
6- Statistical analysis

These investigations help us to understand mainly the nature of raw materials used in body, slip and glaze parts of the ceramics and their processing, the firing conditions and technology of glazing. The outcomes will be used to form classifications among different groups of ceramics to establish similarities and differences of the materials used for the late 12th to 13th centuries in Kuşadası Kadıkalesi/Anaia together with the knowledge on visual classifications. Furthermore, these informations may then also be used to compare these classes of ceramics with the similar ones produced in the Byzantine territory.

Additionally, these classifications are expected to contribute to the discussions on the naming of *Zeuxippus Related Ceramics* which display a great variety of types within a large geographical context. Another scope of this study is to test whether the chemical groupings of these ceramic groups support their classifications based on visual characteristics by the art historians.

CHAPTER 2

MATERIALS AND METHODS

2.1 Sampling

2.1.1 Classification of Samples

A total of seventy-three glazed ceramic samples has been provided from the collection of Kuşadası Kadıkalesi/Anaia excavations which are directed by Prof. Dr. Zeynep Mercangöz from Ege University. These are mainly *Zeuxippus Ware Related Ceramics* dating to the late 12th-13th centuries. Visual classifications of the samples were carried out by Assist. Prof. Dr. Lale Doğer also from Ege University. As the naming of *Zeuxippus Ware Related Ceramics* is still under development, these classifications are currently on a tentative basis.

Groups of samples investigated are given in Table 2.1.

Table 2.1: General classification of Kuşadası Kadıkalesi/Anaia ceramic samples

Group name	**Subgroup code**	**Subgroup Description**	**Number of samples**
Anaia Zeuxippus Ware Type (ZA)	ZA1	*Green and Orange Stained Ware*	5
	ZA2	*Zeuxippus I and II Ware Type Ceramics*	28
Zeuxippus Ware Family (ZFB)	ZFB1	-	10
	ZFB2	-	5
	ZFB3	*Manganese- brown Stained Ware*	5
	ZFB4	*Incised-manganese Ware*	2
	ZFB5	*Green Stained Incised Ware*	1
	ZFB6	*Frankish Style Ceramics*	9
Green Painted Ceramics (GP)	-	-	4
Zeuxippus Ware Type Slip Painted Ceramics (ZS)	-	-	4

The most frequent types of ceramics excavated in Kuşadası Kadıkalesi/ Anaia are the ones having similar form and decoration characteristics with *Zeuxippus I* and *II Wares* (Megaw 1968) (Table 1.2). This type of ceramics was also recovered in the state of unfinished and defective pieces suggesting their local production in Kadıkalesi. Therefore, they are defined as *Anaia Zeuxippus Ware Type* (ZA). These ceramics are differentiated from the other groups with a characteristic paste. *Green and Orange Stained Ware* is distinguished as a subgroup within *Anaia Zeuxippus Ware Type* with its characteristic decoration of green and orange stains under the glaze.

The other group of samples considered within *Zeuxippus Ware Related Ceramics* is called *Zeuxippus Ware Family* (ZFB) which is further divided into six subgroups. These samples also appear to be similar with *Zeuxippus I* and *II Wares* to some extent as far as the forms and decorations are concerned but may not certainly be local productions of Kuşadası Kadıkalesi/Anaia.

Other smaller groups of ceramic samples are *Green Painted Ceramics* (GP) and *Zeuxippus Ware Type Slip Painted Ceramics* (ZS). *Green Painted Ceramics* have emerged as a new group of Late Byzantine ceramics in the excavations at Western Anatolia for the recent years. They are considered out of *Zeuxippus Ware Related Ceramics* since they have a different type of decoration technique with underglaze paints. *Zeuxippus Ware Type Slip Painted Ceramics* also appear as an individual group which display a different decoration scheme than the common 12th century *Slip Painted Ware*. These ceramics are considered to be imported from other Byzantine sites (personal communication with L. Doğer 2011).

Further information about the samples can be found in Table 2.2.

Table 2.2: Detailed classification of Kuşadası Kadıkalesi/Anaia ceramic samples.

Anaia Zeuxippus Ware Type (ZA1)	**Sample code**	**Excavation Code**	**Subgroup Definition**	**Description**
	ZA1-1	B62	Green and Orange Stained Ware	body piece, incised + stained
	ZA1-2	ACE.2		base piece, incised + stained
	ZA1-3	2001.9031		rim piece, incised + stained
	ZA1-4	AJL.1		base piece, incised + stained
	ZA1-5			rim piece, incised + stained
Anaia Zeuxippus Ware Type (ZA2)	ZA2-6	A2	Zeuxippus I	base piece, incised
	ZA2-7	ASL	Zeuxippus I	base piece, incised
	ZA2-8	CFM	Zeuxippus I	rim piece, incised
	ZA2-9	APV/ Ç. 67	Zeuxippus I	base piece, incised
	ZA2-10	ATP	Zeuxippus I	base piece, incised
	ZA2-11	ATC	Zeuxippus I	base piece, incised
	ZA2-12		Zeuxippus I	base piece, incised
	ZA2-13	BFU	Zeuxippus I	rim piece, monochrome glazed
	ZA2-14	AAC.3 2002 surface	Zeuxippus I	base piece, incised
	ZA2-15	BNC	Zeuxippus II	rim piece, stained
	ZA2-16	CFB	Zeuxippus I	base piece, incised
	ZA2-17	ADM-2	Zeuxippus I	rim piece, monochrome glazed
	ZA2-18	ABJ-21	Zeuxippus I	rim piece, incised
	ZA2-19	AAU 13	Zeuxippus I	rim piece, incised
	ZA2-20	BBJ	Zeuxippus I	rim piece, incised

Table 2.2 (cont'd) Detailed classification of Kuşadası Kadıkalesi/Anaia ceramic samples.

Anaia Zeuxippus Ware Type (ZA2)	**Sample code**	**Excavation Code**	**Subgroup Definition**	**Description**
	ZA2-21	AFO-1	Zeuxippus I	base piece, incised
	ZA2-22		Zeuxippus I	rim piece, champlevé
	ZA2-23	CJL	Zeuxippus I	base piece, monochrome glazed
	ZA2-24	AND-2	Zeuxippus I	body piece, incised
	ZA2-25	ARG	Zeuxippus I	rim piece, incised
	ZA2-26	BLC	Zeuxippus I	undefined, monochrome glazed
	ZA2-27	2001.7.4 AOB	Zeuxippus I	base piece, incised
	ZA2-28	BYB	Zeuxippus I	body piece, incised
	ZA2-29	AAU.8	Zeuxippus I	body piece, champlevé
	ZA2-30	ANA	Zeuxippus II	base piece, incised+ stained
	ZA2-31	A2E	Zeuxippus II	body piece, incised+ stained
	ZA2-32	APU	Zeuxippus I	body piece, incised
	ZA2-33	ARG	Zeuxippus I	body piece, incised
Zeuxippus Ware Family (ZFB1)	ZFB1-39	BPR		base piece, incised
	ZFB1-42	ARK		base piece, incised
	ZFB1-43			rim piece, incised
	ZFB1-44	BYB		body piece, champlevé
	ZFB1-47	BLA 182		base piece, incised
	ZFB1-48	BCO.77		base piece, incised

Table 2.2 (cont'd) Detailed classification of Kuşadası Kadıkalesi/Anaia ceramic samples.

Zeuxippus Ware Family (ZFB1)	**Sample code**	**Excavation Code**	**Subgroup Definition**	**Description**
	ZFB1-49	BJI.148		base piece, incised
	ZFB1-50	BRZ.222		body piece, incised
	ZFB1-51	CHU		body piece, incised
	ZFB1-54	BKP.191		base piece, incised+ champlevé
Zeuxippus Ware Family (ZFB2)	ZFB2-55	CCN		rim piece, monochrome glazed
	ZFB2-56	B2		handle piece, monochrome glazed
	ZFB2-57	BLP		body piece, monochrome glazed
	ZFB2-58	BZK		rim piece, monochrome glazed
	ZFB2-59	CGO		rim piece, monochrome glazed
Zeuxippus Ware Family (ZFB3)	ZFB3-60	AHY	Manganese-brown Stained Ware- 2nd quality	base piece, stained
	ZFB3-61	2001.2239	Manganese-brown Stained Ware- 1st quality	body piece, stained+ incised
	ZFB3-62	BTJ.161		body piece, stained
	ZFB3-63	BJD		rim piece, stained + incised
	ZFB3-64			base piece, stained+ incised

Table 2.2 (cont'd) Detailed classification of Kuşadası Kadıkalesi/Anaia ceramic samples.

Zeuxippus Ware Family (ZFB4)	**Sample code**	**Excavation Code**	**Subgroup Definition**	**Description**
	ZFB4-65	BYO	Incised-manganese Ware	body piece, stained+ incised
	ZFB4-66	BJP		base piece, monochrome glazed+ incised
Zeuxippus Ware Family (ZFB5)	ZFB5-67	AAS	Green Stained Incised Ware	base piece, stained+ incised
Zeuxippus Ware Family (ZFB6)	ZFB6-76	BUT-A1	Frankish Style Ceramics	rim piece, monochrome glazed
	ZFB6-77	BG2.103		rim piece, slip painted
	ZFB6-78	ASC		base piece, stained
	ZFB6-79			rim piece, monochrome glazed
	ZFB6-80	AZF		base piece, stained
	ZFB6-81	AHZ-2		rim piece, monochrome glazed
	ZFB6-83	CME 73		body piece, monochrome glazed
	ZFB6-84	CIF. 213		body piece, incised
	ZFB6-85	AFJ.3		rim piece, stained
Green Painted Ceramics (GP)	GP-68			base piece, underglaze painted
	GP-69	AKS		base piece, underglaze painted
	GP-70	CLA-76		base piece, underglaze painted

Table 2.2 (cont'd) Detailed classification of Kuşadası Kadıkalesi/Anaia ceramic samples.

Green Painted Ceramics (GP)	**Sample code**	**Excavation Code**	**Subgroup Definition**	**Description**
	GP-72	AKC		base piece, underglaze painted
Zeuxippus Ware Type Slip Painted Ceramics (ZS)	ZS-86	BVR.225		base piece, slip painted
	ZS-87	BIV-A2		base piece, slip painted
	ZS-89	ARP		rim piece, slip painted
	ZS-92	BFC		body piece, slip painted

Photographs of the investigated samples are given in Figure 2.1. Most of them show the inner sides of the sherds which have the decorations. Some additional photographs of the other sides are listed in Appendix A.

ZA1-1 ZA1-2

ZA1-3 ZA1-4

ZA1-5 ZA2-6

Figure 2.1: Photographs of the ceramic samples investigated

ZA2-7 ZA2-8

ZA2-9 ZA2-10

ZA2-11 ZA2-12

Figure 2.1 (cont'd) Photographs of the ceramic samples investigated

ZA2-13 ZA2-14

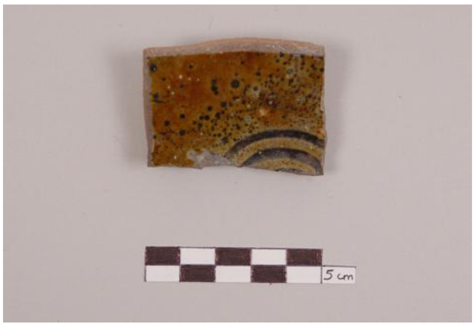
ZA2-15 ZA2-16

ZA2-17 ZA2-18

Figure 2.1 (cont'd) Photographs of the ceramic samples investigated

ZA2-19

ZA2-20



ZA2-21

ZA2-22*

ZA2-23

ZA2-24

Figure 2.1 (cont'd) Photographs of the ceramic samples investigated (*: outer side)

ZA2-25

ZA2-26

ZA2-27

ZA2-28

ZA2-29*

ZA2-30

Figure 2.1 cont'd Photographs of the ceramic samples investigated (*:outer side).

ZA2-31

ZA2-32

ZA2-33

ZFB1-39

ZFB1-42

ZFB1-43

Figure 2.1 (cont'd) Photographs of the ceramic samples investigated

ZFB1-44 ZFB1-47

ZFB1-48 ZFB1-49

ZFB1-50 ZFB1-51

Figure 2.1 (cont’d) Photographs of the ceramic samples investigated

ZFB1-54

ZFB2-55

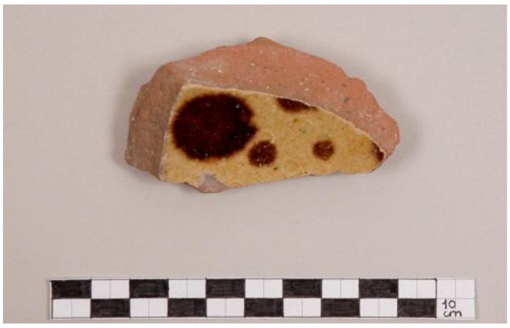
ZFB2-56

ZFB2-57

ZFB2-58

ZFB2-59

Figure 2.1 (cont'd) Photographs of the ceramic samples investigated



ZFB3-60

ZFB3-61*

ZFB3-62

ZFB3-63

ZFB3-64

ZFB4-65

Figure 2.1 (cont'd) Photographs of the ceramic samples investigated (*: outer side).

ZFB4-66*

ZFB5-67

ZFB6-76

ZFB6-77*

ZFB6-78

ZFB6-79

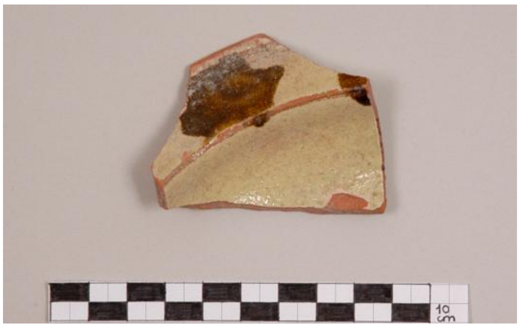
Figure 2.1 (cont'd) Photographs of the ceramic samples investigated (*: outer side).

ZFB6-80

ZFB6-81

ZFB6-83

ZFB6-84



ZFB6-85

GP-68

Figure 2.1 (cont'd) Photographs of the ceramic samples investigated

GP-69

GP-70

GP-72

ZS-86

ZS-87

ZS-89*

ZS-92

Figure 2.1 (cont'd) Photographs of the ceramic samples investigated (*:outer side)

2.2 Methods

2.2.1 Visual Examination

Colors of the body, slip, glaze and paint layers were assigned by using the catalogues named as Munsell Soil Color Charts and Munsell Glossy Finish Collection.

2.2.2 Thin Section Analysis

Thin sections of seventy-three samples were prepared in Thin Section laboratory of Geological Engineering Department of Middle East Technical University (METU). The procedure was similar to what was described by Kerr (1977, p.7-10), as follows. A slab of pottery is cut from the ceramic sample perpendicularly which is then consolidated with an epoxy resin. The cut side is polished in order to obtain a smooth surface. Then, the slab is affixed on a microscopic slide and ground away with abrasives to a uniform thickness of 0.03 mm.

Thin sections were examined using an Olympus CX31 optical microscope in the laboratories of the same department. After the examination of thin sections, representative and most significant samples were selected for further analyses. The photographs of the thin sections were taken in Geological Engineering Department and Materials Conservation Laboratory at Faculty of Architecture in METU.

2.2.3 X-Ray Diffraction Analysis (XRD)

Powdered and unoriented specimens of nineteen representative samples selected from the collection were analyzed with Rigaku Ultima IV X-ray diffractometer at METU Central Laboratory. CuK_α radiation was used. Scanning was made between 3-90 [2Θ]° with a scan speed of 2 deg./min.

2.2.4 Scanning Electron Microscopy - Energy Dispersive X-Ray Analysis (SEM-EDX)

Twenty-three representative samples were selected on the basis of thin section results and observed color of the glazes. They have been cut to about 2 cm^3 pieces and then coated with an alloy of gold and palladium for SEM-EDX analysis in the Central Laboratory (METU). Quanta 400F field emission SEM instrument was used for the investigations.

2.2.5 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Thirty samples were selected for ICP-OES/ICP-MS analyses which were performed at the Central Laboratory of METU. Samples investigated were cut into fragments and polished on an abrasive wheel in order to remove the slip and glaze layers at the Thin Section Laboratory of Geological Engineering Department (METU). Then, they were ground in an agate mortar and transferred to the Central Laboratory for the analysis. Duplicate analyses were carried out for each sample. There, they were first dried at 110°C for two hours and were digested using Anton Paar Multiwave digestion system. Samples which were taken into solution forms were analysed for their Fe, Al, Na, Mg, K, Ca, Si, Ti and Mn contents by ICP-OES technique using a Perkin Elmer Optima 4300 DV ICP-OES spectrometer. Determinations for Rb, Sr, Ba, V, Cr, Co, Ni, Zn, Pb, Tl, Zr, Nb, Ta, Y, La, Ce, Nd and Th were performed by ICP-MS technique using a Perkin Elmer Sciex ELAN DRCII ICP-MS spectrometer.

2.2.6 Statistical Analysis

The chemical composition data of thirty samples obtained from ICP-OES and ICP-MS measurements were treated statistically by a special software named Statistical Package for the Social Sciences (SPSS). Hierarchical Cluster Analysis was performed using Pearson correlation and the nearest neighbour method. Two different tests were carried out first by using all of the major and trace elements measured and then by using only trace elements involved. In addition, bi-plots for the elements of interest and ternary diagrams were also carried out using another software called Origin 5.0.

2.2.7 Raman Spectrometry

Thirty representative samples were chosen for investigating their glaze layers by using non-destructive Raman Spectrometry investigations. Sixteen of these samples (ZA1-1, ZA1-2, ZA1-3, ZA1-4, ZA1-5, ZA2-6, ZA2-7, ZA2-8, ZA2-9, ZA2-12, ZA2-15, ZA2-16, ZA2-17, ZA2-22, ZA2-31, ZA2-33) were analysed in Laboratoire Dynamique Interactions et Réactivité (LADIR) (CNRS, Université Pierre et Marie Curie) in Paris during the author’s stay in France as a TUBİTAK fellow between October 2008-August 2009. Three Raman spectrometers, “Labram Infinity” (Jobin Yvon), “HR800” (Jobin Yvon) and “HE532” (Jobin Yvon Horiba) were used for the micro analysis of the ceramic glazes.

532 nm Nd:YAG laser line was used during the measurements with “Labram Infinity” while Ar^+/Kr^+ laser operating at 514 nm was used for the measurements of “HR800”. Backscattering illumination and collection of the scattered light were made through an Olympus confocal microscope (long focus Olympus x50 objective, total magnification x 500) in these instruments. The laser power on the samples was about 1-2 mW. “HE532” as the mobile Raman spectrometer was also equipped with a green 100 mW Nd:YAG laser at 532 nm

(Laser Quantum Torus, Stockport, UK) which directly injects the laser beam into an optic fiber leading up to the Horiba Jobin-Yvon Superhead (Longjumeau, France). A Nikon x50 ultra long-working distance objective was used during the measurements. The laser power at the samples was about 1-2 mW.

Fourteen of the samples (ZFB1-42, ZFB1-47, ZFB1-51, ZFB2-59, ZFB3-64, ZFB4-65, ZFB5-67, ZFB6-78, ZFB6-81, ZFB6-84, ZFB6-85 GP-68, GP-72, ZS-89) were analysed in METU-Central Laboratory. Renishaw invia Raman spectrometer was used for the measurements with an air cooled DPSS laser at 532 nm. The laser power used was 0.5- 10 mW.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Visual Examination

Detailed visual descriptions for the slip and glaze parts of the ceramic samples are listed in Table 3.1. Most of the samples have both slips and glazes only on the inner sides. They are sometimes present only on the outer sides of the sherds. The glaze colors which are observed visually usually display tones of yellow, brown and green.

Bodies of the ceramic samples investigated mostly display tones of red, brown and yellow in 2.5 and 5YR scales according to Munsell Soil Color charts which indicates the oxidizing firing conditions of the kilns. Colors of the glaze and paints were also determined according to the Munsell Book of Color. Results of the body, glaze and paint colors recorded are listed in Table B.1 (Appendix B).

An example for a ceramic drawing is given in Figure 3.1.

Table 3.1: Detailed visual descriptions of Kuşadası Kadıkalesi/Anaia ceramic samples investigated (+: present, -: absent)

Sample code	**Presence of slip on the sides**	**Presence of glaze on the sides**	**Observed glaze color**
ZA1-1	In:? Out:-	In:+ Out:-	Yellow, orange, green
ZA1-2	In:+ Out:-	In:+ Out:-	Yellow, orange, green
ZA1-3	In:+ Out:+	In:+ Out:-	Yellow, orange, green
ZA1-4	In:+ Out:-	In:+ Out:-	Yellow, orange, green
ZA1-5	In:+ Out:+	In:+ Out:+	Yellow, orange, green
ZA2-6	In:+ Out:-	In:+ Out:-	Yellow
ZA2-7	In:+ Out:-	In:+ Out:+	In:yellow Out:brown
ZA2-8	In:+ Out:+	In:+ Out:+	Honey brown
ZA2-9	In:+ Out:-	In:+ Out:-	Green
ZA2-10	In:- Out:-	In:+ Out:-	Brown
ZA2-11	In:+ Out:-	In:+ Out:-	Yellow
ZA2-12	In:+ Out:-	In:+ Out:-	Green
ZA2-13	In:+ Out:+	In:+ Out:-	Green
ZA2-14	In:+ Out:-	In:+ Out:-	Green
ZA2-15	In:+ Out:+	In:+ Out:-	Honey brown, green
ZA2-16	In:- Out:-	In:+ Out:-	Brown
ZA2-17	In:+ Out:+	In:+ Out:+	Green
ZA2-18	In:+ Out:+	In:+ Out:-	Brown

Table 3.1 (cont'd) Detailed visual descriptions of the ceramic samples

Sample code	**Presence of slip on the sides**	**Presence of glaze on the sides**	**Observed glaze color**
ZA2-19	In:+ Out:+	In:+ Out:+	Green
ZA2-20	In:+ Out:+	In:+ Out:+	Honey brown
ZA2-21	In:- Out:-	In:+ Out:-	Brown
ZA2-22	In:+ Out:+	In:+ Out:+	Light and olive green
ZA2-23	In:+ Out:-	In:+ Out:-	Green
ZA2-24	In:- Out:-	In:+ Out:+	Honey brown
ZA2-25	In:+ Out:+	In:+ Out:-	Honey brown
ZA2-26	+	+	Honey brown
ZA2-27	In:- Out:-	In:+ Out:-	Brown
ZA2-28	In:+ Out:-	In:+ Out:-	Dark yellow
ZA2-29	In:- Out:+	In:- Out:+	Green
ZA2-30	In:+ Out:-	In:+ Out:-	Yellow, honey brown
ZA2-31	In:+ Out:-	In:+ Out:-	Yellow, honey brown
ZA2-32	In:+ Out:-	In:+ Out:-	Honey brown
ZA2-33	In:+ Out:-	In:+ Out:-	Honey brown
ZFB1-39	In:+ Out:-	In:+ Out:-	Yellow
ZFB1-42	In:- Out:-	In:+ Out:-	Honey brown
ZFB1-43	In:+ Out:+	In:+ Out:+	Honey brown
ZFB1-44	In:+ Out:+	In:+ Out:+	Olive green

Table 3.1 (cont'd) Detailed visual descriptions of the ceramic samples

Sample code	**Presence of slip on the sides**	**Presence of glaze on the sides**	**Observed glaze color**
ZFB1-47	In:+ Out:-	In:+ Out:-	Honey brown
ZFB1-48	In:+ Out:-	In:+ Out:-	Honey brown
ZFB1-49	In:- Out:-	In:+ Out:-	Honey brown
ZFB1-50	In:+ Out:+	In:+ Out:-	Yellow
ZFB1-51	In:+ Out:+	In:+ Out:+	Yellow
ZFB1-54	In:+ Out:-	In:+ Out:-	Yellow
ZFB2-55	In:- Out:-	In:+ Out:+	Brown
ZFB2-56	In:- Out:-	In:+ Out:+	Honey brown/green
ZFB2-57	In:+ Out:+	In:+ Out:?	Greenish yellow
ZFB2-58	In:- Out:-	In:+ Out:+	Honey brown/green
ZFB2-59	In:+ Out:+	In:+ Out:+	Honey brown
ZFB3-60	In:+ Out:-	In:+ Out:-	Yellow, purple
ZFB3-61	In:- Out:+	In:- Out:+	Light green, purple
ZFB3-62	In:+ Out:-	In:+ Out:+	Yellow, purple
ZFB3-63	In:? Out:+	In:+ Out:+	Yellow, purple
ZFB3-64	In:+ Out:+	In:+ Out:+	Yellow, purple
ZFB4-65	In:+ Out:+	In:+ Out:+	In:light green,purple Out:green
ZFB4-66	In:+ Out:+	In:+ Out:+	In:green Out:light green

Table 3.1 (cont'd) Detailed visual descriptions of the ceramic samples

Sample code	**Presence of slip on the sides**	**Presence of glaze on the sides**	**Observed glaze color**
ZFB5-67	In:+ Out:-	In:+ Out:-	Yellow, green
ZFB6-76	In:+ Out:+	In:+ Out:-	Light green
ZFB6-77	In:+ Out:+	In:+ Out:+	Yellow, brown
ZFB6-78	In:+ Out:-	In:+ Out: -	Yellow, purple
ZFB6-79	In:+ Out:+	In:+ Out:-	Cream
ZFB6-80	In:+ Out:-	In:+ Out:-	Yellow, purple
ZFB6-81	In:+ Out:-	In:+ Out:-	Dark green
ZFB6-83	In:- Out:-	In:+ Out:-	Honey brown
ZFB6-84	In:+ Out:-	In:+ Out:+	In:Yellow Out:Honey brown
ZFB6-85	In:+ Out:+	In:+ Out:-	Yellow, brown
GP-68	In:- Out:-	In:+ Out:-	Transparent
GP-69	In:- Out:-	In:+ Out:-	Transparent
GP-70	In:- Out:-	In:+ Out:-	Transparent
GP-72	In:- Out:-	In:+ Out:-	Yellow
ZS-86	In:+ Out:-	In:+ Out:-	Brown, green
ZS-87	In:+ Out:-	In:+ Out:-	Brown, honey brown
ZS-89	In:+ Out:-	In:+ Out:-	Brown, yellow
ZS-92	In:+ Out:-	In:+ Out:-	Brown, green

Figure 3.1: The drawing of *Anaia Zeuxippus Ware Type* sample ZA1-5 (diameter: 19 cm) (drawn by Ulaş Deniz).

3.2 Mineralogical and Micromorphological Analysis of the Body, Slip and Glaze Layers

3.2.1 Body

Mineralogical and micromorphological analyses of the body parts were carried out by thin section, XRD and SEM analyses.

Ceramic pastes are observed to be cryptocrystalline and always matrix-supported, displaying grains with no contact to each other, as seen in their thin section images (Figure 3.2a). Grains are usually moderately sorted in the ceramic matrices (Figure 3.2b), although poor (Figure 3.2c) and well sorting (Figure 3.2a) are also observed in some of the samples. The grains, whether they are individual mineral grains or rock fragments in the matrix, display a variety of shapes such as angular, subangular, subrounded and rounded (Appendix C). The first three shapes are more abundant, indicating that these grains have possibly been added to the ceramic bodies as temper (Figure 3.2c).

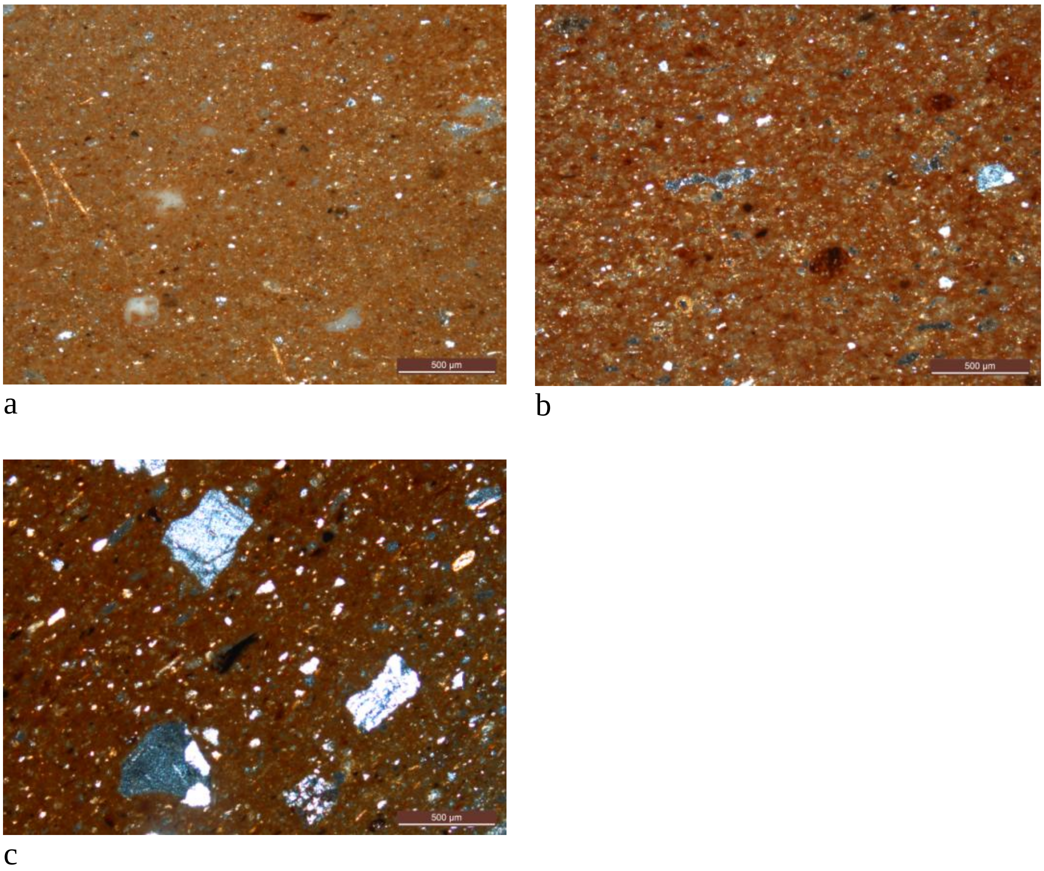
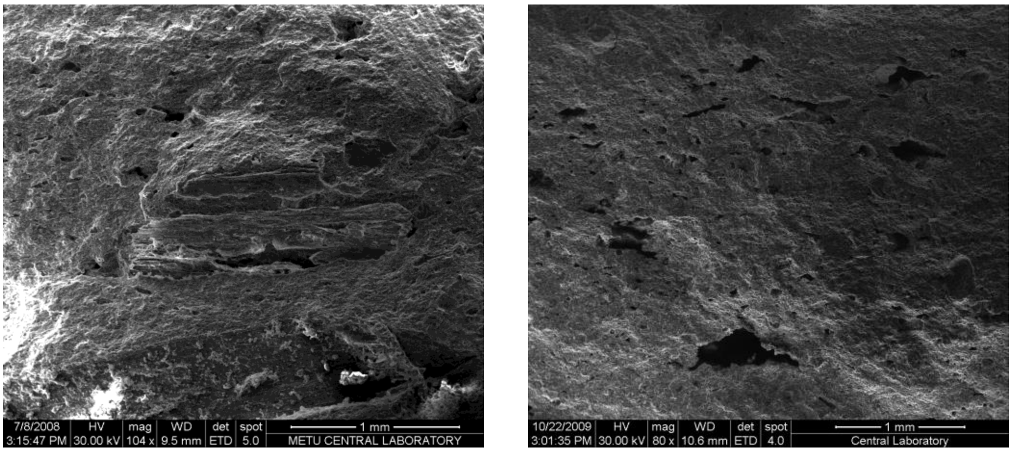


Figure 3.2: Thin section images of ceramic bodies with XPL, a) *Zeuxippus Ware Family* sample ZFB1-39 showing the typical matrix-supported paste and well sorted grains, b) *Anaia Zeuxippus Ware Type* sample ZA1-1 showing moderately sorted grains, c) *Zeuxippus Ware Family* sample ZFB6-76 showing poorly sorted and angular grains.

All ceramic samples display porous texture (Figure 3.3a-b), most of which also present partial vitrification when viewed by SEM (Figure 3.4). Some of the samples seem to have a higher degree of vitrification (Figure 3.5).The pores are sometimes found to be filled with secondary micritic calcite as a result of precipitation from pore water during burial in the soil.



a b

Figure 3.3: Representative SEM images of ceramic bodies displaying porosity; a) *Anaia Zeuxippus Ware Type* sample ZA1-5, b) *Anaia Zeuxippus Ware Type* sample ZA2-15

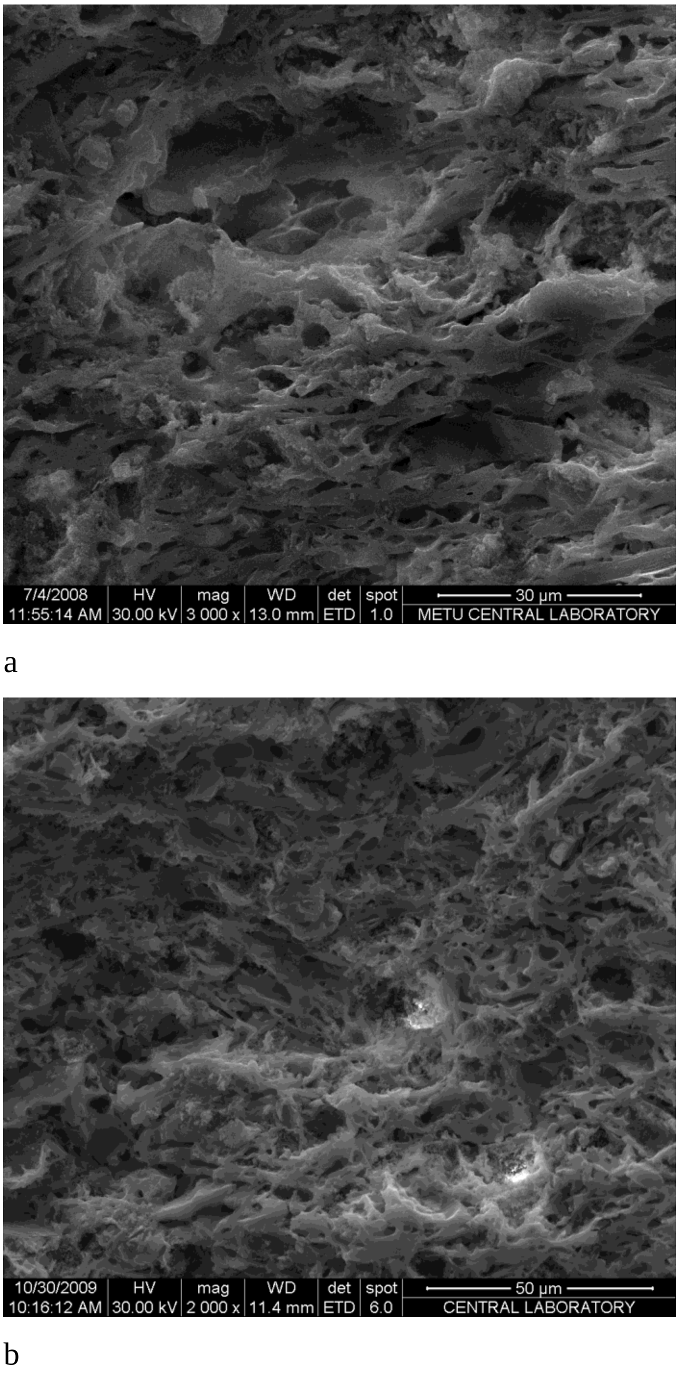


Figure 3.4: Representative SEM images of ceramic bodies displaying partial vitrification; a) *Anaia Zeuxippus Ware Type* sample ZA1-3, b) *Anaia Zeuxippus Ware Type* sample ZA2-16

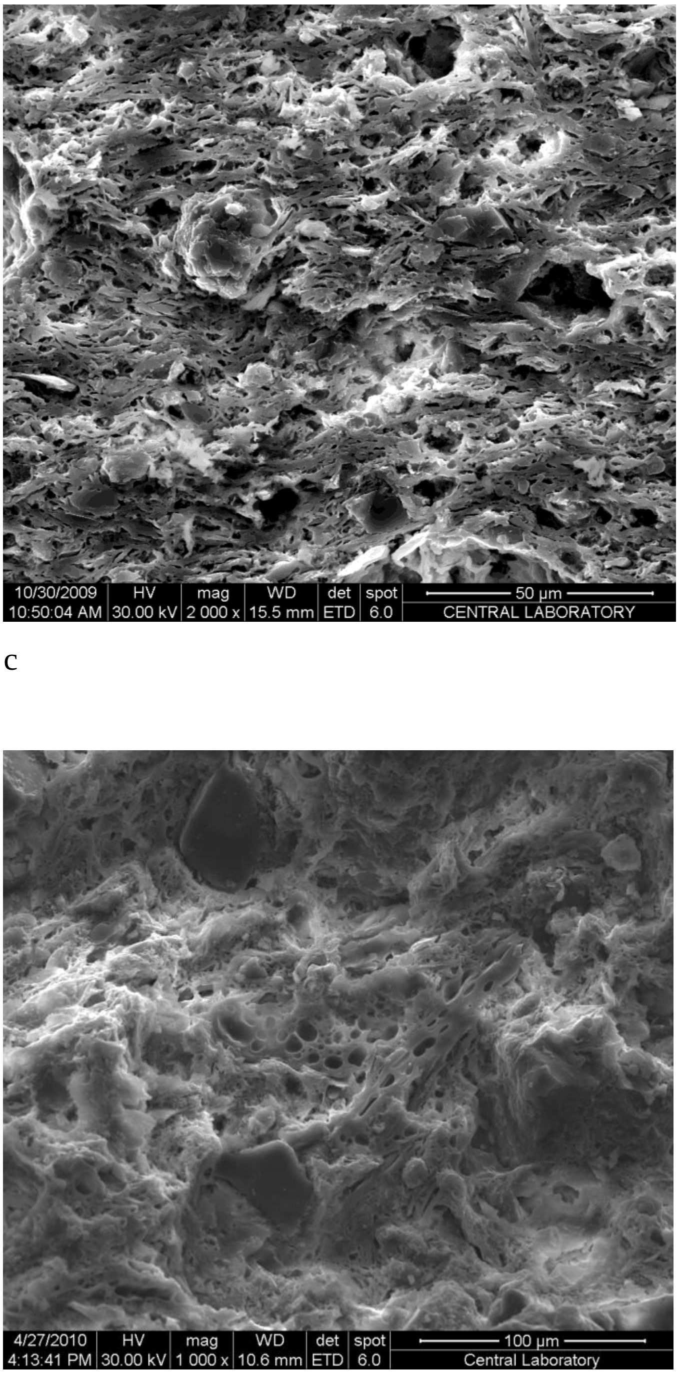


Figure 3.4 (cont'd) Representative SEM images of ceramic bodies displaying partial vitrification; c) *Anaia Zeuxippus Ware Type* sample ZA2-22, d) *Zeuxippus Ware Family* sample ZFB1-51

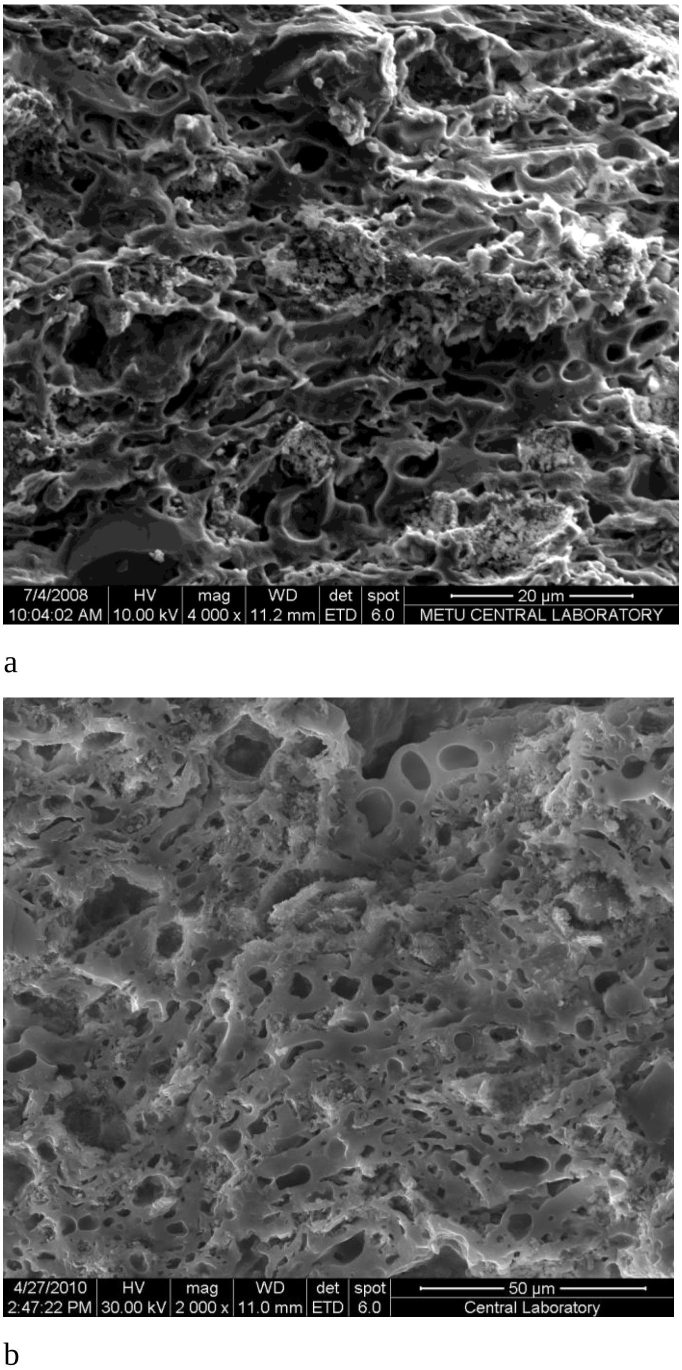
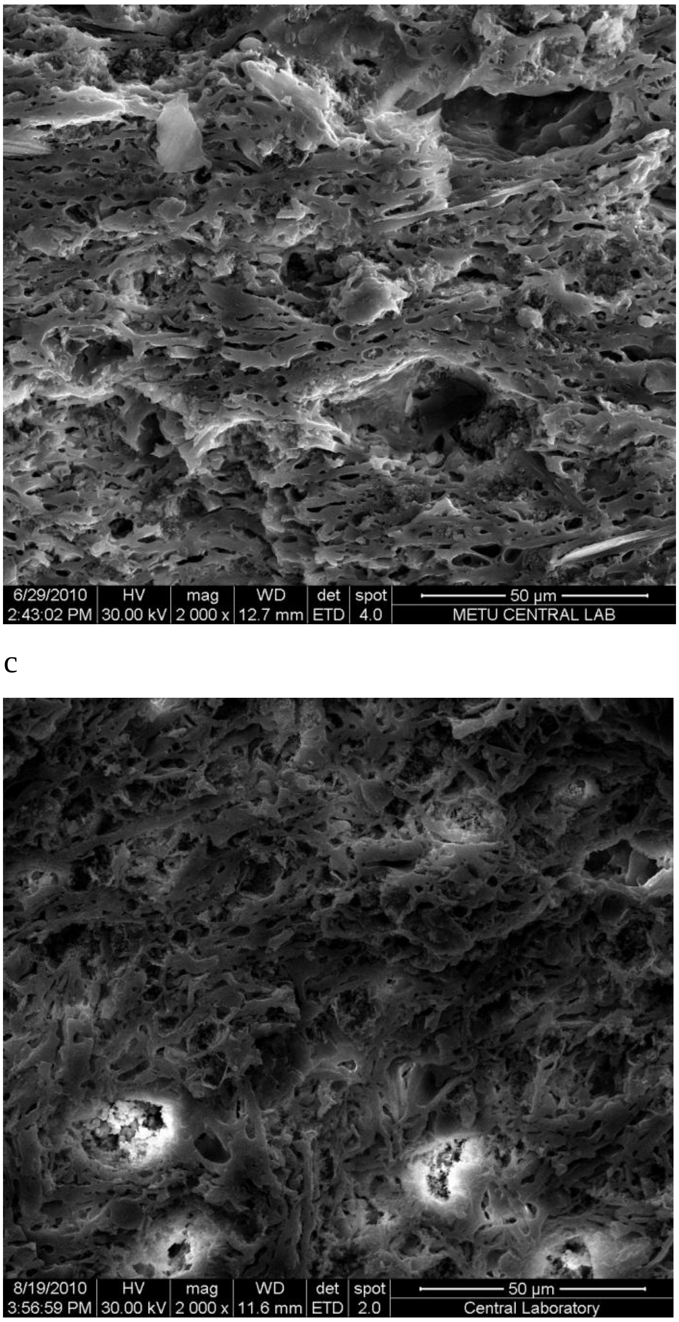


Figure 3.5: Representative SEM images of ceramic bodies displaying higher degree of vitrification; a) *Anaia Zeuxippus Ware Type* sample ZA1-1, b) *Zeuxippus Ware Family* sample ZFB1-42.



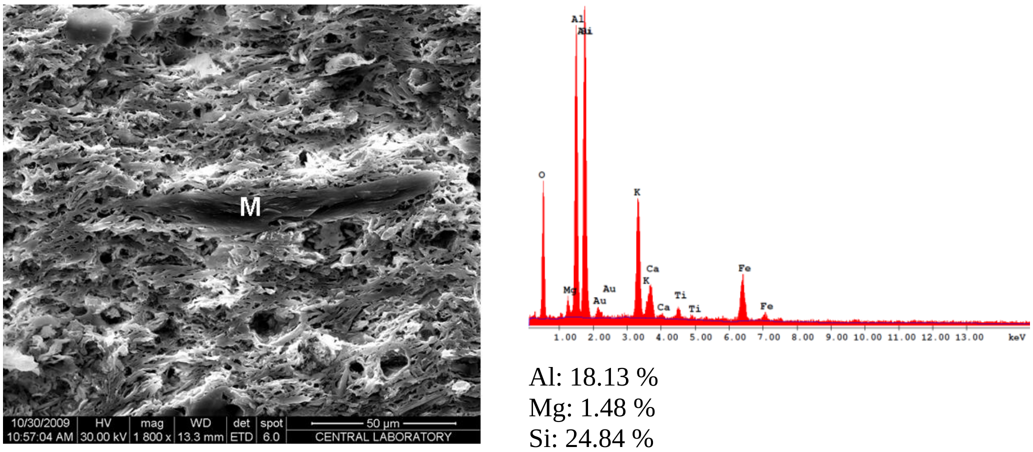
c

d

Figure 3.5 (cont'd) Representative SEM images of ceramic bodies displaying higher degree of vitrification, c) *Zeuxippus Ware Family* sample ZFB3-64, d) *Zeuxippus Ware Family* sample ZFB6-81

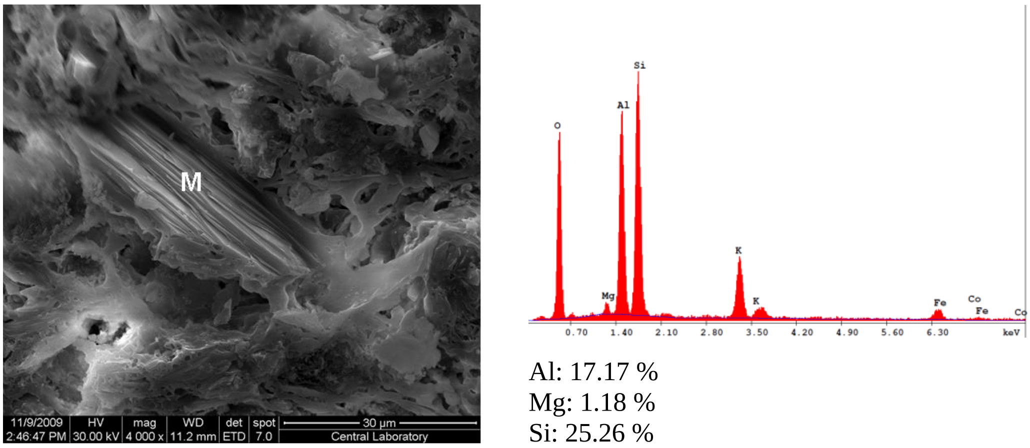
The mineralogy of the samples does not include much variety and is most of the time uniform. Common minerals detected by optical microscopy in ceramic bodies are quartz, feldspars (plagioclase), micas (biotite and muscovite) and iron-oxide minerals such as hematite. Less common minerals are calcite and amphiboles (hornblende) (Figure 3.6). There are also opaque minerals which could not be identified by the optical microscope. Some of these minerals such as quartz, feldspars (albite), hematite, calcite and mica were also identified by either XRD analysis (Table 3.2) or by SEM-EDX (Figure 3.7).

Figure 3.6: Thin section image of *Zeuxippus Ware Family* sample ZFB1-51 with XPL, magnification x10 (H: hornblende)



a

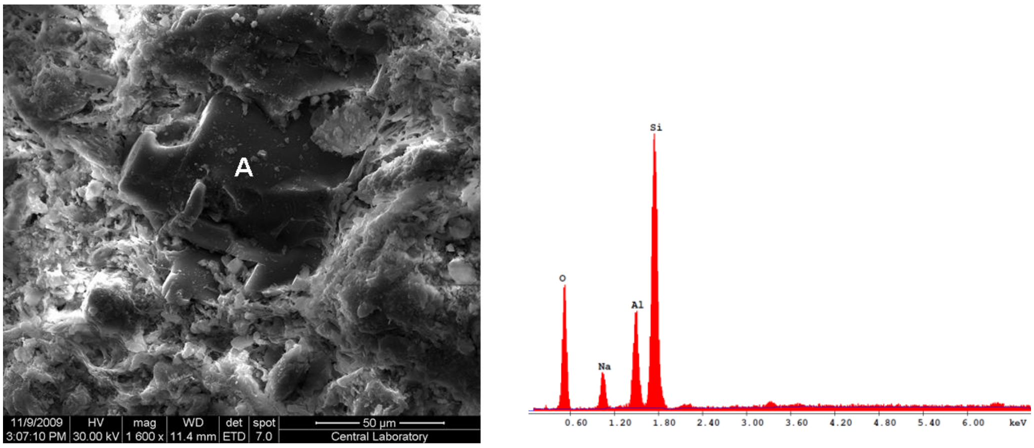
Al: 18.13 %
Mg: 1.48 %
Si: 24.84 %
K: 9.41 %
Fe: 6.36 %
O: 33.37 %



b

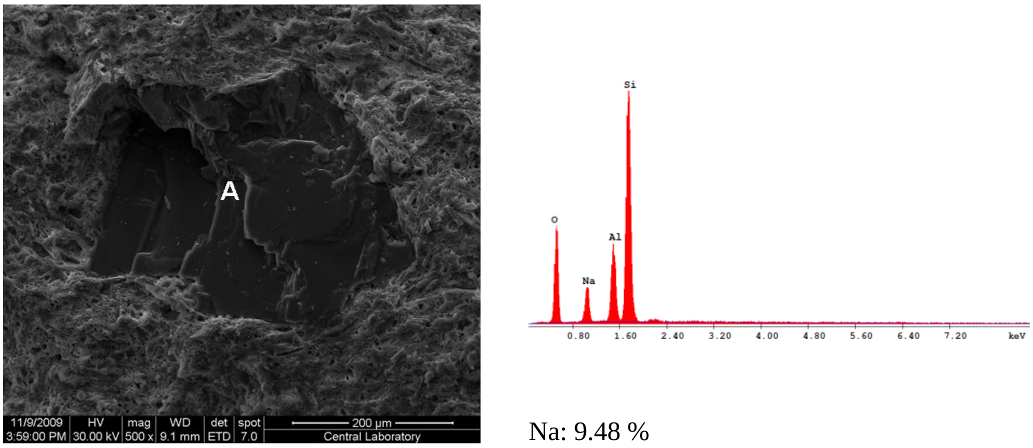
Al: 17.17 %
Mg: 1.18 %
Si: 25.26 %
K: 6.11 %
Fe: 2.03 %
O: 47.98 %

Figure 3.7: Images of minerals identified and their compositions in weight percent for *Anaia Zeuxippus Ware Type* ceramic bodies by SEM-EDX, a) sample ZA2-22, b) sample ZA2-8. Note the high levels of Al, K and Si detected (M: mica).



c

Na: 7.94 %
Al: 11.77 %
Si: 35.82 %
O: 44.47 %



Na: 9.48 %
Al: 11.59 %
Si: 35.48 %
O: 43.44 %

d

Figure 3.7 (cont'd) Images of minerals identified and their compositions in weight percent for *Anaia Zeuxippus Ware Type* ceramic bodies by SEM-EDX c) sample ZA2-8, d) sample ZA2-11. Note the high levels of Na and Al detected (A: albite)

Table 3.2: d-spacing values (A°) in XRD spectra of Kuşadası Kadıkalesi/Anaia samples

Sample code	**d- spacing values (A°)**	**Mineral phase**
ZA1-1	3.348,1.824	Quartz
	3.211	Plagioclase
ZA1-2	3.353, 4.275	Quartz
	3.202	Plagioclase
	3.034	Calcite
ZA1-3	3.353, 1.819	Quartz
	3.243	Plagioclase
	2.69,2.523	Hematite
ZA2-6	3.348, 4.275	Quartz
	3.22	Plagioclase
	3.044	Calcite
	2.703	Hematite
ZA2-7	3.358	Quartz
	3.262, 3.215, 3.211	Plagioclase
	3.0	Calcite
ZA2-8	3.353, 1.82	Quartz
	3.22, 3.197	Plagioclase
ZA2-9	4.258, 3.348, 1.541	Quartz
	3.035, 2.468, 2.285	Calcite
	9.95, 3.30, 1.994	İllite-mica ?
ZFB1-42	4.267, 3.348,1.812	Quartz
	3.206, 4.059	Plagioclase
	2.996, 2.949, 3.779, 2.458	Mg-calcite
ZFB1-47	4.267, 3.348, 1.82, 1.543	Quartz
	3.197	Plagioclase
	3.035, 2.285	Calcite
	2.70, 2.517	Hematite
ZFB1-51	4.267, 3.348,1.819, 1.543	Quartz
	3.243, 3.202	Plagioclase
	3.035, 2.285	Calcite
	2.696, 2.517	Hematite
ZFB2-59	4.275, 3.35, 1.82, 1.543	Quartz
	3.044, 2.285	Calcite
ZFB3-64	4.275, 3.353, 1.821, 1.543	Quartz
	3.202	Plagioclase
	3.007, 2.287	Calcite
	2.703, 2.517	Hematite
ZFB4-65	4.259, 3.343,1.819, 1.542	Quartz
	3.193	Plagioclase
	2.696, 2.517	Hematite

Table 3.2 (cont'd) d-spacing values (A°) in XRD spectra of Kuşadası Kadıkalesi/ Anaia samples

Sample code	d- spacing values (A°)	Mineral phase
ZFB5-67	4.259, 3.348, 1.819, 1.541	Quartz
	3.202	Plagioclase
	2.693, 2.517	Hematite
ZFB6-76	4.259, 3.348, 1.819, 1.542	Quartz
	4.037, 3.238, 3.193	Plagioclase
	3.023, 2.281	Calcite
ZFB6-78	4.259, 3.348, 1.819, 1.542	Quartz
	3.197	Plagioclase
ZFB6-81	4.259, 3.348, 1.817	Quartz
	4.051, 3.215, 3.197	Plagioclase
	2.696, 2.514, 1.842	Hematite
	2.988, 2.945, 3.760, 2.458	Mg-calcite
ZBB6-84	4.267, 3.353, 1.82, 1.543	Quartz
	4.044, 3.249, 3.202	Plagioclase
ZS-89	4.275, 3.353, 1.821, 1.544	Quartz
	3.238, 3.206	Plagioclase
	2.693, 2.520	Hematite

According to the XRD results, quartz was detected in all samples analyzed, most of the time displaying its initial four most intensive peaks (d= ~ 3.34, 4.26, 1.82, 1.54 A°). The intensity of quartz peaks shows the abundance of quartz in the raw material of these ceramics. Together with quartz, feldspar/ plagioclase was also detected in almost all the samples (Table 3.2, Figure 3.8). Some of the samples in groups of *Anaia Zeuxippus Ware Type* as ZA1-2, ZA2-6, ZA2-7, ZA2-9 and of *Zeuxippus Ware Family* as ZFB1-47, ZFB1-51, ZFB2-59, ZFB3-64, ZFB6-76 display peaks of calcite (calcium carbonate) which most of the time seems to indicate secondary calcite coming as a result of burial under the soil. Calcite was observed in the form of micritic calcite in thin sections for these cases. However, in some of the samples such as ZFB3-64, the calcite peaks in

XRD traces may refer to limestone fragments which are also observed under the optical microscope. The presence of primary calcite indicates a firing temperature not more than 900°C for the body parts, as calcite decomposes at temperatures between 650 - 900° C to CaO.

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

High temperature minerals such as spinel, cristobalite and mullite were not detected by XRD analyses which supports predictions for a firing temperature not exceeding 850°C for the ceramic bodies investigated (Grim 1968, p.596). The presence of angular quartz grains in almost all Kuşadası Kadıkalesi/Anaia sample bodies analysed may also support this prediction, indicating firing temperatures below 1000°C (Tite 1989). An evidence of relatively low temperatures of firing also comes from the analyses of a ninth century Byzantine ceramic sample from İznik (Kapur et al. 1998).

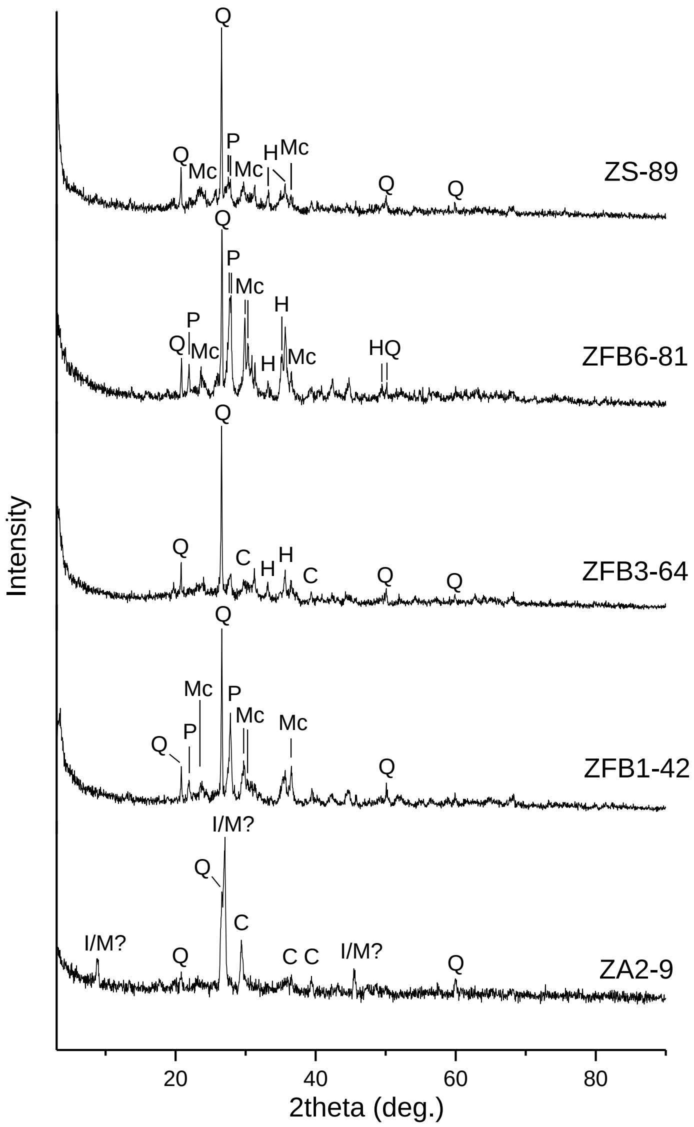


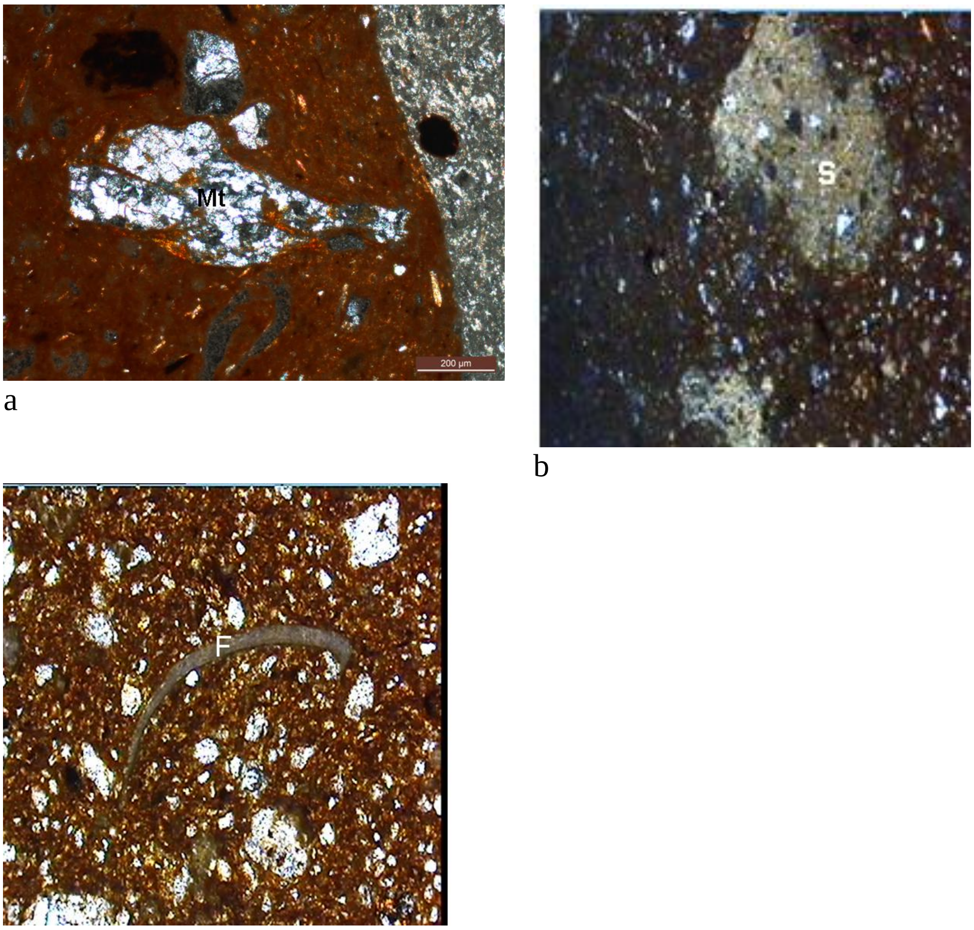
Figure 3.8: Representative XRD spectra for bodies of *Anaia Zeuxippus Ware Type* sample ZA2-9, *Zeuxippus Ware Family* samples ZFB1-42, ZFB3-64, ZFB6-81 and *Zeuxippus Ware Type Slip Painted* sample ZS-89 (Q: quartz, P:plagioclase, I-M: Illite-mica, C: calcite, Mc: Mg-calcite, H: hematite).

Due to the presence of excess amounts of iron in their clay matrix, ceramic bodies investigated in the optical microscope usually have the varying tones of red and brown colors when observed with crossed polars. This may indicate that they were fired under oxidizing atmospheric conditions in the kiln. Under these circumstances, all the Fe species found in ceramic bodies are expected to be oxidized into Fe^{3+}. The presence of iron oxides in the bodies is confirmed by the observation of hematite under the optical microscope as well as the detection of hematite in some of the XRD spectra (Table 3.2).

Rock fragments which are usually of metamorphic origin were observed in almost all the samples (Figure 3.9a). This is consistent with the metamorphic local geology of the area where the Menderes Massif is located (http://www.mta.gov.tr/v2.0/daire-baskanliklari/jed/index.php?id=500basharita, last accessed date: March 2011). Fragments of limestone were also encountered such as in *Zeuxippus Ware Family* sample ZFB6-80 (Figure 3.9b). Fossil fragments which are commonly used as temper in ceramic pastes were also observed in some *Zeuxippus Ware Family* samples as in ZFB6-78 (Figure 3.9c).

Petrographic characteristics of most Kuşadası Kadıkalesi/Anaia ceramics analyzed resemble those of *Zeuxippus Ware Family* ceramics found in Acre (a town in the Crusader Kingdom of Jerusalem) (Stern and Waksman 2003). These ceramics are considered to have been imported to Acre. They were found to have a finely micaceous matrix tempered with quartz, micas, feldspars and metamorphic rock fragments etc., pointing also to a metamorphic terrain.

In addition, the mineralogy of Late Byzantine ceramics from Sardis (Manisa) which were local productions, seems to show affinity with that of Kuşadası Kadıkalesi/Anaia samples as they contain much quartz, plagioclases, micas and metamorphic rock fragments (Scott and Kamilli 1981).



a

b

c

Figure 3.9: Thin section images of ceramic bodies, a) *Anaia Zeuxippus Ware Type* sample ZA2-25, XPL, (Mt: Metamorphic rock fragment), b) *Zeuxippus Ware Family* sample ZFB6-80, XPL, magnification x4 (S: sedimentary rock fragment), c) *Zeuxippus Ware Family* sample ZFB6-78, PPL, magnification x4 (F: fossil fragment)

In the light of these observations, a classification of ceramic bodies can be proposed on the basis of two criteria by applying the charts prepared by Terry and Chilingar (1955) (Appendix C).

1- using their mica content, 2- their grain/ matrix ratio by area

Ceramic bodies can be classified into three groups according to their mica content:

Group 1: bodies with the low mica content (~ 0-2 %)

Group 2: bodies with medium mica content (~ 3-7 %)

Group 3: bodies with the high mica content (~ 10-25 %).

Kuşadası Kadıkalesi/Anaia ceramic bodies were found to be mostly in group 2 and group 3, displaying a micaceous matrix while group 1 was encountered to a smaller extent (Figure 3.10). Some of the samples fall into the intermediate groups as 1-2 (~ 2-3 %) and 2-3 (~ 7-10 %) (Table 3.3, Figure 3.11).

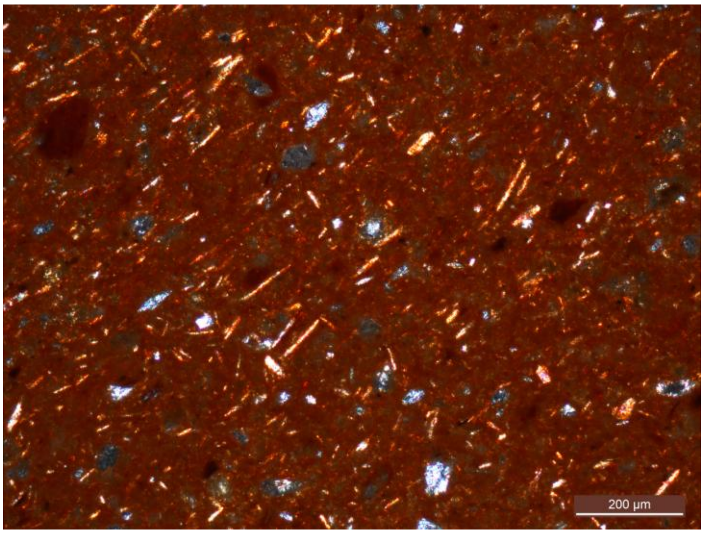


Figure 3.10: Thin section image of *Anaia Zeuxippus Ware Type* sample body ZA1-3 with XPL. Fibreous crystals refer to mica minerals.

Table 3.3: Classification of sample bodies according to their mica contents

Group	**Mica content**	**Sample codes**	**Total**
1	~ 0-2 %	ZA2-7, ZA2-10, ZA2-12, ZFB1-42, ZFB2-55, ZFB2-56, ZFB2-58, GP-68, ZFB6-78, ZFB6-79, ZFB6-84, ZS-86	12
1-2	~ 2-3 %	ZA2-21, ZFB1-39, ZFB1-48, ZFB3-60, ZFB3-63	5
2	~ 3-7 %	ZA1-1, ZA2-11, ZA2-13, ZA2-14, ZA2-15, ZA2-16, ZA2-17, ZA2-22, ZA2-26, ZA2-27, ZA2-30, ZFB1-43, ZFB1-44, ZFB1-49, ZFB1-50, ZFB3-61, ZFB6-76, ZFB6-77, ZFB6-80, ZFB6-81, ZFB6-83, ZS-87	22
2-3	~ 7-10 %	ZA2-18, ZA2-32, ZFB1-51, ZFB3-62, ZFB4-66, ZS-92	6
3	~ 10-25 %	ZA1-2, ZA1-3, ZA1-4, ZA1-5, ZA2-6, ZA2-8, ZA2-9, ZA2-19, ZA2-20, ZA2-23, ZA2-24, ZA2-25, ZA2-28, ZA2-29, ZA2-31, ZA2-33, ZFB1-47, ZFB1-54, ZFB2-57, ZFB2-59, ZFB3-64, ZFB4-65, ZFB5-67, GP-69, GP-70, GP-72, ZFB6-85, ZS-89	28

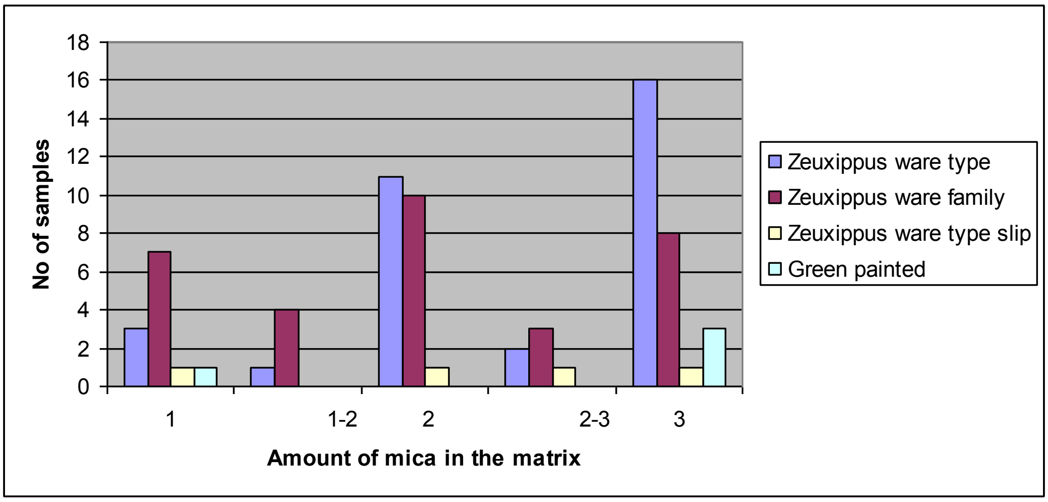


Figure 3.11: Distribution of the number of samples per each sampling group with respect to their mica content (1: ~ 0-2 %, 1-2: ~ 2-3 %, 2: ~ 3-7 %, 2-3: ~ 7-10 %, 3: ~ 10-25 %)

As can be seen in Figure 3.11; most of the samples in *Anaia Zeuxippus Ware Type* (ZA) , *Zeuxippus Ware Family* (ZFB) and *Green Painted* (GP) groups fall into group 2 and/or 3. However, *Zeuxippus Ware Family* ceramics includes a considerable number of its samples in group 1. It is not possible to argue on *Zeuxippus Ware Type Slip Painted* (ZS) and *Green Painted* (GP) ceramic groups since they have a small number of samples.

The presence of considerable amounts of fine mica in ceramic bodies is usually interpreted as coming from the use of a micaceous clay type. As long as the particle sizes of mica fragments are not large, it is more likely that they are already present in the clay matrix, especially in the case of primary clays which are deposits remaining more or less in the same location as the parent rock from which they developed. Consequently, observation of both micaceous and non-micaceous bodies in Kuşadası Kadıkalesi/Anaia ceramics strongly suggests that at least two different types of clay sources have been used in the production of these samples. These different types of clays may also indicate the activity of different workshops at Kadıkalesi/Anaia for the mentioned period. However, different clay sources could have been used in the same workshop. Previously, it was also pointed out that a range of ceramic types from a variety of raw materials could have been produced at a single site during the Medieval times (François et al. 2003). Using a variety of clay sources in the local production of Medieval ceramics, even in the same category of ceramic types, was also mentioned for Ephesus which is located about 25 km north of Kadıkalesi (Sauer and Waksman 2005).

Anaia Zeuxippus Ware Type ceramics which are believed to be local productions of Kuşadası Kadıkalesi/Anaia consist of mostly micaceous bodies. This characteristic can be attributed as the general characteristic of the local production. This characteristic is also in accordance with the micaceous content of Western Anatolia soils. In a similar study, locally produced Byzantine ceramics from Ephesus dating to the 14th and 15th centuries were also reported to have micaceous bodies (Sauer and Waksman 2005). In addition, ceramics with micaceous bodies are very well-known in Western Anatolian archaeological contexts dating as early as prehistoric times (Seifert and Yalçın 1995; Mee 1998).

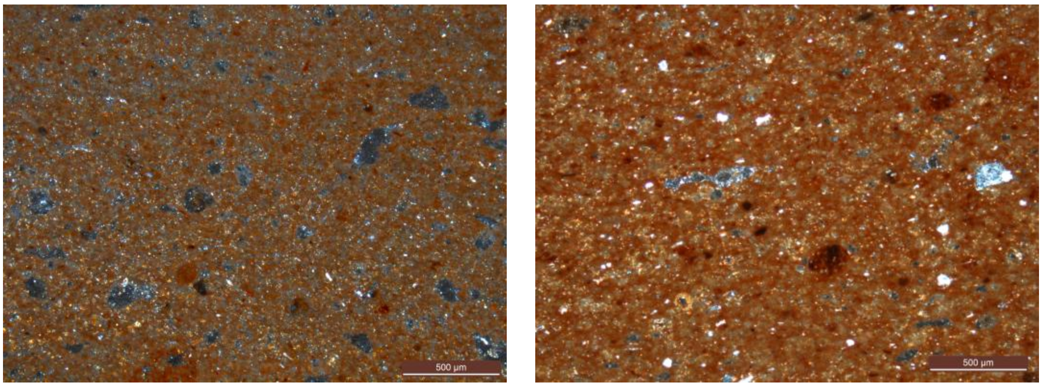
Again based on the same charts (Terry and Chilingar 1955), ceramic bodies can also be classified according to their grain/matrix ratios:

Group A: bodies with the low grain/matrix ratio (~2-3 %)

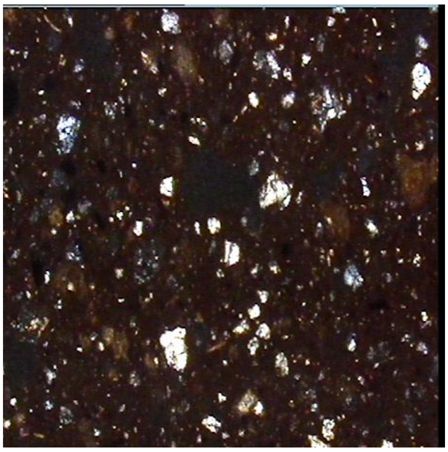
Group B: bodies with medium grain/matrix ratio (~5-10 %)

Group C: bodies with the high grain/matrix ratio (~15-20 %)

Groups observed according to grain/matrix ratios may point to variations in processing the raw materials or differences in the raw material sources. Particularly, ceramic bodies belonging to Group C with the high grain/matrix ratios (~ 15-20 %) can be considered to have intentionally added tempers. Most of the bodies of the samples investigated fall into group C while some of them can be classified in group B. Only a few of the bodies belongs to group A (Figure 3.12). Transitional groups as A-B and B-C with intermediate ratios as ~ 3-5 % and ~ 10-15 % are also present among the samples (Table 3.4, Figure 3.13).



a) Group A b) Group B



c) Group C

Figure 3.12: Thin section images of sample bodies presenting groups of grain/ matrix ratios in XPL; *Anaia Zeuxippus Ware Type* samples a) ZA2-16, b) ZA1-1, *Zeuxippus Ware Family* samples c) ZFB6-76, d) ZFB6-78 (magnification x4)

Table 3.4: Classification of sample bodies according to their grain/matrix ratios.

Group	**Grain/matrix ratio**	**Sample codes**	**Total**
A	~ 2-3 %	ZA2-16, ZFB1-39, ZS-86	3
A-B	~ 3-5 %	ZA2-12, ZA2-18, ZA2-22, ZA2-26, ZA2-28, ZFB1-43, ZFB1-44, ZFB1-54, ZFB3-62, ZFB6-81, ZS-87	11
B	~ 5-10 %	ZA1-1, ZA1-2, ZA1-3, ZA2-13, ZA2-20, ZFB1-49, ZFB2-57, ZFB2-59, ZFB3-63, GP-70, ZFB6-83, ZFB6-85	12
B-C	~ 10-15 %	ZA2-7, ZA2-17, ZA2-23, ZA2-29, ZFB2-55, ZFB3-61, ZFB3-64, ZFB5-67, ZFB6-77, ZFB6-79, ZS-89, ZS-92	12
C	~ 15-20 %	ZA1-4, ZA1-5, ZA2-6, ZA2-8, ZA2-9, ZA2-10, ZA2-11, ZA2-14, ZA2-15, ZA2-19, ZA2-21, ZA2-24, ZA2-25, ZA2-27, ZA2-30, ZA2-31, ZA2-32, ZA2-33, ZFB1-42, ZFB1-47, ZFB1-48, ZFB1-50, ZFB1-51, ZFB2-56, ZFB2-58, ZFB3-60, ZFB4-65, ZFB4-66, GP-68,GP-69, GP-72, ZFB6-76, ZFB6-78, ZFB6-80, ZFB6-84	35

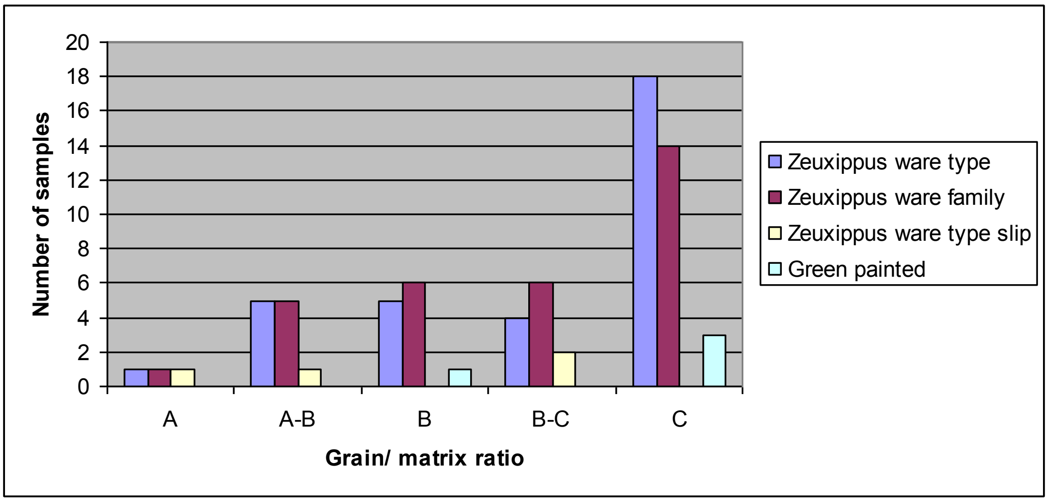


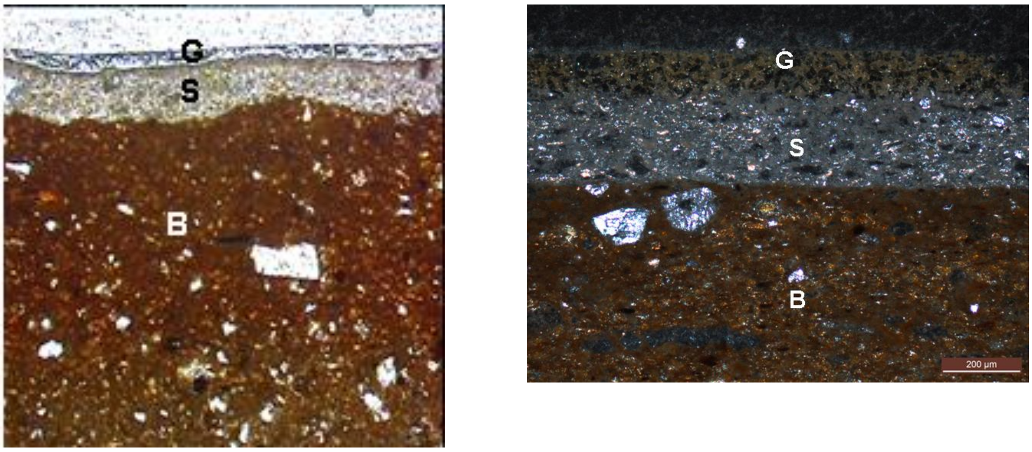
Figure 3.13: Distribution of the number of samples per each sampling group with respect to their grain/matrix ratios. (A: ~ 2-3 %, A-B: ~ 3-5 %, B: ~ 5-10 %, B-C: ~ 10-15 %, C: ~ 15-20 %).

As can be seen in Figure 3.13, *Anaia Zeuxippus Ware Type* (ZA) samples are mostly cumulated in group C, occasionally found in groups A-B and B. Only one of its samples belongs to group A. Similar observations are obtained for the group of *Zeuxippus Ware Family* (ZFB). Samples of *Zeuxippus Ware Type Slip Painted* (ZS) group mostly fall into B-C category whereas samples of *Green Painted* (GP) ceramics into group C. However, it should be noted that the number of samples is very few in the last two groups (ZS and GP) in order to be able to reach a solid conclusion.

When we combine the outcomes of these two classifications, it is possible to say that micaceous ceramics (groups 2 and 3) fall into groups B, C and B-C with relatively higher grain/matrix ratios. The observation of most *Zeuxippus Ware Family* samples falling into groups 2 and 3 may also give a hint that they may be local productions.

3.2.2 Slip

Some of the slip layers which are observed in most of the samples by the naked eye could not be detected during the optical microscope and SEM investigations. The observed slips by the optical microscope appear to have either a vitreous matrix or non-vitreous matrix which includes minerals. These minerals are mainly identified as quartz, feldpars and opaque minerals in some cases. Some of the slip layers have a vitreous matrix where minerals are embedded also (Figure 3.14). The details about the slip layers are listed in Table 3.5. Some of the slip layers that could be identified by SEM are shown in Figure 3.15-3.16.



a

b

Figure 3.14: Thin section images of ceramic samples showing body, slip and glaze parts, a) *Anaia Zeuxippus Ware Type* sample ZA2-31, PPL, magnification x4, b) *Anaia Zeuxippus Ware Type* sample ZA2-33, XPL (B: body, S: slip, G: glaze)

Table 3.5: Details of slip layer characteristics observed by optical microscopy and SEM (√: present, X: absent, -: no SEM analysis)

Sample code	**Characteristics of slips observed by optical microscopy**	**Slips visible by SEM**
ZA1-1	Matrix including mineral grains	X
ZA2-8 (out)		√
ZA2-9		-
ZA2-11		√
ZA2-15		√
ZA2-18		-
ZA2-20		-
ZA2-24		-
ZA2-25		-
ZFB3-60		-
ZFB3-63		-
ZFB3-64		√
ZFB6-77		-
ZFB6-78		X
ZFB6-79		-
ZS-89		X
ZA1-2	Vitreous matrix	-
ZA1-3		√
ZA1-5		√
ZA2-8 (in)		√
ZA2-10		-
ZA2-14		-
ZA2-17		-
ZA2-19		-
ZA2-22		X
ZA2-23		-
ZA2-28		-
ZFB1-43		-
ZFB1-44		-
ZFB1-50		-
ZFB1-54		-
ZFB2-59		X
ZFB3-62		-
ZFB5-67		X
ZFB6-80		-
ZFB6-81		√

Table 3.5 (cont'd) Details of slip layer characteristics observed by optical microscopy and SEM (√: present, X: absent, -: no SEM analysis)

Sample code	**Characteristics of slips observed by optical microscopy**	**Slips visible by SEM**
ZA1-4	Vitreous matrix which also includes minerals	√
ZA2-12		-
ZA2-27		-
ZA2-31		X
ZA2-32		-
ZA2-33		-
ZFB1-51		X
ZFB2-58		-
ZFB4-65		√
ZFB4-66		-
ZFB6-76		√
ZFB6-83		-

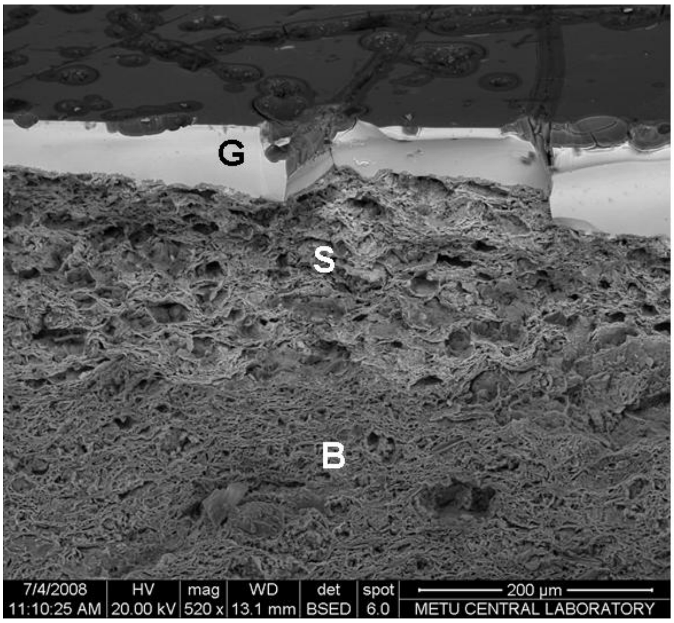
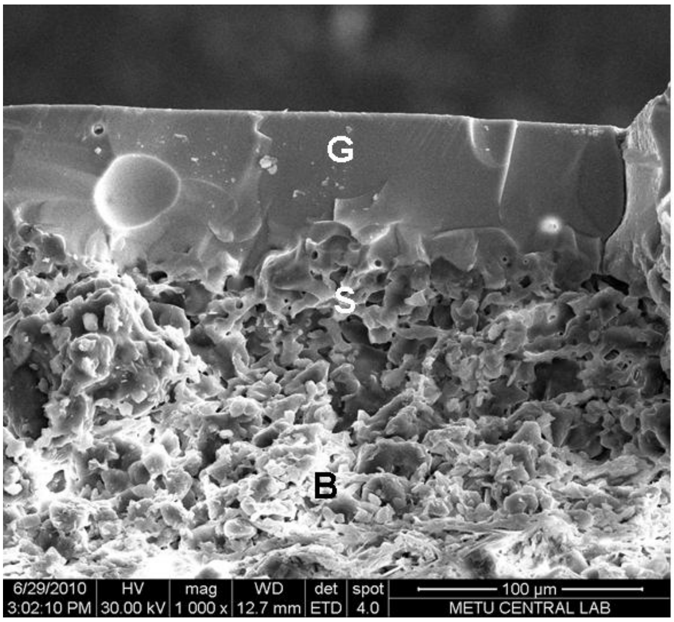
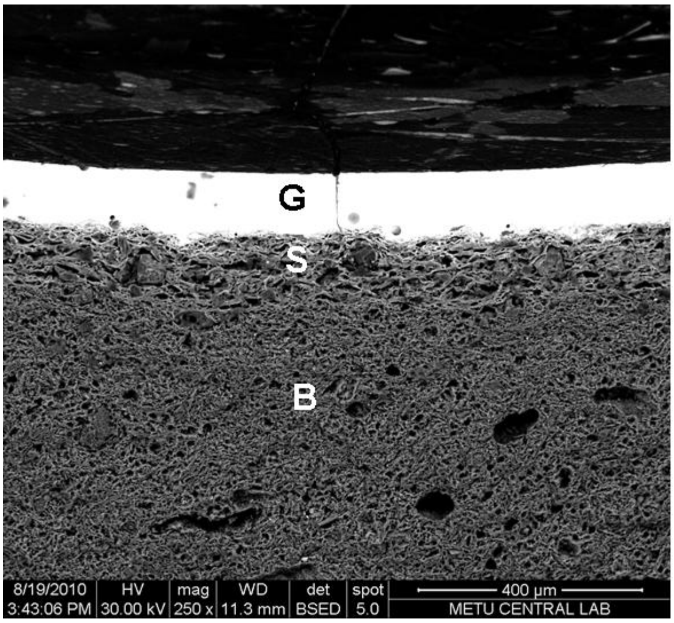


Figure 3.15: Representative SEM images of ceramic samples displaying body, slip and glaze parts, a) *Anaia Zeuxippus Ware Type* sample ZA1-3 (B: body, S: slip, G: glaze).



b



c

Figure 3.15 (cont'd) Representative SEM images of ceramic samples displaying body, slip and glaze parts, b) *Zeuxippus Ware Family* sample ZFB4-65 c) *Zeuxippus Ware Family* sample ZFB6-81 (B: body, S: slip, G: glaze)

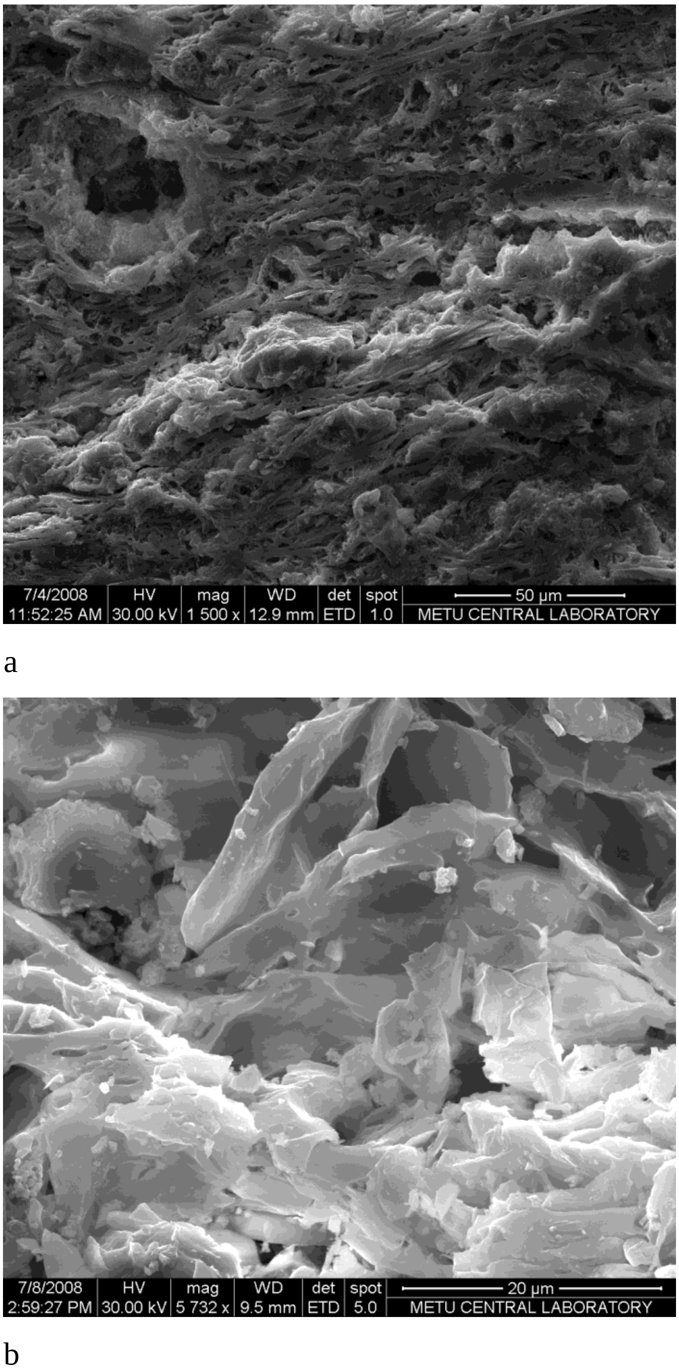
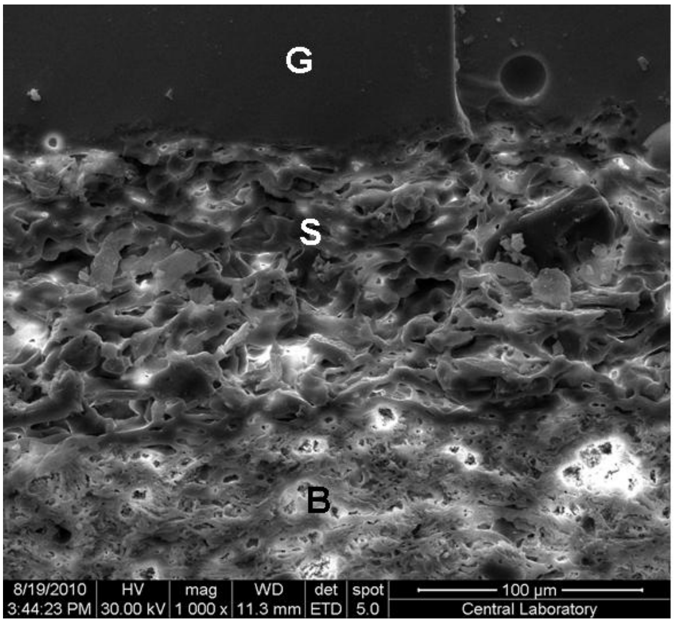


Figure 3.16: Close-up SEM images of slip layers, a) *Anaia Zeuxippus Ware Type* sample ZA1-3, b) *Anaia Zeuxippus Ware Type* sample ZA1-5



c

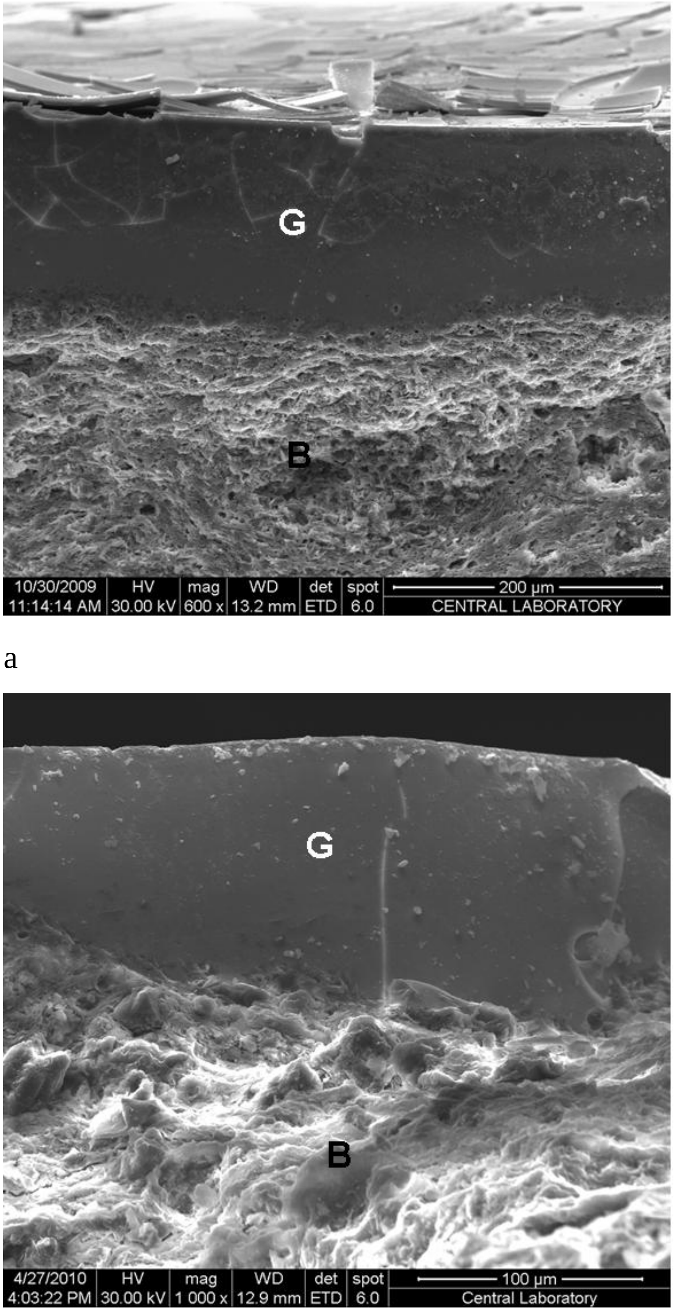
Figure 3.16 (cont’d) Close-up SEM images of slip layers, c) *Zeuxippus Ware Family* sample ZFB6-81 (B: body, S: slip, G: glaze)

3.2.3 Glaze

Representative images of glaze layers visible by SEM are listed in Figure 3.17. The thickness of some glaze layers was measured with a ruler from the SEM images. They vary from one sample to another. The thickness of the glaze also may vary on the same pot (Table 3.6- Figure 3.17f) .

Table 3.6: Measured thickness of the glaze layers (μm)

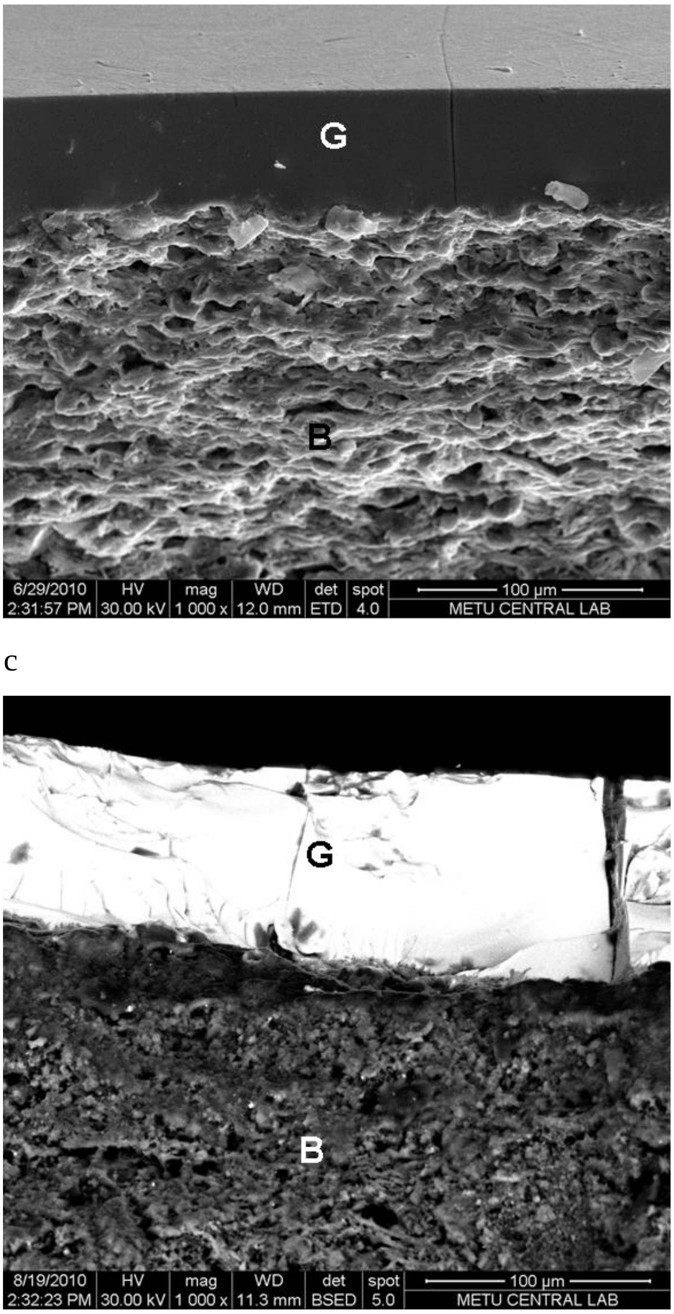
Sample code	**Thickness of the glaze/ μm**
ZA1-1	~200-300
ZA1-3	~45-108
ZA1-4	~74
ZA1-5	~51-93
ZA2-8	~109-136
ZA2-15	~122
ZA2-16	~63-76
ZA2-22	~138-155
ZA2-30	~128
ZA2-31	~37-59
ZFB1-42	~92-100
ZFB1-47	~89-99
ZFB1-51	~76-118
ZFB2-59	~20-52
ZFB3-64	~50-74
ZFB4-65	~34-74
ZFB5-67	~97
ZFB6-76	~63-97
ZFB6-78	~97-116
ZFB6-81	~107-134
ZFB6-84	~25-86
ZS-89	~54-101



a

b

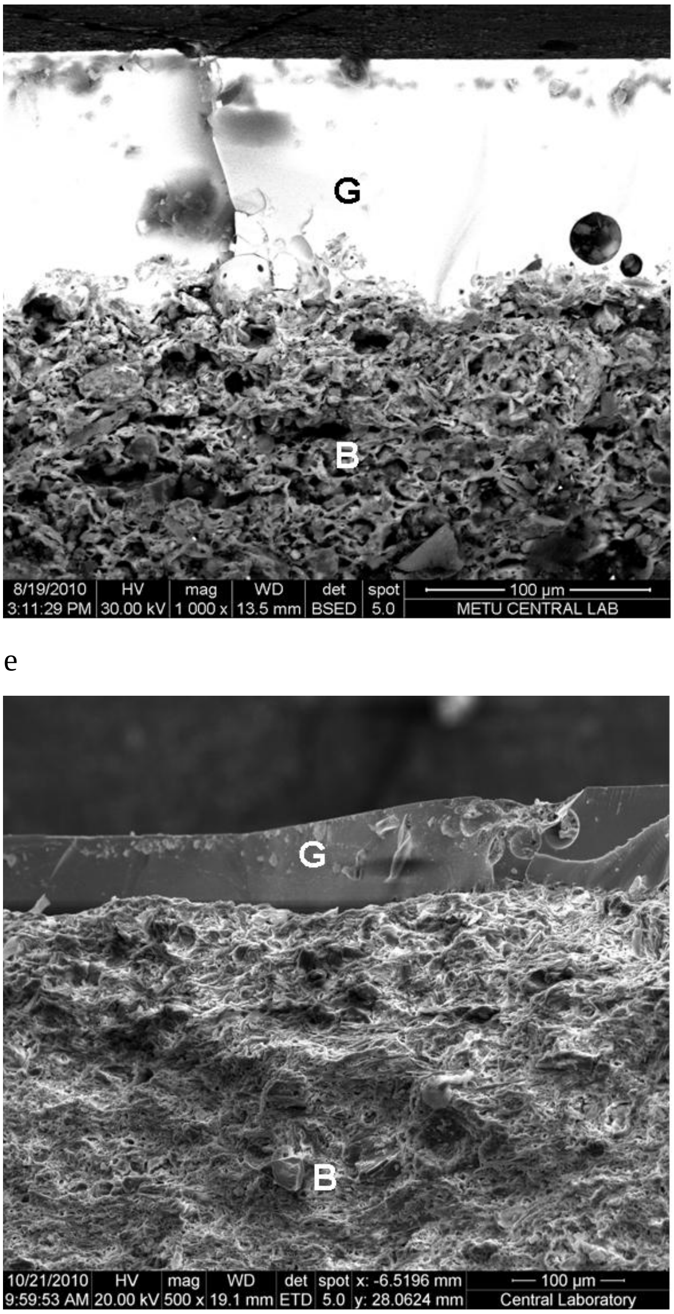
Figure 3.17: SEM images of some ceramic bodies showing body and glaze layers; a) *Anaia Zeuxippus Ware Type* sample ZA2-22; b) *Zeuxippus Ware Family* sample ZFB1-51 (B: body, G: glaze)



c

d

Figure 3.17 (cont'd) SEM images of some ceramic bodies showing body and glaze layers; *Zeuxippus Ware Family* samples c) ZFB3-64, d) ZFB6-76 (B: body, G: glaze)

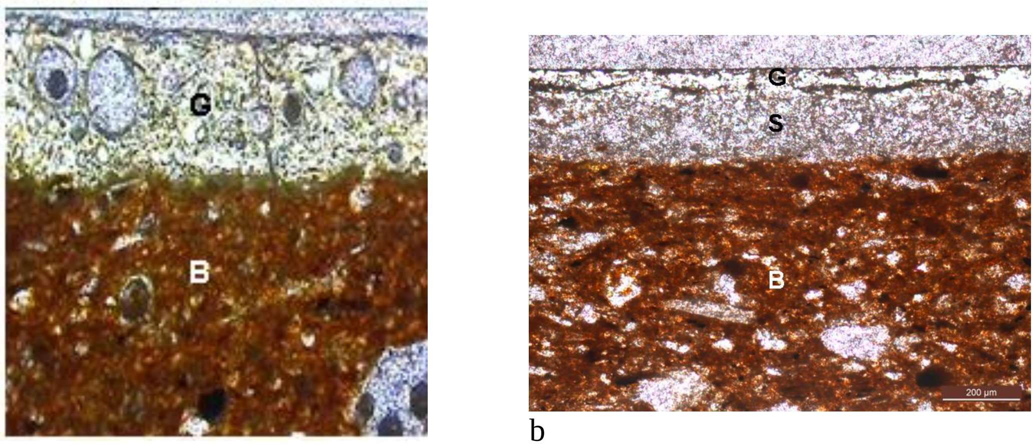


e

f

Figure 3.17 (cont'd) SEM images of some ceramic bodies showing body and glaze layers; e) *Zeuxippus Ware Family* sample ZFB6-78, f) *Zeuxippus Ware Type Slip Painted* sample ZS-89 (B: body, G: glaze)

Glaze layers studied are usually amorphous, displaying vesicles and cracks in some locations (Figure 3.17-3.18). Some of the glaze layers show devitrification products as observed in the glazes of samples ZA2-13 and ZFB6-77. Furthermore, some of the glaze layers are observed in tones of yellow (ZA2-25, ZA2-29, ZA2-32, ZA2-33, ZFB1-43, ZFB2-55, ZFB3-61, ZFB3-63, ZFB3-64, ZFB5-67, ZFB6-77, ZFB6-83, ZS-89), brown (ZFB3-62) and green (ZFB4-65, ZFB4-66) under the optical microscope (Figure 3.18).



a

b

Figure 3.18: Thin section images of some ceramic samples showing body, slip and glaze layers with PPL, a) *Zeuxippus Ware Family* sample ZFB5-67 showing vesicles, magnification x10, b) *Zeuxippus Ware Family* sample ZFB4-65 (B: body, S: slip, G: glaze)

The glaze layers are well differentiated from the body parts indicating relatively low firing temperatures not exceeding about 850°C, as also seen in thin section and SEM images.

3.3 SEM-EDX Analysis

3.3.1 Body

Chemical compositions of the body parts of the samples with oxide concentrations normalized to 100 % are listed in Table 3.7. For the original data converted into oxide forms see Appendix D.

Table 3.7: Compositions of the body parts analyzed by SEM-EDX (% by weight)
*: Measurements are taken from two different areas.

Sample code	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**Na_2O**	**TiO_2**
ZA1-1*	9.82	21.63	42.85	1.90	9.95	13.84	-	-
	2.92	27.47	48.97	6.55	6.23	6.66	1.20	-
ZA1-3	3.48	23.62	50.19	4.58	6.79	10.26	1.05	-
ZA1-4	4.68	22.20	50.10	3.29	9.50	10.20	-	-
ZA1-5	4.75	22.73	52.78	3.02	7.85	7.90	0.38	0.59
ZA2-8	3.40	21.36	50.53	3.81	10.58	10.32	-	-
ZA2-11	4.97	20.78	48.36	3.03	13.46	9.39	-	-
ZA2-15	4.96	21.74	50.05	2.69	12.16	8.40	-	-
ZA2-16	5.91	18.80	46.01	2.99	12.48	13.05	-	0.75
ZA2-22	3.77	19.71	51.62	3.57	11.51	8.91	-	0.91
ZA2-30	3.96	15.64	55.28	2.89	10.66	10.13	-	1.43
ZA2-31	5.52	18.53	46.37	2.52	16.72	8.89	0.54	0.89
ZFB1-42	5.08	21.05	49.45	2.99	11.83	8.81	-	0.78
ZFB1-47	4.72	22.27	49.59	2.74	11.71	8.39	-	0.56
ZFB1-51	4.86	19.07	52.43	2.47	9.99	9.58	0.89	0.68
ZFB2-59	4.72	19.51	52.28	2.82	12.96	7.03	-	0.67
ZFB3-64	3.92	22.09	50.26	3.13	10.76	8.73	0.25	0.86
ZFB4-65	4.13	14.98	57.28	1.43	11.16	8.84	0.63	1.55
ZFB5-67	4.45	13.47	42.40	2.41	22.51	13.63	0.20	0.92
ZFB6-76	5.84	16.72	54.58	2.53	11.95	6.15	1.53	0.70
ZFB6-78	2.29	16.58	58.57	3.32	5.72	13.52	-	-
ZFB6-81	6.42	18.75	43.58	2.07	13.06	12.81	-	3.30
ZFB6-84	2.89	18.98	54.22	3.01	7.23	10.54	1.79	1.32
ZS-89	4.14	18.34	46.88	2.54	14.07	14.02	-	-

Compositional values in weight percent range between about 2-10 % for MgO, 10-25 % for Al_2O_3, 35-60 % for SiO_2, 1-7 % for K_2O, 5-25 % for CaO, 5-15 % for Fe_2O_3, up to 2 % for Na_2O and up to 3 % for TiO_2. Thin section and XRD analyses reveal high abundances of quartz and feldspar minerals in the bodies which are in accordance with the high percentages of SiO_2 and Al_2O_3 found in EDX measurements. The use of kaolinite may also have contributed to the high amounts of Al_2O_3 although it was not detected by XRD due to its collapse when heated above 550°C (Richardson 1972). The raw materials used for the bodies also seem to be rich in CaO and Fe_2O_3 while they are rather poor in Na_2O and TiO_2 contents. Impurities of calcium in the clays as well as the use of calcite as temper may have contributed to the observed calcium content of the body. Relatively high amounts of Fe_2O_3 are well reflected in the reddish bodies of the ceramics.

3.3.2 Slip

Chemical compositions of the slip parts of samples analyzed by SEM-EDX are listed in Table 3.8. The original data converted into oxide forms are given in Table D.2. Compositional values in weight percent range between about 10-35 % for Al_2O_3, 35-80 % for SiO_2, 1-5 % for K_2O, up to 9 % for CaO, 1-10 % for Fe_2O_3, up to 1 % for Na_2O, up to 2 % for TiO_2 and up to 3 % for MgO.

Table 3.8: Compositions of the slip parts analyzed by SEM-EDX (oxide concentrations normalized to 100 %) (% by weight)

Sample code	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	Na_2O	PbO	TiO_2
ZA1-3	-	24.55	44.95	3.60	0.92	5.74	-	20.24	-
ZA1-4	1.58	27.47	64.70	2.82	0.99	2.43	-	-	-
ZA1-5	0.76	21.63	61.47	3.06	-	2.17	0.53	8.84	1.54
ZA2-8	3.19	22.13	49.20	4.03	9.01	11.24	-	-	1.19
ZA2-11	0.97	29.22	61.73	3.84	-	2.51	-	-	1.72
ZA2-15	0.86	20.78	51.97	2.22	1.09	1.42	-	21.12	0.53
ZA2-30	1.36	34.72	52.97	1.61	1.39	2.15	-	5.79	-
ZFB1-47	1.09	26.14	65.35	2.79	1.27	3.35	-	-	-
ZFB3-64	1.61	18.98	47.49	4.39	1.27	4.39	0.80	19.86	1.19
ZFB4-65-in	0.86	9.85	75.44	1.63	1.05	0.64	0.44	9.48	0.61
ZFB4-65-out	1.19	10.86	76.37	1.98	1.88	1.03	0.37	5.48	0.83
ZFB6-76	2.04	29.28	57.17	4.91	3.42	0.88	0.77	1.05	0.45
ZFB6-81	-	17.15	62.86	3.91	-	2.25	-	12.58	1.23
ZFB6-84	1.67	17.95	49.83	3.88	2.21	3.60	1.35	19.12	0.38

As in the case of the body parts, slips analyzed have relatively high amounts of SiO_2 and Al_2O_3 as a result of the presence of quartz and feldspars in the raw materials used in their production. The results are similar to those of Byzantine slips from Ephesus and İznik (Demirci et al. 1996). High Al_2O_3 content (as $\geq$20 %) may also indicate the use of kaolinitic type of clays as the raw material. Additionally, the contents of MgO, CaO and Fe_2O_3 are usually lower than those of the body parts. The detection of PbO in most of the slips may indicate the diffusion of lead ions from the glaze towards the slip during the firing process.

3.3.3 Glaze

Chemical compositions of the glaze layers of samples analyzed by SEM-EDX are listed in weight percent (Table 3.9). The original data converted into oxide forms are also given in Table D.3. All the glazes have a lead-oxide-silica composition with varying amounts of SiO_2 between ~ 10 - 40 % and more than 40 % PbO. Therefore, they can be classified as high-lead glazes according to their PbO content (Tite et al. 1998). Amounts of PbO vary between ~ 40 -80 % for different samples suggesting that different lead compositions were used in the glaze application during manufacturing. PbO amounts also vary within the same sample indicating the inhomogeneity of the glaze compositions. Amounts of alumina (Al_2O_3) found are relatively high (~ up to 10 %) which may partly result from the diffusion from the body constituents during firing. This may also be partly due to the intentional addition of clay to the glaze suspension in order to give strength to the glaze (Tite et al. 1998). The alkali contents (K_2O + Na_2O) were found to be very low, being ~ 2 % at the most.

Chemical compositions of the glazes analyzed are found to be in good correlation with the results of previous studies for Byzantine ceramic and tile glazes (especially having tones of brown and green) (Henderson and Mango 1995; Demirci et al. 1996; Armstrong et al. 1997; Vogt et al. 1997; Demirci et al. 2002)

Table 3.9: Compositions of the glaze parts analyzed by SEM-EDX (oxide concentrations normalized to 100 %) (% by weight)

Sample code	Observed color	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	Na_2O	PbO	TiO_2	NiO	Sb_2O_3	CoO	ZnO	MnO	CuO
ZA1-1	Yellow	1.43	6.63	34.88	0.79	1.66	3.25	-	51.35	-	-	-	-	-	-	-
ZA1-3	Green	0.77	5.12	35.54	-	2.02	3.56	0.33	52.65	-	-	-	-	-	-	-
ZA1-4	Green	-	7.01	26.97	0.52	1.24	3.07	-	61.17	-	-	-	-	-	-	-
ZA1-5	Yellow	-	1.97	12.52	-	0.26	0.97	-	84.27	-	-	-	-	-	-	-
	Orange	-	6.59	41.68	0.86	0.51	1.23	-	49.11	-	-	-	-	-	-	-
ZA2-8	Honey brown	-	4.02	33.16	-	0.73	3.42	-	58.67	-	-	-	-	-	-	-
ZA2-11	Yellow	-	5.22	21.06	-	0.99	1.07	-	71.33	-	-	0.33	-	-	-	-
ZA2-15	Honey brown	0.76	8.01	41.29	-	-	1.43	-	48.49	-	-	-	-	-	-	-
ZA2-16	Brown	-	5.21	25.47	-	0.82	5.04	-	62.94	-	-	-	0.52	-	-	-
ZA2-22	Green-1	-	2.66	16.20	-	1.09	1.98	-	77.79	-	0.25	-	-	-	-	-
	Green-2	-	3.86	27.08	-	2.09	3.19	-	62.84	-	0.94	-	-	-	-	-
ZA2-30	Yellow	-	6.72	36.29	-	-	1.38	-	54.28	-	0.39	0.91	-	-	-	-
ZA2-31	Yellow-1	-	7.32	41.82	-	-	1.42	-	48.15	-	-	1.17	-	0.12	-	-
	Yellow-2	-	4.80	38.42	-	0.68	1.37	-	54.44	-	-	0.27	-	-	-	-
	Yellow-3	-	4.95	28.76	0.55	0.93	1.16	-	63.10	-	-	0.53	-	-	-	-
ZFB1-42	Honey brown	0.63	9.66	39.01	0.76	1.19	3.23	-	44.98	0.52	-	-	-	-	-	-
ZFB1-47	Honey brown	0.47	6.48	34.35	0.28	0.96	3.22	-	53.87	0.35	-	-	-	-	-	-
ZFB1-51	Yellow	0.47	8.89	34.33	0.70	0.28	1.23	-	53.75	0.33	-	-	-	-	-	-
ZFB2-59	Honey brown	0.72	5.13	33.27	0.49	0.58	2.98	0.21	56.25	0.28	-	-	-	-	0.07	-
ZFB3-64	Purple	-	4.74	32.91	0.76	0.93	1.23	-	58.24	-	-	-	-	-	1.18	-

Table 3.9 (cont'd) Compositions of the glaze parts analyzed by SEM-EDX (oxide concentrations normalized to 100%) (% by weight)

Sample code	**observed color**	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**Na_2O**	**PbO**	**TiO_2**	**NiO**	**Sb_2O_3**	**CoO**	**ZnO**	**MnO**	**CuO**
ZFB4-65	Green	0.87	3.97	40.32	0.51	2.14	1.09	0.34	47.42	-	-	-	-	-	0.22	3.10
	Purple	0.48	3.13	32.22	0.53	0.87	0.80	0.25	58.67	0.56	-	-	-	-	2.16	0.31
ZFB5-67	Green-1	0.32	3.27	18.70	0.38	0.73	0.87	0.13	74.15	0.37	-	-	-	-	0.24	0.83
	Green-2	0.19	3.07	19.70	0.40	1.00	1.04	-	72.73	0.37	-	-	-	-	0.20	1.29
ZFB6-76	Light green	0.69	5.81	35.15	0.66	3.01	0.55	-	54.12	-	-	-	-	-	-	-
ZFB6-78	Purple	0.67	7.98	34.69	0.79	1.16	1.33	-	51.90	-	-	-	-	-	1.45	-
	Yellow	1.04	10.08	40.44	0.94	1.77	2.85	-	42.87	-	-	-	-	-	-	-
ZFB6-81	Green	-	3.97	32.97	-	2.06	1.14	-	58.15	-	-	-	-	-	-	1.69
ZFB6-84	Yellow	0.44	5.81	25.85	0.66	0.94	1.63	0.27	64.22	0.17	-	-	-	-	-	-
	Honey brown	1.27	7.19	36.13	1.39	2.85	3.39	0.63	46.69	0.42	-	-	-	-	-	-
ZS-89	Brown	-	5.84	30.95	-	1.07	8.23	-	53.91	-	-	-	-	-	-	-

In general, according to the results obtained by EDX, some of the oxide contents tend to decrease such as MgO, CaO and Fe_2O_3 from the body towards the glaze. These variations for some samples are shown in Figure 3.19. This is also apparent in the compositional mapping images by SEM-EDX for *Zeuxippus Ware Family* sample ZFB2-59 throughout its body, slip and glaze layers (Figure 3.20).

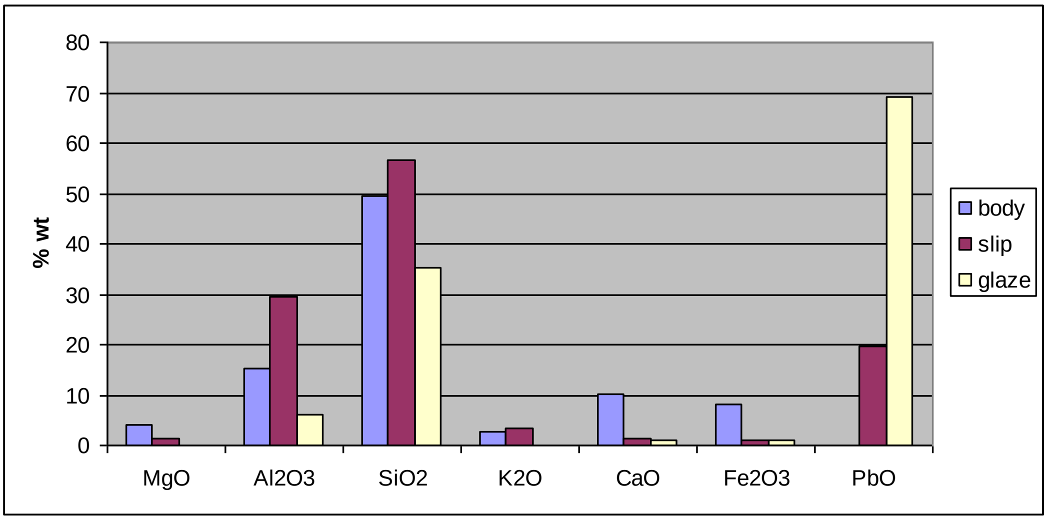
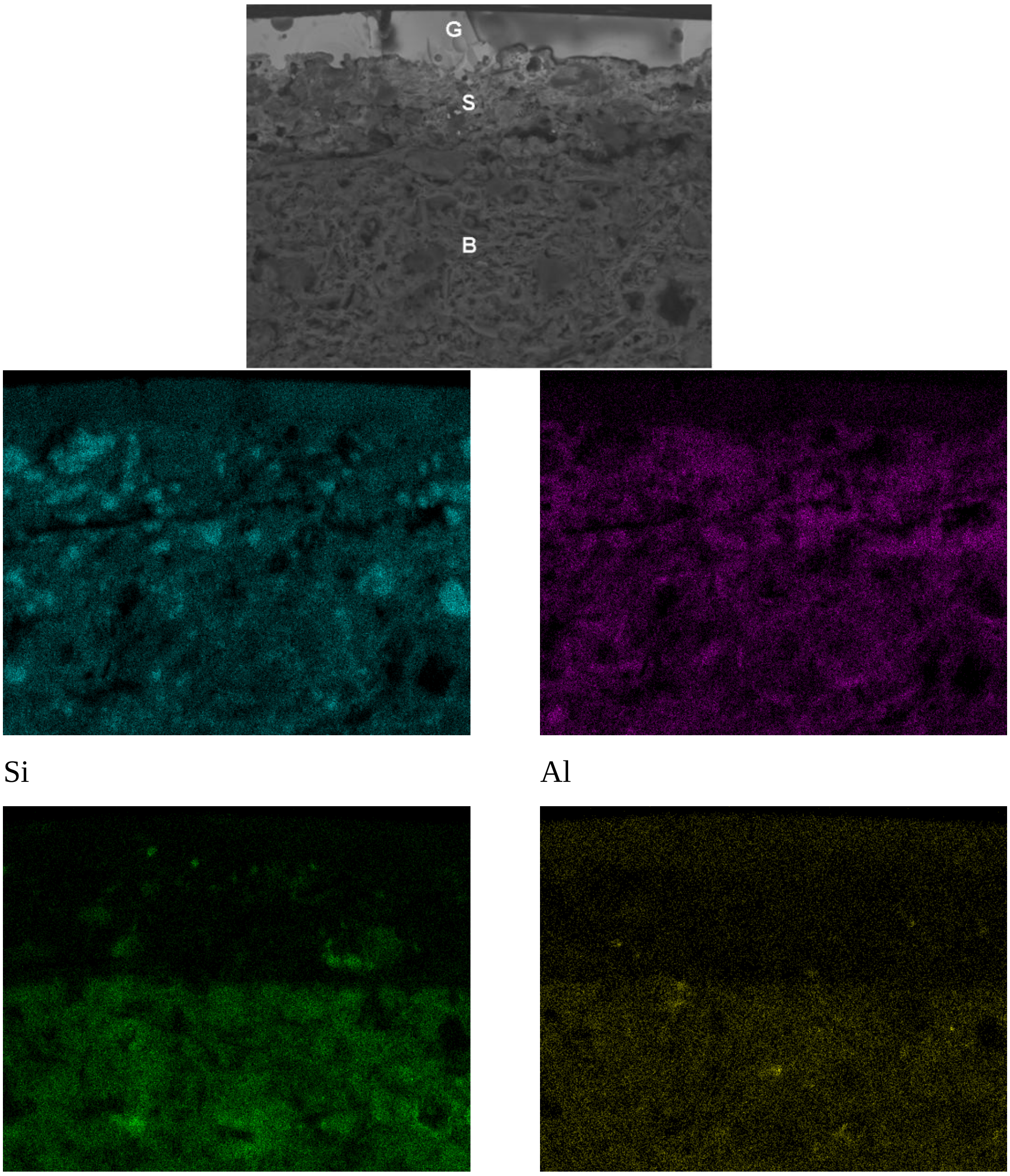


Figure 3.19: Variation of the oxide contents detected by SEM-EDX for some of the representative samples (ZA1-4 for MgO, ZA2-30 for Al_2O_3, ZA1-5 for SiO_2, ZA2-11 for K_2O, ZFB3-64 for CaO, ZFB4-65 for Fe_2O_3, ZFB6-84 for PbO).



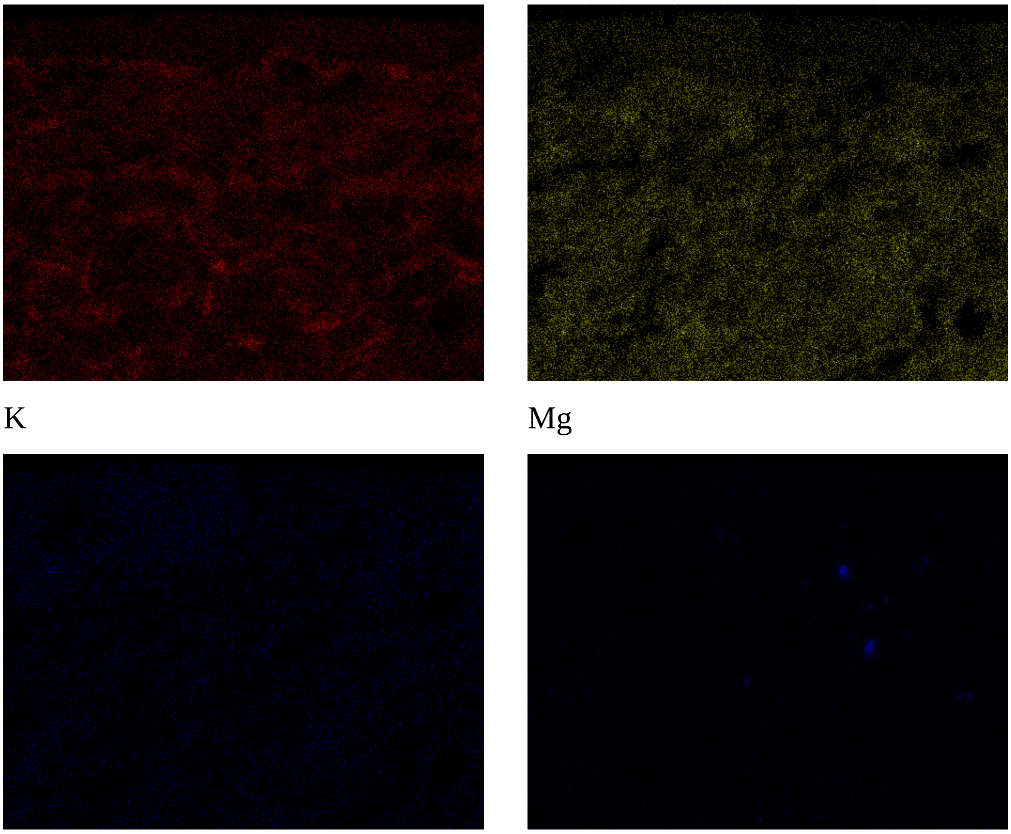
Si

Al

Ca

Fe

Figure 3.20: SEM-EDX mapping images of *Zeuxippus Ware Family* sample ZFB2-59 showing different concentrations for several elements through the body, slip and glaze layers (B: body, S: slip, G: glaze)



K

Mg

Na

Ti

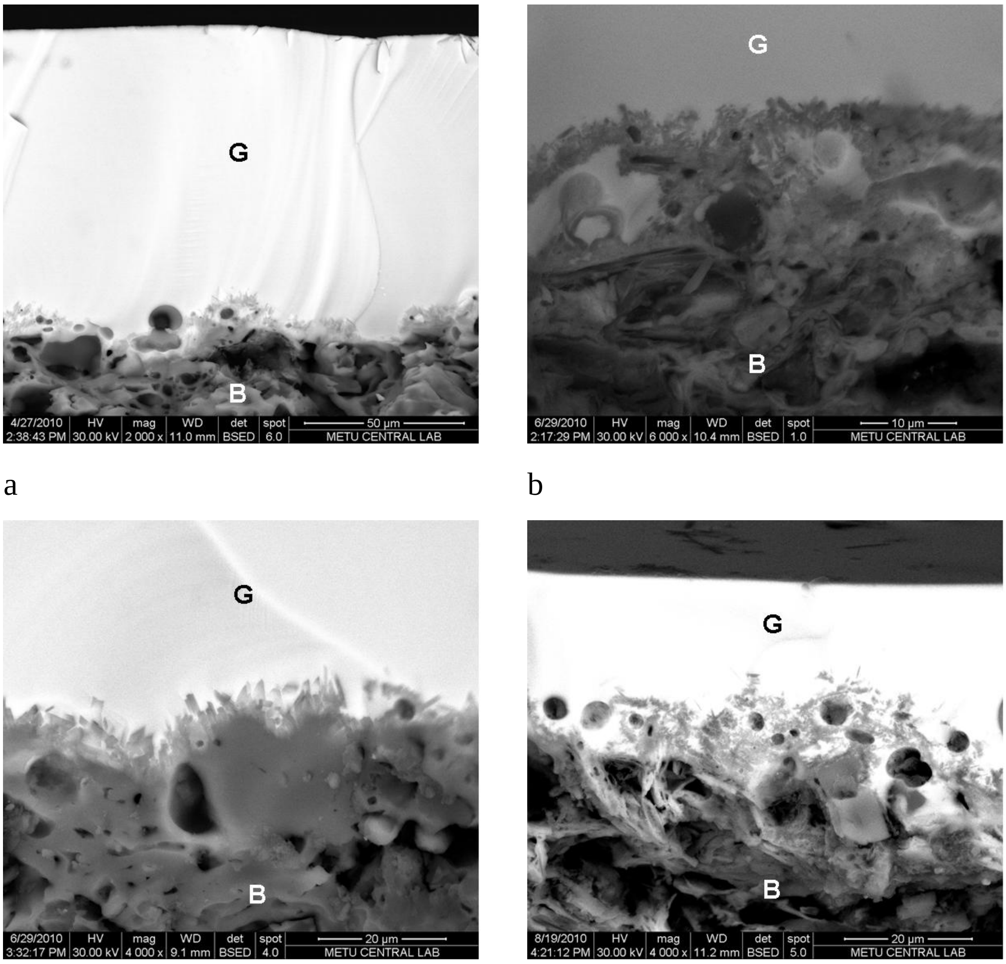
Figure 3.20 (cont'd) SEM-EDX mapping images of *Zeuxippus Ware Family* sample ZFB2-59 showing different concentrations for several elements through the body, slip and glaze layers.

Regarding the compositional mapping images of sample ZFB2-59, silicon contents seem to be homogeneous throughout the body, slip and glaze layers. However in some places in the body and slip layers, the contents tend to increase. On the contrary, aluminum contents are homogeneous in the body and slip layers but seem to decrease when it comes to the glaze. Potassium and magnesium contents also show a similar trend as the aluminum content.

3.3.3.1 The Glazing Technology

When a lead-silica mixture is used for glaze production, certain crystals at the body-glaze interface form during the firing process. The mechanism for the formation of these crystals is based on the fact that certain elements such as aluminum, potassium, calcium, iron and magnesium diffuse from the body through the glaze layer during firing. In case of applying the glaze mixture to an unfired body, the diffusion from the body into the glaze will be greater due to the greater surface area and reactivity of unreacted clay minerals in the body. On the contrary, when the same glaze mixture is applied to a biscuit-fired body, the diffusion from the body to the glaze will be less since the body will already have been fused. Therefore, concentration of the crystals at the body-glaze interface will be higher when an unfired body is used. However, the concentration of these crystals are also dependent on other factors such as the composition of the body, firing temperature and firing time as well as the cooling rate (Tite et al. 1998). These crystals have the structure of feldspars as ($(K,Pb)AlSi_3O_8$) with the substitution of potassium by lead ions coming from the glaze. Therefore, each crystal formed at the interface may have a different compositional range (Molera et al. 2001).

For some of the Kuşadası Kadıkalesi/Anaia ceramics which are *Zeuxippus Ware Family* samples, a layer of Pb-rich feldspar crystals at the glaze-body interface was observed (Figure 3.21). As discussed above, each crystal analyzed shows a variable chemical composition. Al_2O_3 and K_2O amounts in the crystals at the interface are significantly higher than those of their surrounding glaze layers whereas the PbO amounts are usually lower. The thickness of these crystal layers varies from ~ 5- 8 μm which can be considered to be relatively small, indicating that bodies of these ceramic samples were probably fired before the application of the glaze layer (Molera et al. 2001).



a b

c d

Figure 3.21: SEM images showing crystals on the interface of the body and glaze parts of *Zeuxippus Ware Family* samples; a) ZFB1-42, b) ZFB2-59, c) ZFB5-67, d) ZFB6-84 (B: body, G: glaze)

The compositions of these interface crystals were analyzed by SEM-EDX from at least one point (Table 3.10). The original data converted into oxide forms are listed in Table D.4.

Table 3.10: Compositions of the interface crystals analyzed by SEM-EDX (oxide concentrations normalized to 100 %) (% by weight)

Sample code	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**Na_2O**	**PbO**	**TiO_2**
ZFB1-42	0.43	15.06	32.63	2.15	1.34	1.95	-	45.98	0.44
	0.23	17.67	42.51	2.18	1.25	1.71	-	34.07	0.36
	0.56	19.10	45.40	2.34	1.07	1.57	-	29.53	0.42
ZFB1-47	0.50	22.09	44.71	3.42	0.81	1.54	-	26.32	0.59
	0.21	14.98	39.71	2.25	0.92	2.44	-	39.19	0.29
ZFB2-59	-	19.91	43.27	4.46	-	2.59	0.51	29.26	-
	-	16.22	46.23	5.06	-	1.58	-	30.61	0.29
	-	18.43	44.52	4.87	-	2.29	-	29.58	0.30
ZFB5-67	0.76	21.22	38.13	5.58	0.82	1.19	0.14	31.77	0.37
	0.90	21.49	40.38	5.63	0.72	0.97	0.32	29.17	0.41
ZFB6-84	1.04	16.57	37.57	1.30	9.76	4.21	1.05	28.49	-

Colorants

Development of glaze colors usually depends on various factors such as the chemical compositions of glaze and body parts as well as the firing temperature and atmosphere. As discussed above, several elements tend to diffuse from the body into the glaze layers during the firing process. Among these elements, iron is the major one which induces the formation of glaze colors (Molera et al. 2001). According to the results obtained by SEM-EDX analyses, iron compounds seem to be responsible for the glaze colors as yellow, orange, honey brown, brown as well as green in some cases with compositions ranging from ~ 0.5 to 8 % Fe_2O_3 as in the case of Kuşadası Kadıkalesi/Anaia glazes (Table 3.9). As it is well-known, different oxidation states of iron can produce different colors with the same glaze composition (Molera et al. 1997). The yellow to brown colors are generally related to Fe^{3+} whereas Fe^{2+} is responsible for the green color. For the yellow glazes , ~ 1-3 % Fe_2O_3 was detected in the absence of alkalis or with very low alkali amounts in some cases (~ 1 % K_2O + Na_2O). Furthermore, glazes with tones of brown were also found to contain ~ 1-8 % Fe_2O_3 in the same conditions with up to ~ 2 % K_2O + Na_2O at the most. Results for the brownish glazes are in good correlation with the results of previous analyses for other Byzantine glazes from Ephesus in Western Anatolia having a similar color (Demirci et al. 2002).

In the case of *Anaia Zeuxippus Ware Type* sample ZA2-22, ~ 2-3 % Fe_2O_3 is responsible for the green glaze in the absence of any detected copper and alkali content. The body of ZA2-22 is glazed on both sides which leads to a reduction in the paste (Figure 2.1-A.1). This is also evident with the dark gray color of the body. Therefore, iron is probably diffused in the form of Fe^{2+} from the body into the glaze, forming the observed green color.

Concerning the other green glazes, copper was detected as ~ 1-3 % CuO. In sample ZFB5-67 from *Zeuxippus Ware Family* group, the green stained glaze was found to contain ~ 1 % CuO with very low alkali content (~ 0.5 % K_2O + Na_2O). Belonging to one of the most distinguished subgroups among *Zeuxippus Ware Family* ceramics, *Incised-manganese* ceramic sample ZFB4-65 having a green glaze on the outer side also contain ~ 3 % CuO together with ~ 1 % K_2O + Na_2O. The green glaze of sample ZFB6-81 as a *Frankish Style* ceramic has also about 2 % CuO without any detected alkali content. Another point for the green glazes is that their Fe_2O_3 contents seem to decrease in the presence of CuO.

In some of *Anaia Zeuxippus Ware Type* samples such as ZA2-11, ZA2-30 and ZA2-31 which have a yellow glaze, antimony was detected which might also had acted as a coloring agent. Detection of antimony in the glazes may suggest the addition of a pigment into the glaze mixture. This pigment may be a *Naples yellow* type of pigment which was also detected in sample ZA2-31 by Raman spectrometry. Detailed discussion for *Naples yellow* pigment is given in section 3.5.3. For the purple regions of the glazes, manganese was detected as ~ 1-2 %

MnO which gives purple color to the glaze by its sole presence. Similar results for the colorants were reported for Late Byzantine ceramic glazes from Sardis (Manisa) in Western Anatolia (Scott and Kamilli 1981) and from Serres (Northern Greece) (Wisseman et al. 1997) and 9th-11th century white bodied tiles from Constantinople (Vogt et al. 1997).

3.4 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) Analyses

Chemical compositions determined by ICP-OES/ICP-MS measurements, of the body parts belonging to thirty representative Kuşadası Kadıkalesi/Anaia samples are given in Table 3.11.

In a close examination of Table 3.11 which gives the results of ICP-OES/ ICP-MS measurements, it is clear that the chemical composition of the bodies, in general, contain ~ 1.5 – 5 % MgO, ~ 13-20 % Al_2O_3, ~ 43- 65.5 % SiO_2, ~ 2-3 % K_2O, ~ 1-17 % CaO, ~ 5-10 % Fe_2O_3, up to 1.5 % Na_2O, up to 1 % TiO_2 and up to 0.2 % MnO. Among these, particularly the amounts of MgO, Al_2O_3, SiO_2, Fe_2O_3 and Na_2O seem to be in good correlation with the results of SEM-EDX data obtained previously (Section 3.3.1). The abundant quantities of quartz and feldpar minerals in the raw materials of the bodies are well reflected in the SiO_2 and Al_2O_3 amounts recorded. Relatively high amounts of Fe_2O_3 measured are also in accordance with the observed reddish bodies of the ceramics.

Table 3.11: Chemical compositions of the ceramic bodies by ICP-OES/ ICP- MS

Element	**ZA1-1**	**ZA1-3**	**ZA2-7**	**ZA2-9**	**ZA2-12**	**ZA2-15**	**ZA2-16**	**ZA2-17**
Fe_2O_3 (%)	9.09±0.13	8.56±0.11	8.64±0.08	7.92±0.06	8.61±0.16	8.32±0.07	8.12±0.03	8.36±0.10
Al_2O_3 (%)	19.27±0.4	18.89±0.6	18.61±0.45	16.92±0.39	19.83±0.6	18.57±0.37	18.23±0.36	18.57±0.25
Na_2O (%)	0.56±0.009	0.61±0.01	0.47±0.01	0.44±0.01	0.61±0.03	0.54±0.01	0.55±0.01	1.29±0.03
MgO (%)	4.21±0.08	3.81±0.09	4.39±0.08	4.36±0.06	4.46±0.12	3.68±0.06	3.99±0.08	4.62±0.05
K_2O (%)	2.84±0.05	2.82±0.08	2.68±0.06	2.43±0.06	2.84±0.07	2.59±0.05	2.74±0.06	1.74±0.02
CaO (%)	10.41±0.14	10.08±0.17	9.68±0.15	10.98±0.13	10.49±0.18	11.81±0.11	11.40±0.17	13.06±0.13
SiO_2 (%)	45.7±0.8	44.9±0.8	46.4±1.1	45.1±0.6	47.27±1.1	46.4±1.1	44.5±1.1	46.2±0.6
TiO_2 (%)	0.715±0.006	0.721±0.010	0.729±0.008	0.698±0.006	0.698±0.012	0.732±0.003	0.668±0.005	0.742±0.010
MnO (%)	0.165±0.001	0.173±0.001	0.161±0.001	0.123±0.001	0.130±0.001	0.169±0.001	0.169±0.001	0.155±0.001
Rb (mg/kg)	168.0±1.7	153.0±2.4	150.0±0.9	120.0±0.7	170.0±1.0	143.0±1.5	155.5±1.6	142.5±1.5
Sr (mg/kg)	286.5±2.4	294.0±3.9	246.9±1.1	214.5±1.7	276.5±2.8	239.5±1.4	265.0±0.4	256.5±3.0
Ba (mg/kg)	433.5±1.6	486.5±6.1	401.9±2.0	390.5±4.1	432.5±4.4	412.0±4.5	461.5±4.4	447.0±3.2
V (mg/kg)	143.5±1.1	136.5±2.5	139.9±0.9	139.5±1.3	158.5±2.2	132.0±0.7	134.5±0.9	149.0±1.7
Cr (mg/kg)	272.5±1.2	266.5±4.1	301.5±2.2	293.0±3.3	244.5±3.1	299.5±3.6	262.5±2.1	245.5±1.7
Co (mg/kg)	31.8±0.2	28.5±0.4	32.6±0.7	27.1±0.5	28.2±0.4	31.8±0.4	30.9±0.5	32.3±0.4
Ni (mg/kg)	227.1±2.3	204.4±5.0	245.6±3.7	225.9±2.3	207.8±2.8	231.1±2.9	213.1±2.9	202.7±3.6
Zn (mg/kg)	140.0±2.8	122.5±4.2	128.0±1.8	100.1±4.0	117.0±3.9	114.5±2.5	123.5±2.2	123.0±2.2
Pb (mg/kg)	400.0±5.1	1345±17	249.5±2.4	311.0±2.3	675.5±4.3	388.5±6.3	385.5±4.9	8745±115
Tl (mg/kg)	0.81±0.05	0.89±0.04	1.06±0.07	1.03±0.02	-	0.79±0.04	-	0.38±0.02
Zr (mg/kg)	59.6±3.4	64.8±1.9	58.9±1.1	61.8±1.7	66.4±1.9	60.1±2.1	55.4±1.0	68.3±2.0
Nb (mg/kg)	16.4±0.1	16.3±0.4	15.8±0.1	13.4±0.2	16.8±0.2	15.5±0.3	15.4±0.1	16.6±0.3
P (mg/kg)	2310±20	1305±29	1410±15	1365±15	1165±17	959±23	1570±33	1665±23
Ta (mg/kg)	1.31±0.08	1.26±0.05	1.16±0.10	1.03±0.08	1.34±0.10	1.19±0.03	1.22±0.04	1.29±0.04
Y (mg/kg)	34.9±0.7	31.7±0.5	30.8±0.3	24.9±0.4	35.8±0.4	30.1±0.4	32.3±0.3	33.4±0.3
La (mg/kg)	47.6±0.7	49.0±0.4	45.0±0.5	36.6±0.5	49.2±0.5	44.0±0.4	45.1±0.6	45.4±0.4
Ce (mg/kg)	90.4±1.1	94.2±1.6	85.0±1.0	69.5±0.8	93.1±1.1	83.7±0.9	86.8±0.9	87.2±0.2
Nd (mg/kg)	41.6±0.6	42.7±1.1	38.8±0.9	31.9±1.1	41.7±1.6	37.9±1.5	39.5±1.1	39.9±0.9
Th (mg/kg)	20.1±0.5	20.9±0.4	17.8±0.3	15.3±0.1	21.4±0.3	18.8±0.3	18.9±0.3	18.5±0.3

Table 3.11 (cont'd) Chemical compositions of the ceramic bodies by ICP-OES/ ICP-MS

Element	**ZA2-22**	**ZA2-31**	**ZA2-33**	**ZFB1-42**	**ZFB1-47**	**ZFB1-48**	**ZFB1-51**	**ZFB2-58**
Fe_2O_3 (%)	8.18±0.03	7.78±0.11	7.68±0.07	8.35±0.08	7.36±0.04	8.55±0.17	7.58±0.01	5.62±0.03
Al_2O_3 (%)	19.07±0.4	16.58±0.28	17.98±0.25	17.68±0.51	16.13±0.34	18.77±0.56	14.22±0.26	14.02±0.23
Na_2O (%)	0.85±0.03	0.87±0.03	0.503±0.011	0.51±0.03	0.55±0.01	0.48±0.01	1.02±0.03	0.86±0.01
MgO (%)	3.66±0.05	4.01±0.06	3.85±0.05	4.62±0.10	3.85±0.08	4.46±0.13	3.36±0.05	1.94±0.03
K_2O (%)	2.96±0.05	2.74±0.05	2.61±0.04	2.42±0.07	2.31±0.06	2.54±0.07	2.18±0.04	2.09±0.04
CaO (%)	11.18±0.03	11.59±0.11	10.51±0.11	12.13±0.14	11.43±0.19	10.91±0.26	7.65±0.07	6.49±0.08
SiO_2 (%)	47.3±0.4	47.7±0.6	45.7±0.9	46.8±0.8	45.7±1.1	48.9±1.9	55.4±0.8	61.8±1.3
TiO_2 (%)	0.917±0.005	0.725±0.006	0.708±0.003	0.739±0.010	0.670±0.006	0.757±0.012	0.862±0.010	0.787±0.006
MnO (%)	0.124±0.001	0.124±0.001	0.149±0.003	0.128±0.001	0.139±0.001	0.128±0.001	0.219±0.002	0.094±0.001
Rb (mg/kg)	162.5±1.9	139.5±0.6	140.5±1.7	129.0±1.2	118.0±1.8	138.5±1.3	92.0±1.2	105.0±1.4
Sr (mg/kg)	264.0±1.5	219.5±2.0	287.0±3.0	218.0±1.3	229.0±2.7	244.0±0.8	151.5±1.1	111.0±0.6
Ba (mg/kg)	574.5±4.2	474.0±3.2	463.5±3.7	428.0±1.4	467.5±7.8	416.0±4.2	464.5±5.6	452.0±3.4
V (mg/kg)	138.0±1.1	121.0±1.3	141.5±2.2	153.5±1.7	136.5±1.2	151.5±0.8	121.0±1.4	110.0±0.9
Cr (mg/kg)	192.5±1.6	290.0±3.3	273.5±3.4	353.5±2.2	329.0±3.8	334.5±2.2	211.0±1.0	115.0±1.2
Co (mg/kg)	26.2±0.2	26.4±0.4	27.1±0.4	31.0±0.3	30.4±0.5	30.0±0.1	30.7±0.3	16.2±0.3
Ni (mg/kg)	136.6±1.6	216.4±3.9	211.4±3.0	268.0±1.3	267.6±2.8	261.1±3.1	156.2±3.0	63.0±1.5
Zn (mg/kg)	112.5±4.9	123.5±2.6	111.5±2.0	112.5±1.3	108.0±3.0	114.5±2.2	104.0±4.7	82.1±1.7
Pb (mg/kg)	906.5±7.4	1190±20	1705±25	845±11.2	178.5±1.5	644.0±6.6	94.4±1.2	1810±10
Tl (mg/kg)	-	0.48±0.02	1.07±0.06	0.79±0.04	1.14±0.08	-	-	0.41±0.02
Zr (mg/kg)	91.9±2.3	46.5±1.4	61.5±1.0	59.3±1.3	44.7±1.8	63.0±1.6	30.2±0.5	69.7±0.5
Nb (mg/kg)	18.3±0.09	14.6±0.1	15.4±0.3	14.4±0.1	13.8±0.3	15.2±0.1	14.2±0.2	14.4±0.2
P (mg/kg)	813±13	2755±41	1340±37	1330±18	1845±33	1335±27	917±16	618±9
Ta (mg/kg)	1.37±0.05	1.14±0.05	1.21±0.05	1.07±0.08	1.04±0.08	1.14±0.06	1.04±0.08	1.13±0.06
Y (mg/kg)	20.3±0.08	27.5±0.1	29.2±0.4	26.9±0.3	25.3±0.3	29.2±0.2	23.2±0.4	20.6±0.6
La (mg/kg)	43.2±0.2	39.7±0.2	44.2±0.9	39.0±0.5	38.0±0.8	42.5±0.4	32.6±0.3	38.2±0.5
Ce (mg/kg)	87.4±0.9	76.9±1.0	83.4±1.2	73.4±1.0	73.1±1.0	80.3±0.5	67.0±0.6	76.4±0.7
Nd (mg/kg)	36.3±1.3	35.0±0.7	37.4±1.3	33.2±1.0	33.6±0.9	36.7±1.4	29.9±1.3	34.9±1.0
Th (mg/kg)	17.7±0.5	15.7±0.4	18.4±0.5	15.3±0.2	15.6±0.2	17.1±0.3	11.9±0.1	13.4±0.1

Table 3.11 (cont'd) Chemical compositions of the ceramic bodies by ICP-OES/ICP- MS

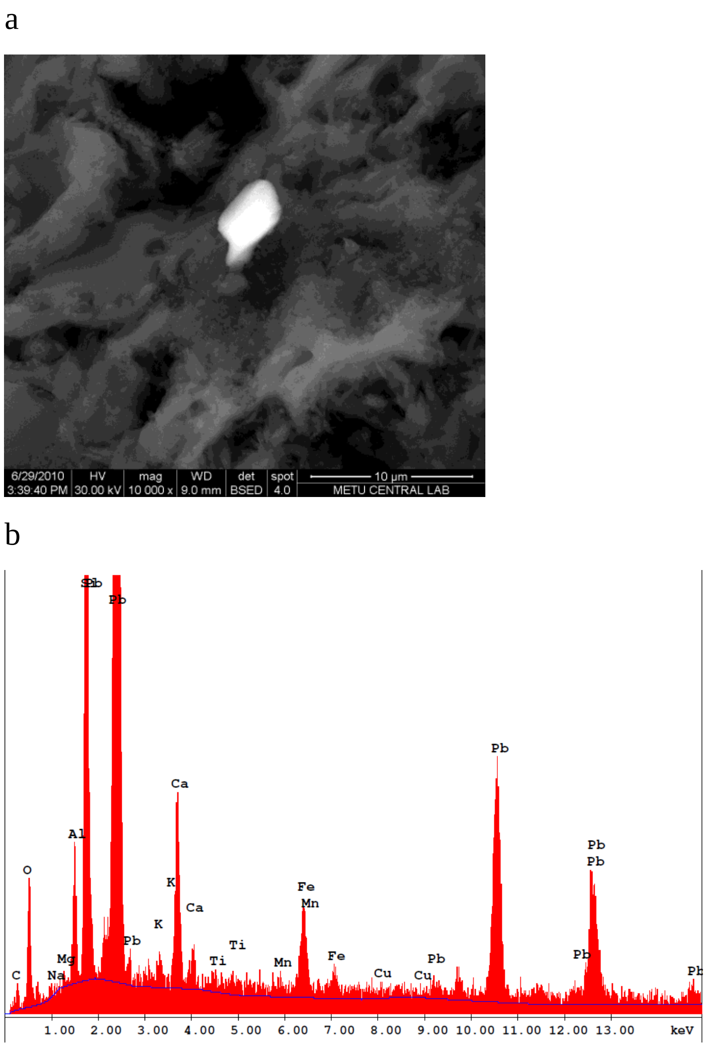
Element	ZFB2-59	ZFB3-60	ZFB3-64	ZFB4-65	ZFB5-67	ZFB6-76	ZFB6-78	ZFB6-81
Fe_2O_3 (%)	5.79±0.04	5.15±0.03	8.92±0.07	6.83±0.06	6.31±0.03	5.87±0.06	5.09±0.01	8.46±0.16
Al_2O_3 (%)	12.86±0.47	12.56±0.18	19.83±0.2	14.34±0.34	14.11±0.32	12.67±0.24	12.50±0.13	18.77±0.43
Na_2O (%)	0.34±0.01	0.86±0.03	0.46±0.004	0.59±0.03	0.39±0.008	1.47±0.04	0.87±0.03	0.71±0.03
MgO (%)	3.55±0.12	1.56±0.02	3.99±0.05	3.26±0.06	3.51±0.08	3.71±0.06	1.56±0.02	3.96±0.08
K_2O (%)	2.12±0.07	1.91±0.02	2.83±0.04	1.83±0.05	2.42±0.05	2.09±0.04	1.90±0.02	2.73±0.07
CaO (%)	13.37±0.28	5.16±0.07	9.28±0.09	6.49±0.09	14.13±0.3	9.65±0.14	4.95±0.03	13.74±0.25
SiO_2 (%)	44.9±1.7	64.6±1.1	46.84±0.4	55.6±1.3	46.8±1.5	53.3±1.3	63.9±0.6	42.9±0.8
TiO_2 (%)	0.602±0.008	0.732±0.006	0.765±0.003	0.825±0.013	0.648±0.006	0.688±0.008	0.722±0.005	0.677±0.013
MnO (%)	0.112±0.001	0.059±0.001	0.142±0.001	0.117±0.001	0.111±0.001	0.132±0.001	0.057±0.001	0.172±0.001
Rb (mg/kg)	90.0±1.2	92.4±0.5	154.0±0.5	94.4±1.3	109.5±1.3	88.4±0.7	92.2±1.0	168.5±0.9
Sr (mg/kg)	170.5±1.4	100.7±0.9	291.5±2.5	218.0±1.3	182.0±2.9	213.5±1.3	102.5±0.8	309.5±6.0
Ba (mg/kg)	371.5±5.5	396.5±4.7	457.5±3.8	573.5±3.5	461.5±4.3	396.5±2.1	395.0±1.9	561.0±8.4
V (mg/kg)	112.0±0.8	98.3±1.3	141.0±1.4	111.0±0.9	109.0±2.5	98.5±1.4	97.3±0.6	143.0±1.3
Cr (mg/kg)	228.5±3.0	99.4±1.4	283.0±1.5	172.5±1.9	254.5±3.8	216.5±3.1	97.2±1.3	239.0±3.0
Co (mg/kg)	16.9±0.4	14.9±0.2	27.9±0.5	22.7±0.4	17.0±0.5	23.3±0.4	16.3±0.5	29.9±0.4
Ni (mg/kg)	132.0±1.7	54.6±0.6	214.4±1.1	138.1±1.9	131.4±3.8	161.2±1.2	54.3±1.4	200.4±2.8
Zn (mg/kg)	85.9±2.3	78.3±2.5	129.0±2.5	138.0±5.8	89.7±1.0	83.1±3.5	79.9±5.2	121.0±1.3
Pb (mg/kg)	590.5±3.4	416.0±6.2	535.5±4.6	319.5±4.7	113.5±2.2	300.0±1.5	436.5±0.4	2595±38
Tl (mg/kg)	0.56±0.02	0.56±0.04	1.19±0.07	1.09±0.06	0.56±0.05	0.58±0.04	-	-
Zr (mg/kg)	42.4±1.0	68.3±1.0	68.1±1.6	65.0±1.6	49.9±1.6	49.4±2.6	61.2±1.2	60.4±1.2
Nb (mg/kg)	12.2±0.3	12.8±0.1	16.4±0.3	17.6±0.2	13.3±0.2	11.1±0.3	12.7±0.1	15.9±0.2
P (mg/kg)	1002±27	728±26	2400±20	1075±17	1560±28	1130±24	740±16	1405±19
Ta (mg/kg)	0.90±0.07	1.01±0.07	1.26±0.08	1.28±0.06	1.01±0.04	0.86±0.05	0.99±0.07	1.29±0.02
Y (mg/kg)	19.7±0.2	18.6±0.1	31.0±0.2	16.8±0.4	21.4±0.3	18.9±0.3	17.9±0.3	33.4±0.6
La (mg/kg)	31.0±0.3	33.4±0.4	47.5±0.7	40.9±0.9	34.4±0.4	29.7±0.2	33.4±0.3	46.2±0.4
Ce (mg/kg)	60.6±1.3	67.9±0.4	89.9±0.8	81.4±0.6	66.9±0.6	60.0±0.2	67.5±1.0	88.5±1.1
Nd (mg/kg)	26.9±0.6	29.9±1.5	41.4±1.3	35.0±1.3	30.6±1.3	26.6±0.8	30.7±1.1	40.2±1.9
Th (mg/kg)	11.0±0.4	11.6±0.3	20.4±0.4	14.2±0.4	12.9±0.2	11.2±0.3	11.7±0.2	20.8±0.3

Table 3.11 (cont'd) Chemical compositions of the ceramic bodies by ICP-OES/ICP-MS

Element	**ZFB6-84**	**GP-68**	**GP-72**	**ZS-86**	**ZS-87**	**ZS-89**
Fe_2O_3 (%)	6.46±0.06	5.90±0.04	5.22±0.01	5.80±0.06	9.88±0.07	8.06±0.07
Al_2O_3 (%)	16.23±0.43	13.88±0.34	12.84±0.21	12.66±0.13	20.40±0.4	17.21±0.28
Na_2O (%)	1.54±0.05	1.54±0.04	1.23±0.04	0.27±0.005	1.01±0.01	0.52±0.007
MgO (%)	2.38±0.06	4.13±0.08	3.73±0.06	3.15±0.03	5.12±0.06	3.71±0.05
K_2O (%)	2.75±0.06	2.39±0.05	2.27±0.04	2.98±0.04	3.35±0.08	2.55±0.04
CaO (%)	5.12±0.08	14.97±0.3	16.78±0.1	1.48±0.03	4.04±0.03	10.17±0.14
SiO_2 (%)	58.2±1.5	47.4±0.8	44.3±0.6	65.5±0.8	44.9±0.8	45.9±0.6
TiO_2 (%)	0.792±0.012	0.634±0.006	0.584±0.006	0.655±0.003	0.926±0.006	0.704±0.003
MnO (%)	0.109±0.001	0.116±0.001	0.099±0.001	0.086±0.001	0.117±0.002	0.130±0.001
Rb (mg/kg)	118.5±1.2	123.5±1.1	113.0±0.5	130.0±1.3	135.5±0.8	133.5±1.0
Sr (mg/kg)	98.2±1.5	266.0±1.2	259.0±1.1	75.4±0.9	292.5±2.6	250.5±2.5
Ba (mg/kg)	539.5±5.5	598.0±5.7	597.0±7.1	223.0±2.6	792.0±5.8	408.5±2.4
V (mg/kg)	111.5±1.0	92.3±0.4	82.2±0.7	161.0±1.3	147.5±1.1	128.5±0.4
Cr (mg/kg)	173.5±2.0	223.5±2.9	180.5±1.2	78.1±0.5	164.0±1.1	284.0±2.3
Co (mg/kg)	20.2±0.4	21.4±0.4	19.2±0.2	19.1±0.5	27.9±0.5	27.4±0.3
Ni (mg/kg)	94.4±1.5	152.2±1.8	126.7±0.4	66.8±1.5	98.7±0.9	216.0±2.3
Zn (mg/kg)	99.4±1.7	79.8±2.9	79.2±3.1	94.4±2.3	156.0±3.1	111.0±4.1
Pb (mg/kg)	1365±13	598.5±8.0	952.5±9.1	158.5±2.0	42.3±0.7	537.5±3.4
Tl (mg/kg)	-	0.30±0.02	-	1.26±0.06	0.88±0.04	1.09±0.06
Zr (mg/kg)	48.4±2.1	38.9±1.0	29.3±0.7	106.0±2.0	12.1±0.8	59.6±1.2
Nb (mg/kg)	13.5±0.1	13.1±0.3	12.2±0.2	13.6±0.3	14.7±0.3	14.2±0.3
P (mg/kg)	688±12	1141±17	1175±22	752±16	918±8	1275±24
Ta (mg/kg)	-	-	1.01±0.02	0.98±0.04	1.04±0.07	1.09±0.05
Y (mg/kg)	18.7±0.4	24.4±0.6	22.9±0.2	28.1±0.4	30.4±0.2	26.7±0.4
La (mg/kg)	38.9±0.6	33.0±0.3	31.5±0.3	35.2±0.3	55.4±0.7	40.0±0.4
Ce (mg/kg)	79.0±0.8	67.1±1.0	64.4±1.0	78.3±0.4	115.0±1.7	75.9±0.2
Nd (mg/kg)	34.6±1.0	29.2±1.0	28.6±1.1	30.8±0.5	53.2±0.8	35.0±0.8
Th (mg/kg)	13.3±0.2	12.9±0.3	12.9±0.3	11.4±0.1	17.4±0.2	16.6±0.3

In the cluster analysis performed by using SPSS, data belonging to calcium, strontium, lead and phosphorous were not included due to several reasons. In the thin section analyses performed, in addition to primary calcite which is expected to be present in the body composition, micritic calcites occurring from secondary processes were also observed (Section 3.2.1). Obviously, this may lead to erroneous results in the statistical analysis. Strontium which is a mobile element and has similar chemical behaviour as that of calcium has not been included in the statistical analysis with similar reasons. Relatively high amounts of lead detected in the bodies (Table 3.11) which were also detected by previous SEM-EDX analysis (Figure 3.22), may result from the diffusion of lead ions from the glaze towards the body part during the firing process. Phosphorous may also be present due to the contamination arising from burial conditions.

Two types of Hierarchical Cluster analyses were carried out; first by using all of the major and trace elements measured, and then by using only trace elements involved (except calcium, strontium, lead and phosphorous) (Figures 3.23-3.24). These Hierarchical Cluster Analyses were performed using Pearson correlation and the nearest neighbour method. In these examinations, abbreviations used are the followings: Anaia Zeuxippus Ware Type: ZA, Zeuxippus Ware Family: ZFB, Green Painted: GP, Zeuxippus Ware Type Slip Painted: ZS.



Element	Wt %	At %	K-Ratio	Z	A	F
C K	5.62	21.50	0.0108	1.1762	0.1634	1.0001
O K	10.58	30.39	0.0175	1.1591	0.1430	1.0002
NaK	0.00	0.00	0.0000	1.0878	0.1953	1.0013
MgK	0.28	0.53	0.0008	1.1159	0.2593	1.0026
AlK	2.62	4.47	0.0098	1.0838	0.3423	1.0039
SiK	12.18	19.93	0.0577	1.1160	0.4246	1.0005
K K	0.82	0.97	0.0039	1.1105	0.4294	1.0040
CaK	4.75	5.44	0.0262	1.1334	0.4872	1.0013
TiK	0.49	0.47	0.0030	1.0223	0.6058	1.0023
MnK	0.50	0.42	0.0040	0.9981	0.7832	1.0149
FeK	3.20	2.63	0.0276	1.0201	0.8261	1.0219
CuK	0.34	0.24	0.0033	1.0013	0.9057	1.0634
PbL	58.63	13.01	0.5016	0.8316	1.0287	1.0000
Total	100.00	100.00				

Figure 3.22: a) SEM image of *Zeuxippus Ware Family* sample ZFB5-67 body showing a lightly colored area which refers to a very rich Pb concentration, b) The EDX analysis results from this lightly colored area.

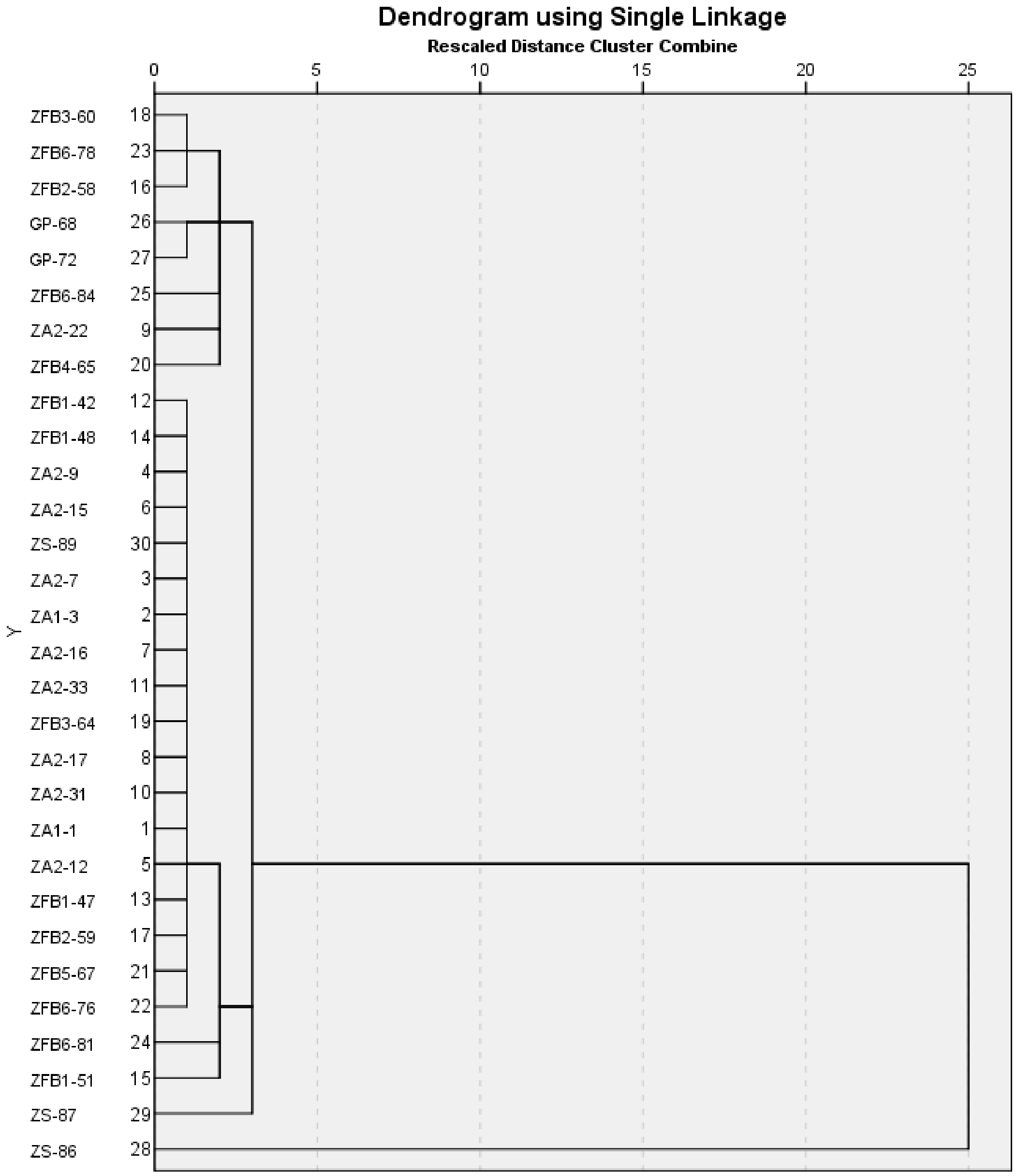


Figure 3.23: Cluster diagram of all elements measured using Pearson correlation and the nearest neighbour method

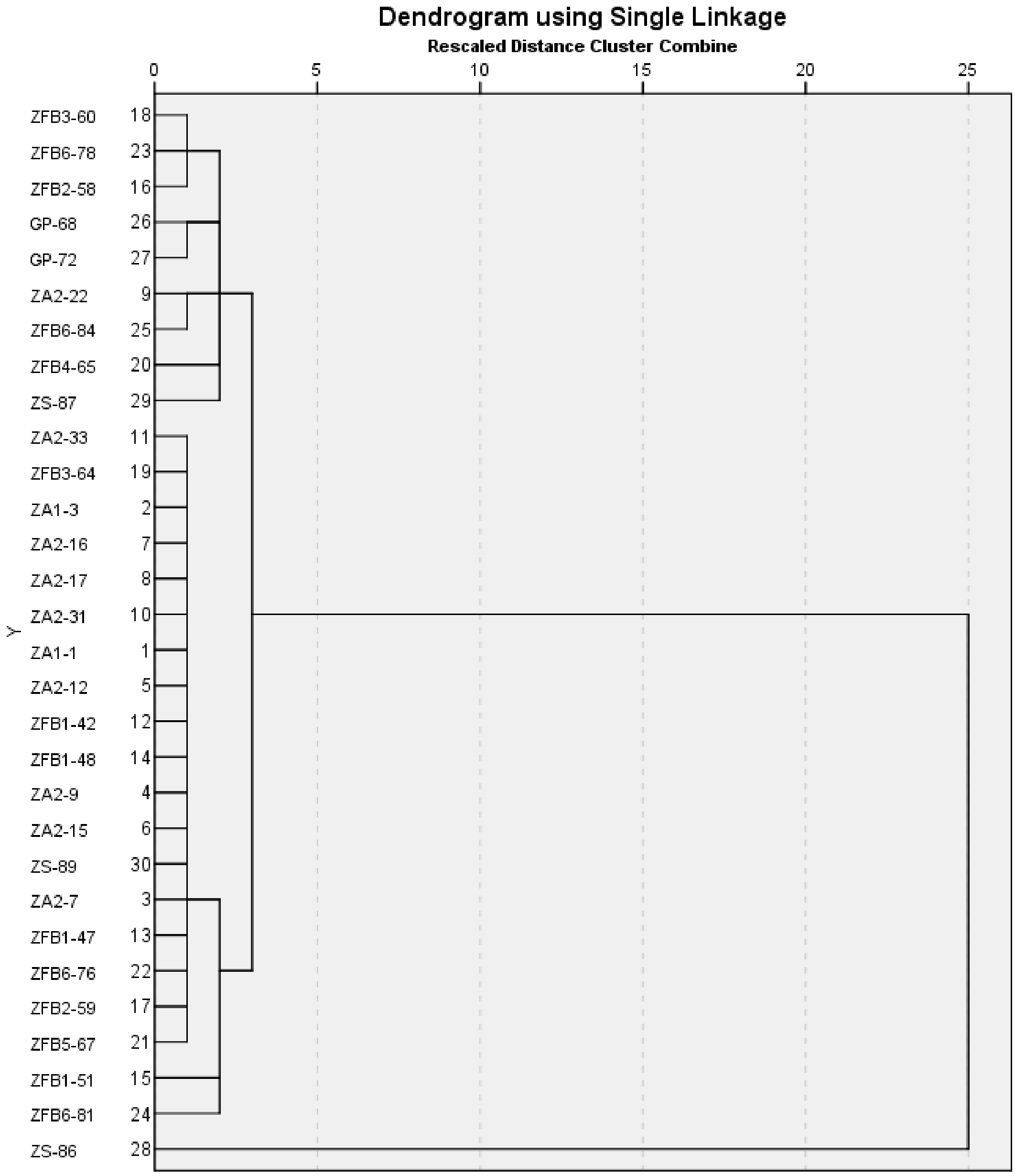


Figure 3.24: Cluster diagram of trace elements measured using Pearson correlation and the nearest neighbour method.

According to both of the cluster diagrams, there are two main groups labeled as Group 1 and Group 2 together with a unique sample (ZS-86) which seems to be completely different from the rest. From the similarity of the cluster diagrams, it is concluded that trace elements are dominant and discriminative elements in the formation of these clusters. Consequently, further discussions will be based on the cluster diagram obtained by the use of only trace elements (Figure 3.24). Group 1 includes samples ZFB3-60, ZFB6-78, ZFB2-58, GP-68, GP-72, ZA2-22, ZFB6-84, ZFB4-65 and ZS87. This group is further divided into four subgroups as Subgroup 1.1, Subgroup 1.2, Subgroup 1.3 and Subgroup 1.4. Group 2 includes samples ZA2-33, ZFB3-64, ZA1-3, ZA2-16, ZA2-17, ZA2-31, ZA1-1, ZA2-12, ZFB1-42, ZFB1-48, ZA2-9, ZA2-15, ZS-89, ZA2-7, ZFB1-47, ZB6-76, ZFB2-59, ZFB5-67, ZFB1-51 and ZFB6-81. This group is also further divided into two subgroups as Subgroup 2.1 and Subgroup 2.2. Subgroup 1.1, which includes samples ZFB3-60, ZFB6-78 and ZFB2-58, is also characterized by their highest grain/matrix ratios (~ 15-20 %) and non-micaceous matrixes (~ 0-2 % - ~ 2-3 %) (Section 3.2.1). Subgroup 1.2 includes samples GP-68 and GP-72 while Subgroup 1.3 consists of samples ZA2-22 and ZFB6-84. Finally, Subgroup 1.4 includes ZFB4-65 and ZS-87.

It is noteworthy to say that Subgroup 2.1 contains most of the samples under investigation. It includes almost all of the ZA samples analyzed (ZA2-33, ZA1-3, ZA2-16, ZA2-17, ZA2-31, ZA1-1, ZA2-12, ZA2-9, ZA2-15, ZA2-7) and half of the ZFB samples (ZFB3-64, ZFB1-42, ZFB1-48, ZFB1-47, ZFB6-76, ZFB2-59 and ZFB5-67). Therefore, this cluster analysis reveals that ZA ceramics form more or less a homogeneous group. In addition, Subgroup 2.2 consists of ZFB1-51 and ZFB6-81.

More detailed comparisons were carried out by drawing bi-plots and ternary diagrams. According to the ternary diagram of K_2O, MgO and Al_2O_3 combination (Figure 3.25), three of the ZFB samples (ZFB3-60, ZFB6-78 and ZFB2-58) are well separated from the rest and they form a coherent group. The other samples appear to be cumulated in one group, except sample ZS-86 which stands out from the rest clearly. These outcomes have been already observed in the cluster analysis previously (Figure 3.24).

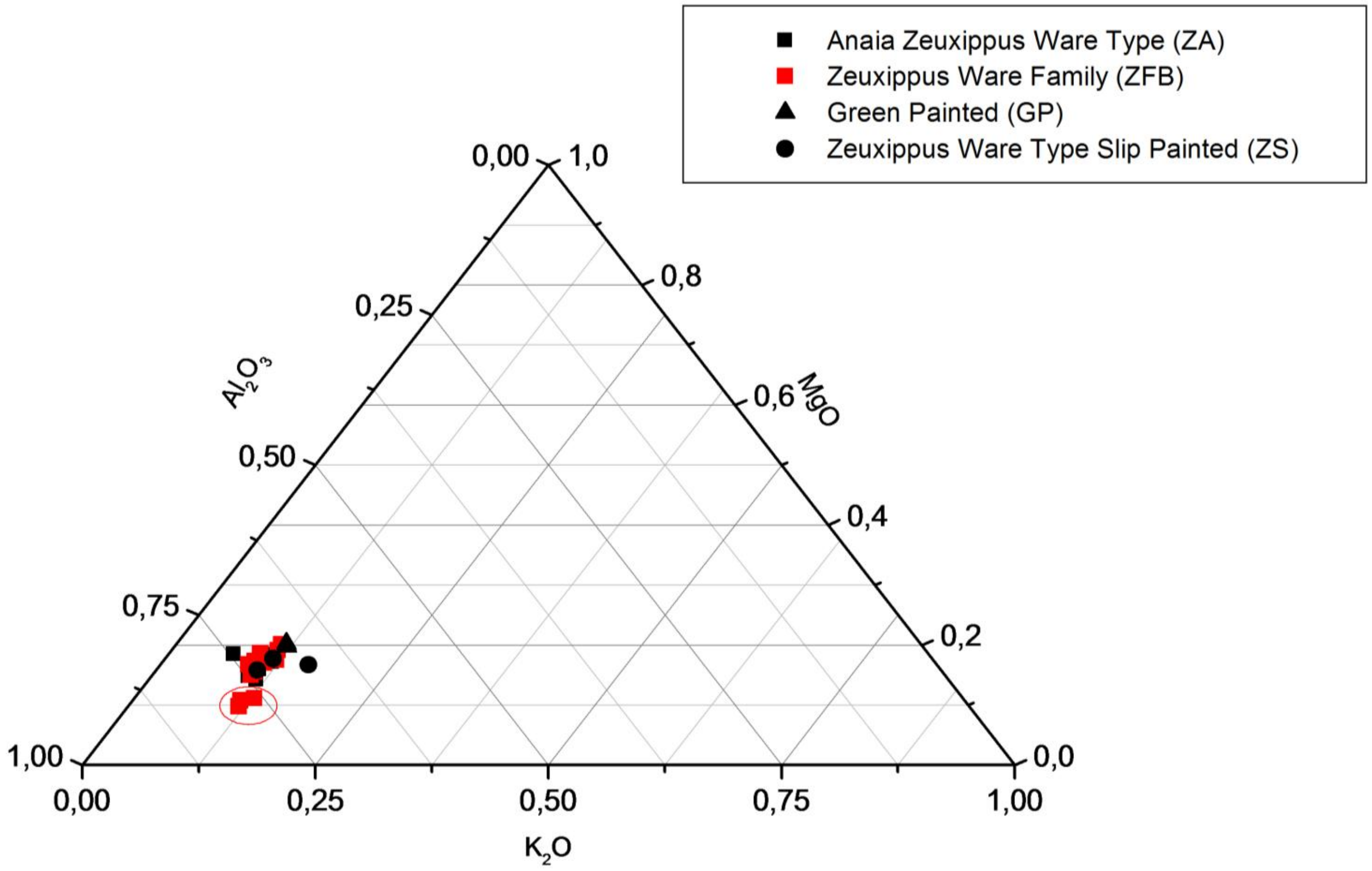


Figure 3.25: Ternary diagram showing the relative amounts of K_2O, MgO and Al_2O_3 of the sample bodies analyzed.

In general, samples analyzed contain relatively high amounts of chromium and nickel (Table 3.11) which may indicate the use of ophiolitic related clay raw materials in their production. This observation is supported by the widespread occurence of ophiolitic rocks around Küçük Menderes river (Section 1.1 and Figure 1.1) (Sauer and Waksman 2005). However, in the Ni-Cr bi-plot (Figure 3.26), samples ZFB3-60, ZFB6-78, ZFB2-58 together with ZS-86 are separated from the rest in terms of their relatively low amounts of chromium and nickel. When the bi-plots of Cr-Zr, Ni-Zr and Ni-Co (Figures 3.27-3.28-3.29) are examined, samples ZFB3-60, ZFB6-78 and ZFB2-58 are found to have medium zirconium and relatively lower cobalt contents. These three samples which belong to Group 1.1 in cluster analysis always appear to be a well separated group in all examinations. Among these three samples, ZFB3-60 and ZFB6-78 have an additional common characteristic as they display purple stains on the yellow glaze.

Another well separated group in all examinations is ZFB1-42, ZFB1-47 and ZFB1-48 with their high nickel and chromium, medium zirconium and high cobalt contents. In cluster analysis, they are all placed in Group 2.1. Also, they were visually classified belonging to the same group.

Samples ZS-86 and ZA2-22 strike with their quite high zirconium contents which may point to the use of raw materials from volcanic origins. However, nickel, chromium and cobalt levels of these two samples are quite different from each other, indicating that they may have been produced from different clay sources. One should also note that in the cluster analysis (Figure 3.24) sample ZS-86 stands out in a completely different position than the rest of all the samples. The possibility of its being an import ceramic was already stated in the visual classification carried out by Doğer (personal communication, 2011). On the other hand, sample ZA2-22 which displays *champlevé* technique also falls apart in several plots as ZS-86 does. However, it is not possible to make a clear comment for this sample based on its location in the cluster analysis.

Another distinctive sample, sample ZS-87 with its low zirconium, medium nickel, chromium and relatively high cobalt contents appears to be well separated from the rest of the samples in most of the plots. This is another sample which may be an import ceramic as in the case of ZS-86.

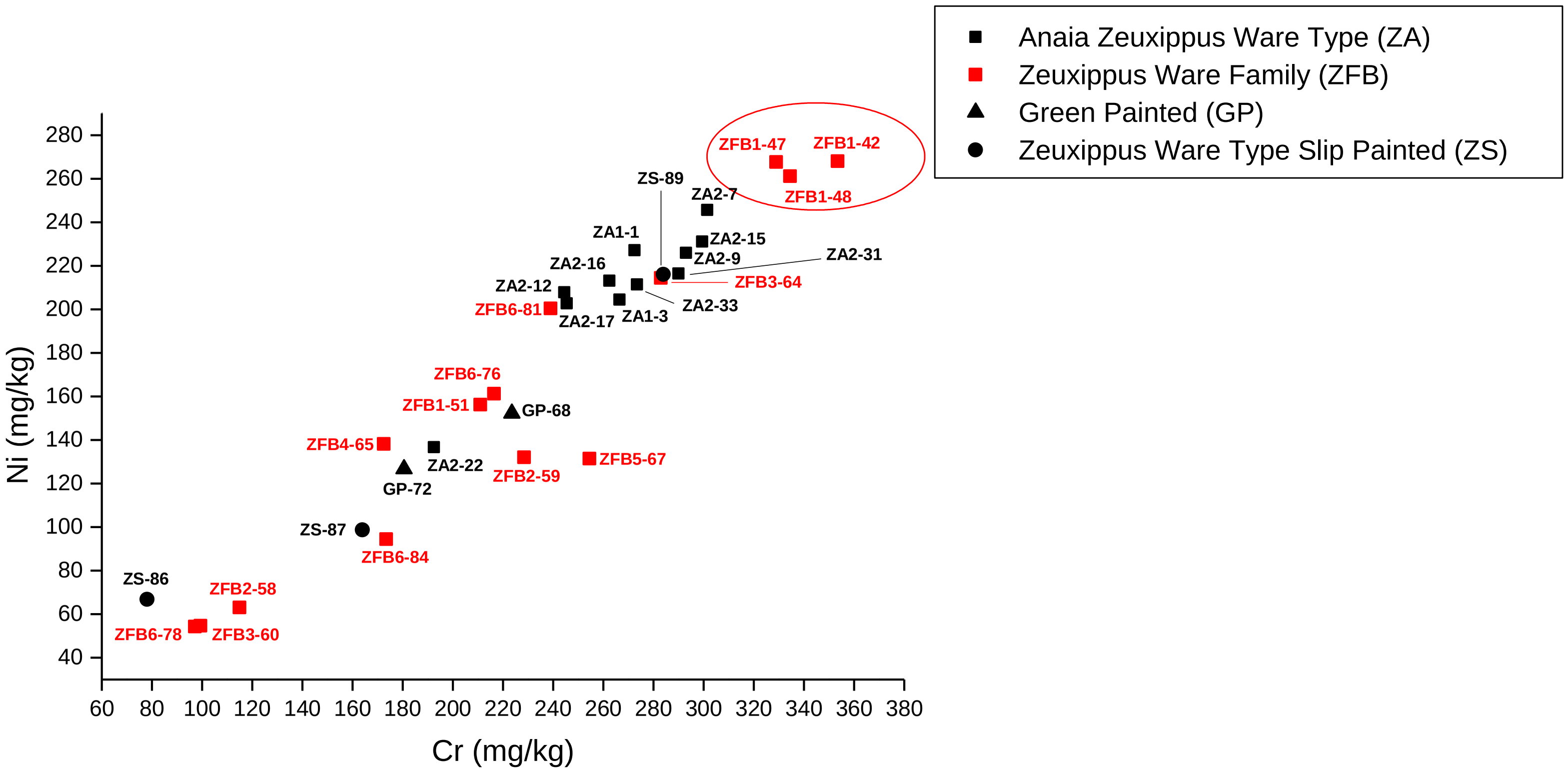


Figure 3.26: The Ni – Cr biplot of the analyzed sample bodies

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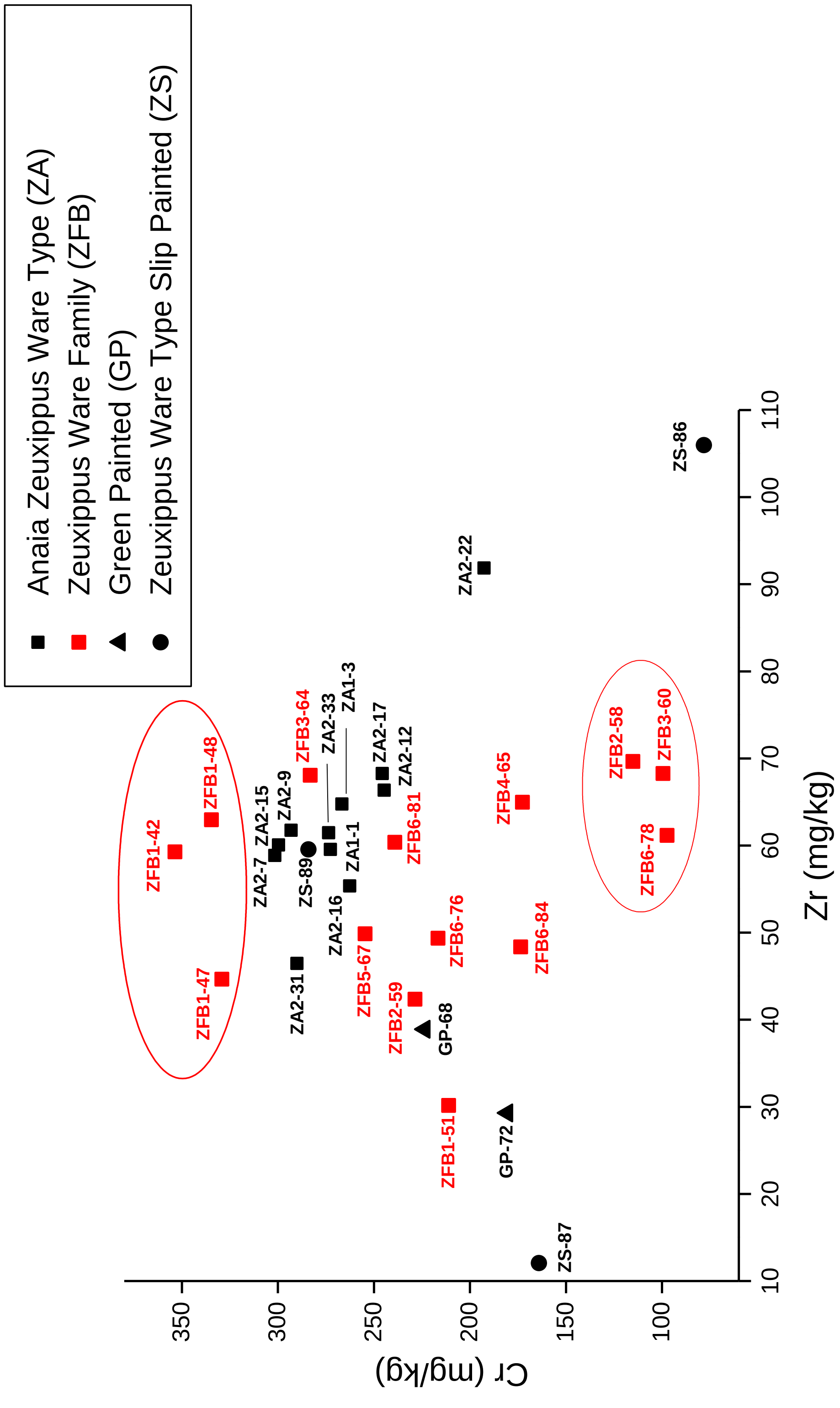

Figure 3.27: The Cr -Zr biplot of the analyzed sample bodies.

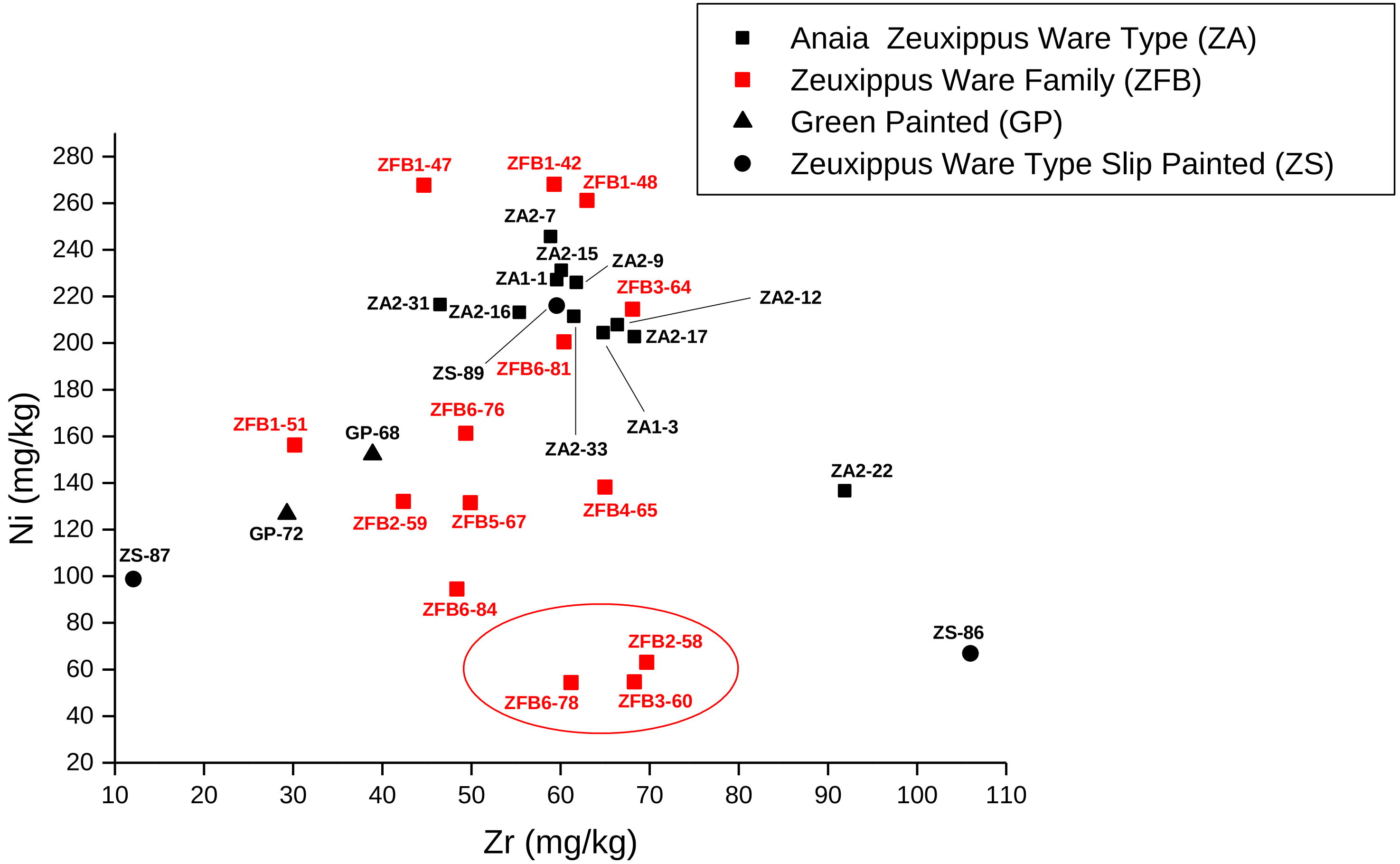

Figure 3.28: The Ni - Zr biplot of the analyzed sample bodies.

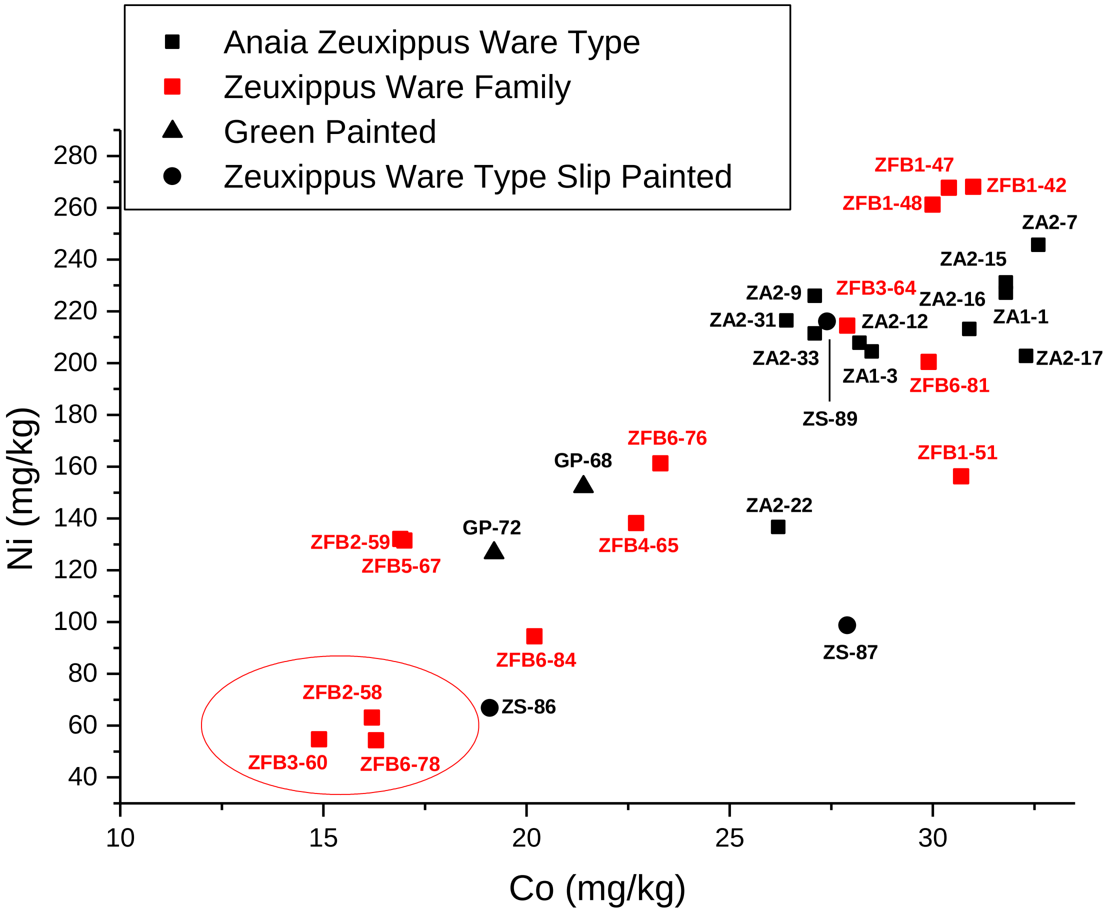

Figure 3.29: The Ni - Co biplot of the analyzed sample bodies

3.5 Raman Spectrometry

Raman spectrometry was performed for the non-destructive analysis of Kuşadası Kadıkalesi/Anaia ceramic glazes. Thirty representative samples were selected for the measurements. Four types of instruments were used for the analyses as mobile HE532, LabRam Infinity, HR800 (Horiba Jobin-Yvon) and Renishaw invia Raman spectrometers (for a detailed description of the instruments see section 2.2.7) (Table 3.12).

Table 3.12: Type of Raman Spectrometers used for the analysis of Kuşadası Kadıkalesi/Anaia glazes (λ = laser wavelength)

Type of Raman spectrometer	**Sample code**
HE532 (λ = 532 nm)	ZA1-2
HR800 (λ= 514 nm)	ZA1-1, ZA1-3, ZA1-4, ZA1-5, ZA2-15, ZA2-16, ZA2-17, ZA2-22, ZA2-31
LabRam Infinity (λ = 532 nm)	ZA2-6, ZA2-7, ZA2-8, ZA2-9, ZA2-12, ZA2-33
Renishaw (λ = 532 nm)	ZFB1-42, ZFB1-47, ZFB1-51, ZFB2-59, ZFB3-64, ZFB4-65, ZFB5-67, ZFB6-78, ZFB6-81, ZFB6-84, ZFB6-85 GP-68, GP-72, ZS-89

3.5.1 Data Processing

All the spectra recorded for various glaze samples using all Raman spectrometers both in LADIR and METU-Central Laboratory were baseline corrected in order to see the bending and stretching massifs better. LabSpec (Dilor) software was used for this procedure (Colomban et al. 2006). A ~ 4 segmented linear baseline was subtracted at around 200, 700, 900 and 1250 cm^{-1} regions. More points are added when the defined baseline crosses the spectrum. The same process was applied for all the spectra obtained.

The peak-fitting process was done by using Origin software peak fitting module (Microcal Software Inc.) according to the procedure previously discussed (Colomban and Tournié 2007; Colomban 2008). In this procedure, Q^n model was used as the basis of deconvolution for the spectra of glass as discussed previously above. Gaussian bands were assumed for the components of Si-O bending and stretching massifs since the samples are amorphous while Lorentzian bands were applied for the narrow peaks of the crystalline phases. The same spectral windows were used for each spectrum. For the Si-O stretching region (~ 700-1200 cm^{-1}), five bands were postulated as Q^0, Q^1, Q^2, Q^3 and Q^4. For the Si-O bending massif, four bands were used with similar bandwidths. The integral area under each component was calculated in order to obtain the polymerization index (Ip) values (see section 1.7). However, due to the baseline correction process, calculated values of Ip become rather biased and should not be considered as absolute values. They can only be used relatively on a comparative basis with literature.

3.5.2 Glassy Si-O Matrix

Representative raw and baseline corrected spectra for the glassy Si-O matrices of Kuşadası Kadıkalesi/Anaia glazes are given in Figure 3.30 and 3.31. Representative spectra of each sample are also given in Figure E.1.

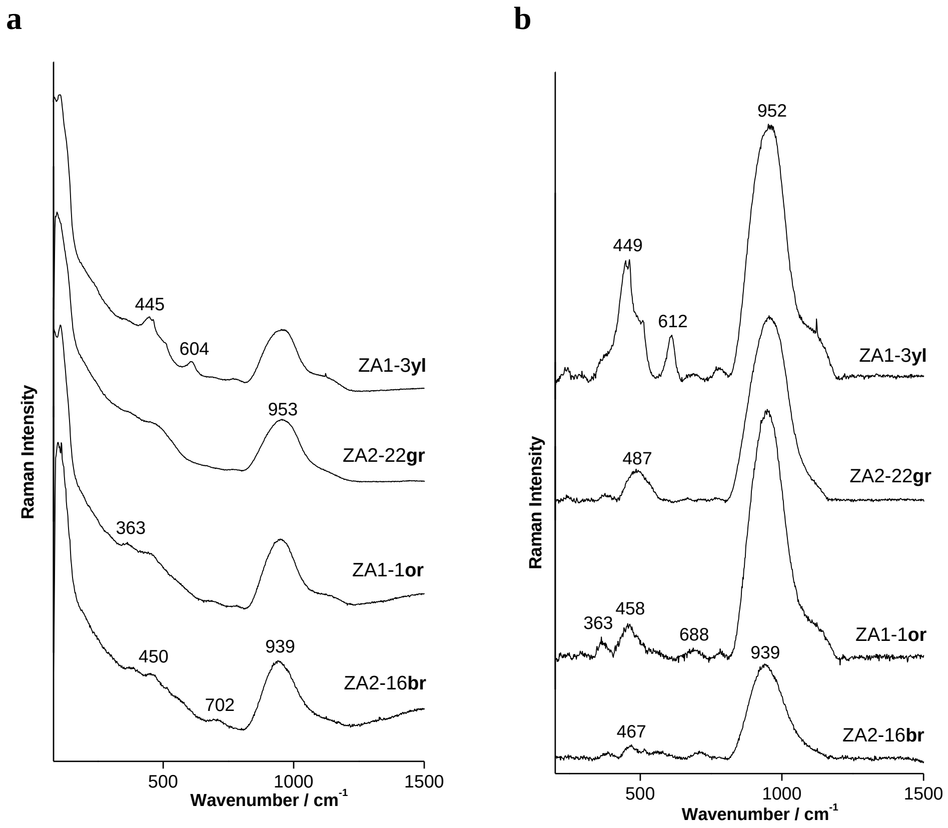

Figure 3.30: Raman spectra of the glassy Si-O matrices for ZA1-1, ZA1-3, ZA2-16, ZA2-22 recorded by HR800 Raman spectrometer a) Raw spectra b) Baseline corrected spectra (or: orange, br: brown, gr: green, yl: yellow)

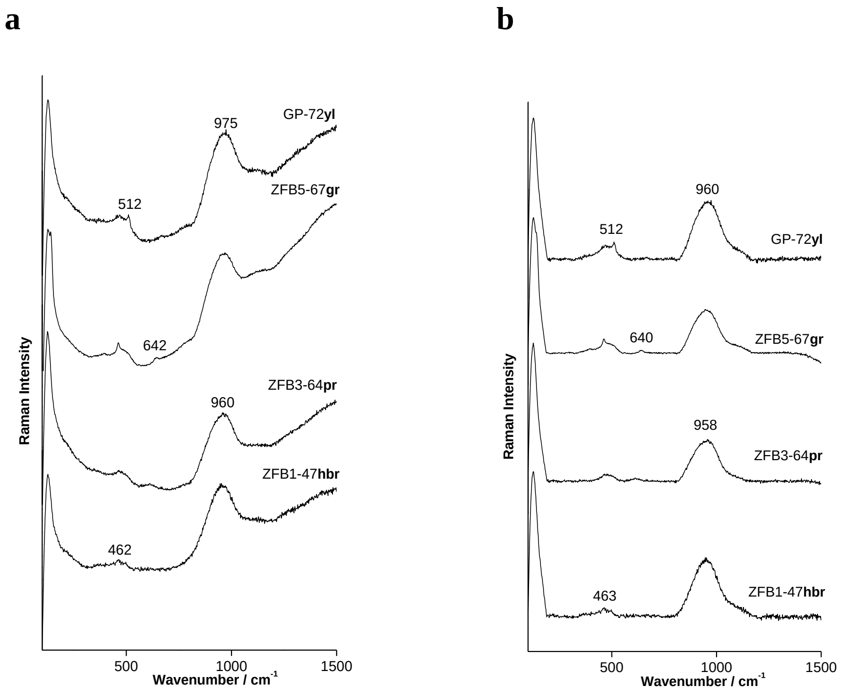

Figure 3.31: Raman spectra of the glassy Si-O matrices for ZFB1-47, ZFB3-64, ZFB5-67, GP-72 recorded by Renishaw invia Raman spectrometer a) Raw spectra b) Baseline corrected spectra (pr: purple, hbr: honey brown, gr: green, yl: yellow)

Maxima of the Si-O bending (δ) and stretching (ν) peaks for Kuşadası Kadıkalesi/Anaia glaze spectra are listed in Table 3.13.

Table 3.13: Maxima of the Si-O bending (δ) and stretching (ν) peaks for Kuşadası Kadıkalesi/Anaia glazes (wavenumbers in cm^{-1}).

Group name	**Sample code**	**Observed Color**	**δmax Si-O**	**νmax Si-O**	**Figure No**
Anaia Zeuxippus Ware Type - Green and Orange Stained Ware	ZA1-1	Brown	501	943	E.1-1
		Orange	458	948	E.1-1
		Yellow	-	952	E.1-1
	ZA1-2	Brown	493	936	E.1-2
		Green	-	947	E.1-3
		Yellow	-	954	E.1-3
	ZA1-3	Orange	-	945	E.1-4
		Green	468	952	E.1-4
		Yellow	462	952	E.1-5
	ZA1-4	Brown	552	941	E.1-6
		Green	486	946	E.1-6
	ZA1-5	Brown	499	948	E.1-7
		Green	471	969	E.1-7
		Yellow-1	-	957	E.1-8
		Yellow-2*	454	957	E.1-9
Anaia Zeuxippus Ware Type- Zeuxippus I Ware Type	ZA2-6	Brown	486	930	E.1-10
		Yellow	462	951	E.1-10
	ZA2-7	Brown	508	939	E.1-11
		Yellow	-	924	E.1-11
	ZA2-8	Brown	-	963	E.1-12
		Honey brown	-	967	E.1-13
	ZA2-9	Brown	484	944	E.1-14
		Green	-	942	E.1-14
	ZA2-12	Brown	533	936	E.1-15
		Green	484	949	E.1-16
	ZA2-16	Brown	469	941	E.1-18
		Honey brown	469	939	E.1-18
	ZA2-17	Green	469	957	E.1-19
	ZA2-22	Green	485	955	E.1-20
		light green	468	965	E.1-20
	ZA2-33	Brown	527	939	E.1-23
		Honey brown	460	934	E.1-23

Table 3.13 (cont'd) Maxima of the Si-O bending (δ) and stretching (ν) peaks for Kadıkalesi/ Anaia glazes (wavenumbers in cm^{-1}).

Group name	**Sample code**	**Observed Color**	**δmax Si-O**	**νmax Si-O**	**Figure No**
Anaia Zeuxippus Ware Type - Zeuxippus II Ware Type	ZA2-15	Honey brown	461	944	E.1-17
		Green	458	943	E.1-17
	ZA2-31	brown-1	-	946	E.1-21
		brown-2	540	955	E.1-21
		Honey brown	470	955	E.1-21
		Yellow	-	980	E.1-22
Zeuxippus Ware Family	ZFB1-42	brown	496	954	E.1-24
		Honey brown	462	942	E.1-24
	ZFB1-47	Honey brown-1	463	952	E.1-25
		Honey brown-2	-	941	E.1-25
	ZFB1-51	Yellow	469	954	E.1-26
Zeuxippus Ware Family	ZFB2-59	Honey brown	480	956	E.1-27
Zeuxippus Ware Family-Manganese-brown Stained Ware	ZFB3-64	Purple	465	958	E.1-28
Zeuxippus Ware Family-Incised-manganese Ware	ZFB4-65	Light green (yellow)	463	947	E.1-29
		Purple	612	976	E.1-29
		Green	-	972	E.1-29
Zeuxippus Ware Family-Green Stained Incised Ware	ZFB5-67	Brown	491	950	E.1-30
		Green	464	948	E.1-30
Zeuxippus Ware Family-Frankish Style Ceramics	ZFB6-78	Purple	461	937	E.1-31
		Yellow-1	463	930	E.1-31
		Yellow-2	461	948	E.1-31
	ZFB6-81	Green	-	969	E.1-32
	ZFB6-84	Yellow	462	925	E.1-33
	ZFB6-85	Brown	-	958	E.1-34

Table 3.13 (cont'd) Maxima of the Si-O bending (δ) and stretching (ν) peaks for Kadıkalesi/ Anaia glazes (wavenumbers in cm^{-1}).

Group name	**Sample code**	**Observed Color**	**δmax Si-O**	**νmax Si-O**	**Figure No**
Green Painted Ceramics	GP-68	Green	511	951	E.1-35
		transparent	460	961	E.1-35
	GP-72	Green-1	459	946	E.1-36
		Green-2	-	961	E.1-36
		Yellow	512	960	E.1-36
Zeuxippus Ware Type Slip Painted Ceramics	ZS-89	Brown	491	944	E.1-37
		Yellow	-	952	E.1-37

(*: outer side)

The Si-O stretching peak maxima of the glassy matrix spectra recorded varying between ca. 920 to 980 cm^{-1} indicate that these glazes have lead based composition (Ricciardi et al. 2009). Some of the spectra don't have Si-O bending massifs which are concealed by peaks corresponding to the crystalline phases (Figure E.1-1, 29, 32, 34, 37).

The Polymerization Index

The polymerization index values calculated from some of these representative spectra range from 0.04 to 0.05 which also show the very high lead content of these glazes (Figure 3.32). According to the classification of glassy silicates as a function of their composition proposed by Colomban et al. (2006), these glazes fall into the family with Ip values below 0.3-0.5 which corresponds to lead-rich silicates processed at low temperatures (< 700°C). As also discussed before, glazes of *Anaia Zeuxippus Ware Type* samples ZA2-16 and ZA2-31 were found to have ~ 50- 62 % PbO by SEM-EDX (Table D.3). Thus, results of Raman spectrometry measurements and SEM-EDX analyses are in accordance with each other. Additionally, results of this study are in good correlation with those of previous studies carried out for the 12th-14th century Byzantine glazes found at Skopje and Prilep in Republic of Macedonia, with Ip values below 0.5 and ~ 50 % PbO contents (Tanevska et al. 2009). Similar results were reported for another set of the 13th-14th century Byzantine glazes from Skopje (Raskovska et al. 2010) and the 6th -11th century Byzantine glazes from İznik and Ephesus in Turkey (Colomban et al. 2006).

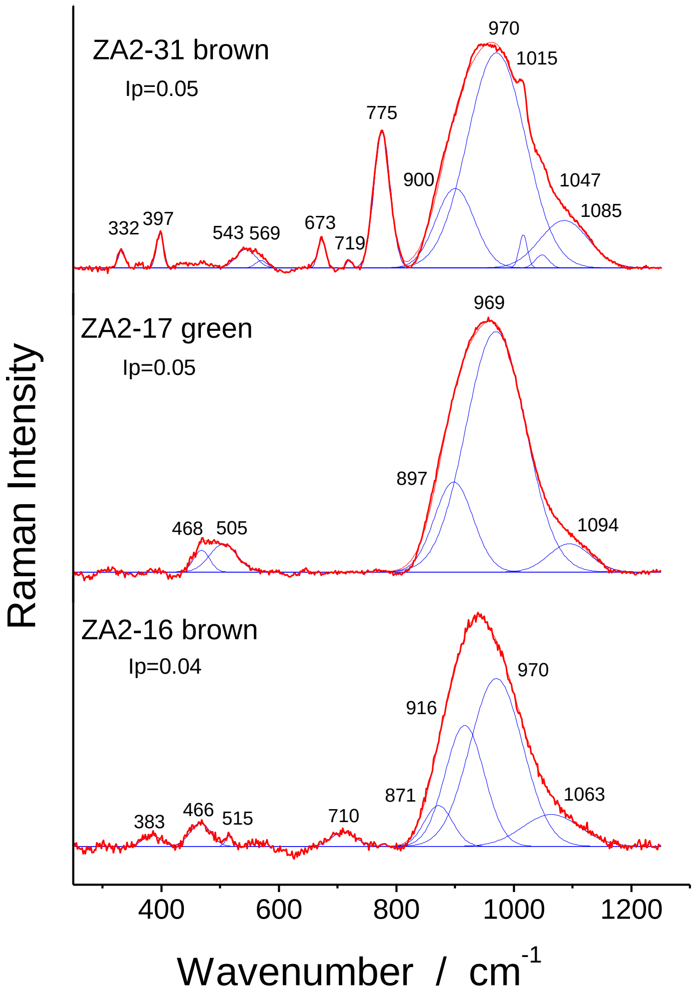

Figure 3.32: Deconvolution of representative Raman spectra according to the Q^n model recorded on samples ZA2-16, ZA2-17 and ZA2-31.

3.5.3 Crystalline Phases

Representative raw and baseline corrected spectra for the crystalline phases of Kuşadasi Kadıkalesi/Anaia glazes are given in Figure 3.33 and 3.34. Wavenumbers of the peaks corresponding to crystalline phases for the glazes analyzed are listed in Table 3.14. Arrangement of the table is on the basis of observed color of glazes. Most of the assigments are made to the common crystalline phases/ pigments found in ceramic glazes.

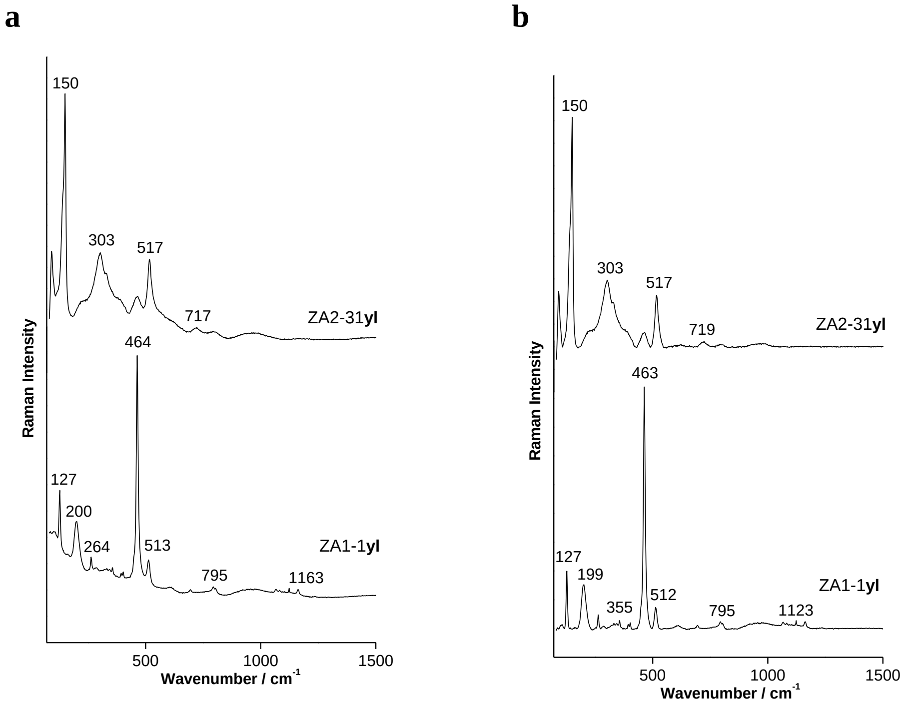

Figure 3.33 : Raman spectra of the crystalline phases for ZA1-1 and ZA2-31 recorded by HR800 Raman spectrometer a) Raw spectra b) Baseline corrected spectra (yl: yellow)

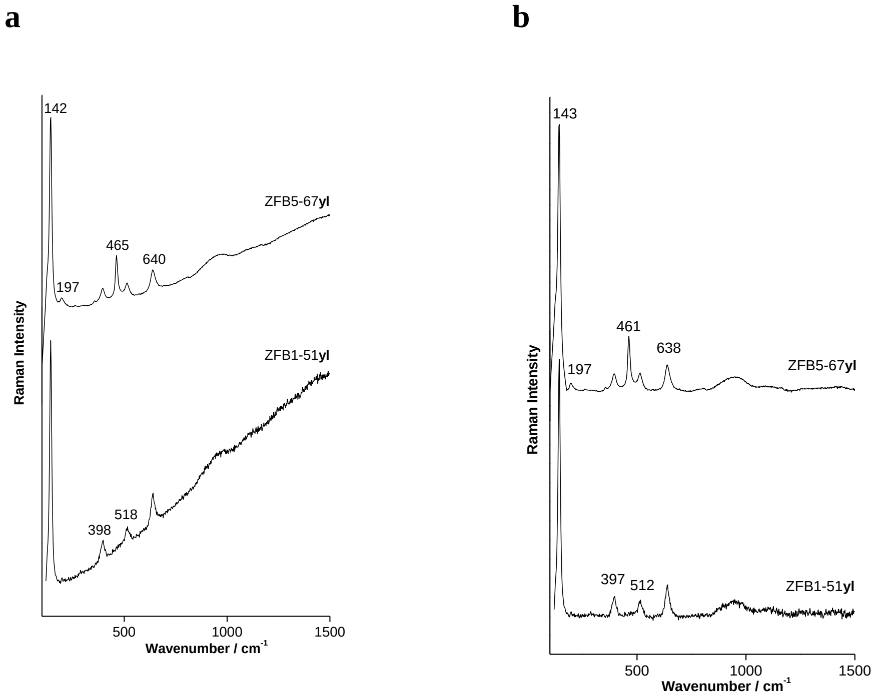

Figure 3.34 : Raman spectra of the crystalline phases for ZFB1-51 and ZFB5-67 recorded by Renishaw invia Raman spectrometer a) Raw spectra b) Baseline corrected spectra (yl: yellow)

Table 3.14: Crystalline phase and pigment assignments by Raman spectrometry for Kuşadası Kadıkalesi/Anaia glazes.

Observed color	**Crystalline phase/ pigment assignment**	**Formula**	**Raman signature (wavenumbers in cm^{-1})**	**sample code**	**Figure no**
Brown (incised regions)	Anorthite?	$CaAl_2Si_2O_8$	246 (250), 765	ZA1-2	E.1-2
	Microcline	$KAlSi_3O_8$	204, 327, 367, 469, 517	ZA2-9	E.1-14
	Magnetite	Fe_3O_4	666	ZA1-2	E.1-2
			307?, 544, 674	ZA1-5	E.1-7
			542, 666	ZA2-7	E.1-11
			664	ZA2-8	E.1-12
			533, 665	ZA2-12	E.1-15
			542, 673	ZA2-31	E.1-21
			302, 527, 662	ZA2-33	E.1-23
	Augite	(Ca,Na)(Mg,Fe, Al) $(Si,Al)_2O_6$	324, 390, 666, 1011	ZA2-7	E.1-11
			325, 393, 668,1011	ZFB5-67	E.1-30
	Hematite	α-Fe_2O_3	222, 666, 1313	ZA2-9	E.1-14
	Goethite	α –FeOOH	205, 244, 390, 484, 1006	ZA2-12	E.1-15
Brown	Hematite	α-Fe_2O_3	222, 413, 1316	ZFB6-85	E.1-34
	Magnetite	Fe_3O_4	665	ZS-89	E.1-37
Yellow	*Naples yellow* varieties	$Pb_2Sb_2O_7$	127, 199, 330, 512	ZA1-1	E.1-1
			150, 330, 517	ZA2-31	E.1-22
	Rutile	TiO_2	242-244, 444-451, 606-612	ZA1-1, ZA1-2, ZA1-3	E.1-1,3,5
			520, 615	ZA1-5	E.1-8
			244, 518, 617	ZA1-5 outer	E.1-9

Table 3.14 (cont'd) Crystalline phase and pigment assignments by Raman spectrometry for Kuşadası Kadıkalesi/Anaia glazes

Observed color	**Crystalline phase/ pigment assignment**	**Formula**	**Raman signature (wavenumbers in cm^{-1})**	**sample code**	**Figure no**
Yellow	Quartz	SiO_2	263, 355, 463	ZA1-1	E.1-1
			469	ZA1-5	E.1-8
			205, 260, 355, 461	ZA2-7	E.1-11
			463	ZA2-31	E.1-22
			206, 268, 360, 468		E.1-22
			463	ZFB4-65	E.1-29
	Feldspar (orthoclase-sanidine)?	$KAlSi_3O_8$	160, 512	ZA1-1	E.1-1
	Feldspar (orthoclase)	$KAlSi_3O_8$	454, 518	ZA1-5 outer	E.1-9
	Anatase	TiO_2	144, 397, 512, 641	ZFB1-51	E.1-26
			143, 395, 513, 638	ZFB5-67	E.1-30
Green	Rutile	TiO_2	242, 443, 606	ZA1-2	E.1-3
			244, 444, 514, 608	ZA2-9	E.1-14
	Anatase	TiO_2	395, 513, 636	ZA2-12	E.1-16
			144, 393, 511, 635	GP-68	E.1-35
	Quartz	SiO_2	205, 354, 463	ZA2-12	E.1-16
			463	ZFB4-65	E.1-29
			202, 262, 353, 462	ZFB6-81	E.1-32
	Microcline?	$KAlSi_3O_8$	198, 400, 517, 615	ZFB4-65	E.1-29

Table 3.14 (cont'd) Crystalline phase and pigment assignments by Raman spectrometry for Kuşadası Kadıkalesi/Anaia glazes

Observed color	Crystalline phase/ pigment assignment	Formula	Raman signature (wavenumbers in cm^{-1})	sample code	Figure no
Orange	Feldspar (microcline)	$KAlSi_3O_8$	111,128, 159, 265?, 290, 358, 451, 466, 515, 929	ZA1-3	E.1-4
	Quartz	SiO_2	128, 265, 358, 466	ZA1-3	E.1-4
Honey Brown	Quartz	SiO_2	202, 354, 463	ZA2-8	E.1-13
	Feldspar (microcline)	$KAlSi_3O_8$	202, 286, 332, 463, 514	ZA2-8	E.1-13
			330, 461, 514	ZA2-15	E.1-17
	Hematite?	α-Fe_2O_3	287, 408, 1324	ZFB2-59	E.1-27
	Goethite?	α –FeOOH	206, 480, 688, 1324	ZFB2-59	E.1-27
	Rutile	TiO_2	242, 448,609, 511, 609	ZS-89	E.1-37

Brown:

The brown regions of the glazes in the form of incised decorations were probably being painted with dark pigments by the Byzantine potters and these pigments were getting fused with the glaze during the firing process thus making the *sgraffitto* pattern clearer (Scott and Kamilli 1981). Most of the brown regions of the glazes (incised decorations) analyzed display peaks which may be considered belonging to magnetite with its most characteristic peak at ca. 662-674 cm^{-1} (de Faria et al. 1997; Froment et al. 2008) (Table 3.14, Figure E.1-2,7,11,12,15,21,23). In addition to magnetite, hematite and goethite were also attributed for the incised brown regions in some *Anaia Zeuxippus Ware Type* ceramic glazes analyzed (ZA2-9 and ZA2-12) (Colomban et al. 2001; Froment et al. 2008) (Table 3.14, Figure E.1-14,15).

In the brown stain of *Frankish Style* ceramic sample ZFB6-85, some of the peaks were attributed to hematite (Table 3.14, Figure E.1-34) while magnetite was also found in the brown glaze of *Zeuxippus Ware Type Slip Painted* sample ZS-89 (Table 3.14, Figure E.1-37) (de Faria et al. 1997). These compounds might have been deliberately added by the potters to the glaze mixtures or may come from the the body layers where the presence of iron compounds is most probable. In fact, the characterization of these iron oxide/hydroxide polymorphs by Raman spectrometry is a complicated matter since the peak wavenumbers of these compounds can easily be shifted depending on the firing temperature.

Presence of feldspar peaks in some *Anaia Zeuxippus Ware Type* ceramic glazes may be due to the contribution from the body layers underneath the glazes. Augite was also clearly detected in *Anaia Zeuxippus Ware Type* sample ZA2-7 and *Zeuxippus Ware Family* sample ZFB5-67 (Table 3.14, Figure E.1-11-30). This is a pyroxene type of mineral suggesting that its signature might also come from the body layer.

Yellow:

In the yellow colored glazes, two polymorphs of TiO_2 as rutile and anatase were detected. In the samples of *Green and Orange Stained Ware* which is a subgroup of *Anaia Zeuxippus Ware Type* ceramics, rutile was detected (Table 3.14, Figure E.1-1,3,5,8,9) while anatase was found in some of the *Zeuxippus Ware Family* samples (Table 3.14, Figure E.1-26,30). The use of rutile and anatase as pigments in glass and ceramic glazes is recent since titanium pigments were first synthesized in the early 20th century (Laver 1997). Thus, presences of rutile and anatase in Kuşadası Kadıkalesi/Anaia glazes probably result from the fact that they usually occur in the raw materials used for making glazes in trace amounts. Raman cross sections of rutile and anatase are both huge making them easily detected even in very small quantities (Ricciardi et al. 2009).

In *Anaia Zeuxippus Ware Type* samples ZA1-1 and ZA2-31, signatures referring to *Naples yellow* type of pigment solid solutions were detected (Table 3.14, Figure E.1-1, 22). *Naples yellow* ($Pb_2Sb_2O_7$) is one of the oldest synthetic pigments, also known as lead antimonate. The evidence of its first use as a pigment for coloring glass comes from the yellow colored glass found in Egypt, dating to 1450 B.C. (Wainwright et al. 1986). It was also encountered in glazes from Mesopotamia dating to 1300-1000 B.C. (Hedges 1976). The use of lead antimonate became very common during the 16th century, especially in the yellow glazes of majolica ceramics (Padeletti et al. 2004). It was also being used frequently in the paintings between the 16th -19th centuries (Dik et al. 2005).

Lead antimonate has a cubic pyrochlore structure with the general formula of $A_2B_2O_7$. Because of its chemistry, it is likely to form large solid solutions with almost any metal that can take octahedral coordination in the B position, such as Sn, Zn and Fe (Eastaugh et al. 2004). In the past, it is known that modifications of *Naples yellow* pigment were produced according to the availability of the raw materials and for achieving different hues (Hradil et al. 2007). The very intense

Raman peak which is found at ca. 130 -145 cm^{-1} as the Pb-O lattice mode is the marker for all lead based yellow pigments including also *Naples yellow*. However, this characteristic peak mentioned above may easily be shifted to according to the composition of the pyrochlore structure, depending on the atomic mass of the cation in B position and the firing temperature (Ruiz-Moreno et al. 2003; Sakellariou et al. 2004; Sandalinas et al. 2006; Rosi et al. 2009). Therefore, it is difficult to identify the exact structure of the solid solutions of *Naples yellow* type of pigments used in ceramic glazes by means of Raman spectrometry.

For Kuşadası Kadıkalesi/Anaia glazes, *Naples yellow* type of pigment species were identified mainly on the basis of the very intense Pb-O lattice mode at 127 and 150 cm^{-1} for samples ZA1-1 and ZA2-31, respectively. Characteristic peaks of *Naples yellow* at around 330 and 510 cm^{-1} are also detected in both of the samples (Colomban et al. 2001). This result seems interesting since the use of *Naples yellow* type of pigments as a pigment in glass and glazes has been scarcely reported between the Roman period and the 16th century (Sakellariou et al. 2004). Very low amounts of Sb_2O_3 were also detected for sample ZA2-31 by SEM-EDX analysis (Table 3.9). However, it is rather difficult to reach a definite conclusion by SEM-EDX analysis as it is a semi-quantitative technique. Therefore, further investigations are required to enlighten this 12th - 13th century use of *Naples yellow* type of pigment in Kuşadası Kadıkalesi/Anaia glazes. Supporting our findings, new evidence found in Byzantine ceramics by SEM-EDX analysis from the Republic of Macedonia, also shows that this type of pigment may have been used during the 12th – 14th centuries (Tanevska et al. 2009).

Quartz was also detected in the yellow glazes of *Anaia Zeuxippus Ware Type* samples ZA1-1, ZA1-5, ZA2-7 and ZA2-31 and *Zeuxippus Ware Family* sample ZFB4-65, most probably coming from the slip layers underneath as it is also the case for feldspar minerals (Table 3.14, Figure E.1-1,8,9,11,22,29).

Green:

Some of the green glazes mainly display the characteristic signature of glass (Figure E.1-17,19,20,30,36). In these cases, metal ions are responsible for the coloring of glazes as discussed previously (Section 1.7). For green glazes, Cu^{2+} and Fe^{2+} ions are expected to have been used (Molera et al. 1997). For some of the other green glazes, rutile was detected in *Anaia Zeuxippus Ware Type* samples such as ZA1-2 and ZA2-9 (Table 3.14, Figure E.1-3,14). These glazes have lighter tones of green. However, in *Anaia Zeuxippus Ware Type* sample ZA2-12 and *Green Painted* sample GP-68 which display a darker tone of green, another TiO_2 polymorph as anatase was detected (Schubnel et al. 1992) (Table 3.14, Figure E.1-16,35). As discussed before, TiO_2 polymorphs can be found in the raw materials of glaze which can be detected easily by Raman spectrometry. Quartz was also detected in *Anaia Zeuxippus Ware Type* sample ZA2-12 and *Zeuxippus Ware Family* samples ZFB5-65, ZFB6-81 which probably come from the slip and body layers below the glaze (Table 3.14, Figure E.1- 16,29,32).

Orange and Honey Brown:

In general, only quartz and feldspar signatures were observed in the orange and honey brown glazes, probably coming from the slip layers underneath (Table 3.14, Figure E.1-4,13,17). However, rutile was assigned in the honey brown glaze of *Zeuxippus Ware Type Slip Painted* sample ZS-89 (Table 3.14, Figure E.1-37).

Purple:

In most of the purple colored glazes, the characteristic signatures of glass were mainly observed indicating that the metal ions were responsible for the observed colors (Figures E.28-29). In this case, manganese ions were used as detected by SEM-EDX analysis (Table 3.9).

CHAPTER 4

CONCLUSION

4.1 Outcomes of the Study

Different groups of Byzantine glazed ceramics which belong to mainly *Zeuxippus Ware Related* productions from Kuşadası Kadıkalesi/Anaia dating to the late 12th-13th centuries were investigated by using several archaeometric methods, including visual, mineralogical, micromorphological, chemical (EDX, ICP-OES, ICP-MS) and Raman Spectrometry techniques together with the statistical analyses. Outcomes of the study have enabled us to classify these ceramic groups on the basis of their detailed material characterization and have shed light on the main characteristics of their production technology. The results of these investigations on the different parts of the ceramics can be summarized as follows:

Body

The mineralogy of the ceramic bodies is most of the time uniform with quartz, feldspars (plagioclase), micas (biotite/muscovite) and iron-oxide which are the commonly detected minerals by optical microscopy, XRD and SEM-EDX analyses. These observations are also confirmed by high amounts of SiO_2 and Al_2O_3 measured by ICP-OES analyses. Relatively high amounts of Fe_2O_3 detected agree well with the observed reddish bodies of the ceramics. Rather high chromium and nickel amounts of most of the bodies analyzed by ICP-MS may indicate the use of ophiolitic related clay raw materials which are located widely around the Küçük Menderes river. Rock fragments, which were observed during the thin section analysis, mostly seem to have a metamorphic origin consistent with the metamorphic local geology of the area where the Menderes Massif is located.

Bodies of the ceramic samples mainly exhibit a cryptocrystalline matrix with moderately or poorly sorted grains. These grains are most of the time angular, subangular or subrounded indicating that they have been added as temper. Particularly, ceramic bodies with the high grain/matrix ratios (~ 15-20%) can be considered to have intentionally added tempers. Ceramic bodies have porous texture and usually display partial vitrification. This partial vitrification and the absence of high temperature phases may indicate firing temperatures probably not exceeding 850°C for the ceramic bodies.

By optical microscopy, it was possible to make classifications for all ceramic bodies on the basis of their grain/matrix ratio and mica content by using the diagrams of Terry and Chilingar (1955). According to these diagrams, most of the samples classified as *Anaia Zeuxippus Ware Type* (ZA) and *Zeuxippus Ware Family* (ZFB) are found to have relatively high grain/matrix ratios as well as high mica contents while a small number of samples display a non-micaceous matrix. The *Anaia Zeuxippus Ware Type* ceramics which are considered to be local productions by art historians (Lale Doğer, personal communication, 2011) mostly have micaceous bodies. This is in accordance with the micaceous content of Western Anatolian soils.

According to the results of the chemical analyses by ICP-OES/ICP-MS and the evaluation by statistical analyses carried out on thirty selected samples, there are two main groups of ceramics together with a unique sample (ZS-86) which seems to be completely different from the rest. A similar classification was already stated by L. Doğer earlier, with small variations in grouping of the samples (personal communication, 2011). Moreover in this study, it is concluded that ZA ceramics make up a more or less homogeneous group while ZFB samples seem to be rather inhomogeneous. Sample ZS-86 stands out as an outlier in the cluster analysis. On the contrary to its low chromium and nickel amounts, this ceramic body has a quite high zirconium content which may point to a volcanic origin for its raw materials used. Its discrepancy in the cluster analysis also strengthens the idea that it might be an import, as also suspected during the visual classification (Lale Doğer, personal communication, 2011).

Slip

In some of the ceramics examined by thin section and SEM analyses, slip layers could not be identified clearly. Therefore it was not possible to make persuasive comments on these parts of the ceramics. In the cases where they were observed, slips display crystalline and/or vitreous matrix under optical microscope. Their raw materials are rich in SiO_2 and Al_2O_3 as measured by SEM-EDX analysis due to the quartz and feldspar minerals used in their production.

Glaze

All the glazes analyzed by SEM-EDX are found to be high-lead glazes with concentrations over 40 % PbO, with varying amounts of SiO_2 between ~ 10-40 % and with low alkali contents of ~2 %. According to the calculations based on SEM-EDX glaze compositions, one can conclude that most of the ceramics analyzed were glazed by using a lead-silica mixture instead of just applying a single lead compound. In some of the glazes, a layer of Pb-rich feldspar crystals at the glaze-body interface was present with relatively small thickness which may indicate that these ceramics were fired prior to the application of the glaze layers.

According to SEM-EDX analyses, iron compounds are the major coloring agents for the observed yellow, orange, honey brown, brown and green colors with compositions varying between ~ 0.5 to 8 % Fe_2O_3. Yellow glazes analyzed were found to have ~ 1-3 % Fe_2O_3 in the absence of alkalis or with very low alkali amounts (~ 1 % K_2O + Na_2O). Similarly, for the brownish glazes, Fe_2O_3 contents change from ~ 1 to 8 % in the presence of up to ~ 2 % alkali content. Some of the green glazes also contain ~ 1- 3 % Fe_2O_3 almost without any alkali contents. Additionally, the green glazes of *Zeuxippus Ware Family* samples were found to contain also copper with ~ 1-3 % CuO in the presence of very low or without alkali contents. For the purple glazes, manganese was detected as ~ 1-2 % MnO**.**

Signatures of crystalline phases in glassy matrices were detected in most of the glazes analyzed by Raman spectrometry. Magnetite was generally suggested for the brown regions of the glazes in the form of incised decorations. This observation most probably confirms that these incised decorations were being painted with pigments by the potters. For the other brown colored glazes, the Raman peaks can be attributed to magnetite as well as hematite. These compounds might have been deliberately added by the potters to the glaze mixtures or may occur due to the contribution from the body layers where the presence of iron compounds is most probable.

Green glazes analyzed by Raman spectrometry usually display the characteristic signature of a glass which means that their color development was achieved by the use of metal ions like Cu^{2+} and Fe^{2+} as confirmed by SEM-EDX analyses. In most of the yellow glazes, rutile and anatase were detected possibly due to their presence in trace amounts in the raw materials used in glaze preparation. For the purple glazes, mainly the characteristic signatures of glass were observed indicating that the metal ions were responsible for the observed colors. These ions were found to be manganese by SEM-EDX analysis.

Raman spectrometry analyses also confirm the use of lead rich compositions fired at temperatures around 700° C or below on the basis of the Si-O stretching maxima of the Raman spectra recorded at 920-980 cm^{-1}. Polymerization indexes of these glazes around 0.05, also confirm the presence of high lead content.

A very striking finding during the examinations of the yellow glaze on two of the samples, is the presence of Raman peaks at 127-150, 330, 512-517 cm^{-1}, which may be assigned to solid solutions of *Naples yellow* type of pigment. This result seems interesting, since the use of *Naples yellow type* pigments, as a colorant for vitreous materials, is known to be very rare between ancient times and the 16th century.

4.2 Significance of the Study

Kuşadası Kadıkalesi/Anaia is a forthcoming Byzantine site which may provide significant information about the production of the late 12th-13th century glazed ceramics in Western Anatolia region. Since there are not many studies focusing on the production technology of Byzantine ceramics, this study may be significant for contributing to the understanding of production technology characteristics of the late 12th-13th century Byzantine ceramics.

One of the most significant outcomes of this study is the observation of Raman peaks which could be assigned to solid solutions of *Naples yellow* type of pigment for some of the yellow glazes of Kuşadası Kadıkalesi/Anaia samples. Detection of this pigment may indicate its probable use in the Byzantine period. A similar suggestion was also given by Tanevska et al. (2009) for the 12th-14th century Byzantine ceramic glazes from the Republic of Macedonia. Consequently, these implications fill the gap between the Roman period and the 16th century when the use of lead antimonate type pigments has not been reported. These findings also support the common opinion suggesting the use of lead-antimonate type pigments had reached Europe from the Eastern Mediterranean via Asia Minor by the Byzantine craftsmen who migrated during the 15th century after the collapse of Byzantium (Dik et al. 2005).

4.3 Recommendations

The characterization of *Naples yellow* type of pigments in Byzantine glazes needs further detailed analyses since the matter has particular significance in the history of ceramic and pigment technology.

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APPENDIX A

CERAMIC PHOTOGRAPHS

ZA1-5 out ZA2-7 out

ZA2-16 out ZA2-20 out

Figure A.1: The photographs of Kuşadası Kadıkalesi/Anaia ceramic samples showing their other sides

ZA2-22 out

ZA2-23 out

ZA2-24 out

ZFB1-43 out

ZFB1-48 out

ZFB1-49 out

Figure A.1 (cont'd) The photographs of Kuşadası Kadıkalesi/Anaia ceramic samples showing their other sides

ZFB1-51 out

ZFB2-58 out

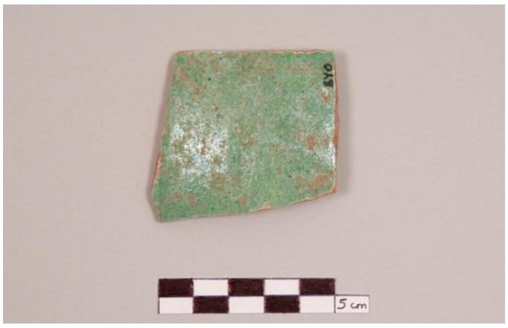
ZFB3-60 out

ZFB3-62 out

ZFB3-63 out

ZFB3-64 out

Figure A.1 (cont'd) The photographs of Kuşadası Kadıkalesi/Anaia ceramic samples showing their other sides



ZFB4-65 out

ZFB4-66 in

ZFB5-67 out

GP-68 out

GP-69 out

GP-70 out

Figure A.1 (cont'd) The photographs of Kuşadası Kadıkalesi/Anaia ceramic samples showing their other sides

GP-72 out

ZFB6-77 in

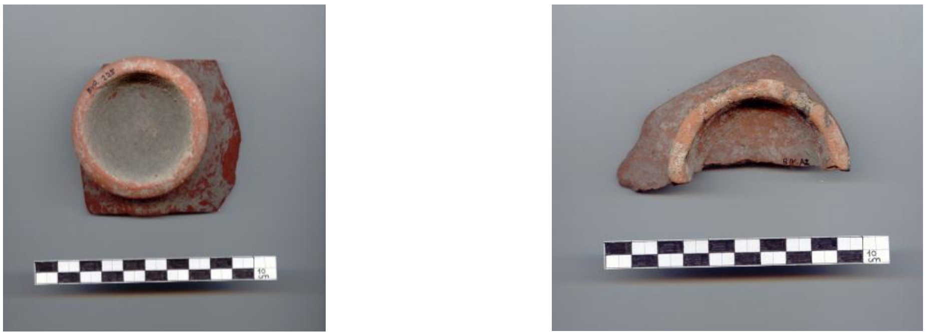
ZFB6-78 out

ZFB6-80 out

ZFB6-84 out

ZFB6-85 out

Figure A.1 (cont'd) The photographs of Kuşadası Kadıkalesi/Anaia ceramic samples showing their other sides



ZS-86 out ZS-87 out

Figure A.1 (cont'd) The photographs of Kuşadası Kadıkalesi/Anaia ceramic samples showing their other sides

APPENDIX B

COLOR EXAMINATION

Table B.1: Colors of the ceramic body, slip, glaze and paint parts examined by Munsell Color System

Sample code	**Body color**	**Glaze Color**
ZA1-1	2.5 YR 7/4, 6/4 (light reddish brown)	yellow: 2.5 Y 8/6, 8.5/6 orange: 10 YR 6/10, 5/10 green: 2.5 GY 6/6, 5/6
ZA1-2	5 YR 7/6, 6/6 (reddish yellow) white slip	orange: 2.5 Y 7/8, 6/8 yellow: 10 Y 9/4 green: 10 GY 7/6
ZA1-3	2.5 YR 6/6 (light red) white slip	orange: 10 YR 6/10 (light), 7.5 YR 4/8 (dark) yellow: 5 Y 9/4 green: 7.5 GY 5/6, 6/6
ZA1-4	2.5 7R 6/6 (light red), 5/6 (red) white slip	green: 10 GY 4/8 (dark), 7.5 GY 8/6 (light)
ZA1-5	2.5 YR 6/4 (light reddish brown), 6/6 (light red) white slip	green: 7.5 GY 4/6 (dark), 6/6 orange: 5 Y 7/10, 6/10 yellow: 5 Y 9/4, 8.5/4
ZA2-6	2.5 YR 6/6 (light red), 5/6 (red)	yellow: 5 Y 9/6, 8.5 /6, 9/4
ZA2-7	2.5 YR 7/6, 6/6 (light red), 5/6 (red)	yellow: 2.5 Y 8/6, 8.5/6
ZA2-8	2.5 YR 6/6, 6/8 (light red) pinkish slip	2.5 Y 8/10, 7/12, 6/10, 5/8 (from the lightest to the darkest)
ZA2-9	2.5 YR 5/8 (red), 6/6 (light red)	5 GY 8/6, 7/6, 5/6 (from the lightest to the darkest)

Table B.1 (cont'd) Colors of the ceramic body, slip, glaze and paint parts examined by Munsell Color System

Sample code	**Body color**	**Glaze Color**
ZA2-10	5 YR 6/6 (reddish yellow), 6/4 (light reddish brown)	2.5 Y 7/10, 6/10, 5/8 (from the lightest to the darkest), 10 YR 5/8
ZA2-11	2. 5 YR 5/4 (reddish brown), 5/6 (red)	5 Y 8.5/4, 8/4, 8.5/6, 8/6, 9/6
ZA2-12	5 YR 6/4 (light reddish brown), 7.5 YR 7/4 (pink) white slip	7.5 GY 7/6, 6/6, 5/6 (from the lightest to the darkest)
ZA2-13	2.5 YR 6/6 (light red), 2.5 YR 5/6, 5/8 (red) cream slip	5 GY 7/8, 6/8, 5/8 (from the lightest to the darkest)
ZA2-14	2.5 YR 6/6 (light red), 5/6 (red)	5 GY 7/6, 6/6, 5/6 (from the lightest to the darkest)
ZA2-15	5 YR 6/4 (light reddish brown), 6/6 (reddish yellow) cream slip	honey brown: 2.5 Y 7/8, 6/8 (from the lightest to the darkest) green: 5 GY 5/8, 5/6, 4/6 (from the lightest to the darkest)
ZA2-16	5 YR 6/4 (light reddish brown), 6/6 (reddish yellow)	10 YR 6/10, 6/12, 5/10, 7.5 YR 4/8
ZA2-17	5 YR 6/2 (pinkish gray), 5/2 (reddish gray)	5 GY 5/6, 6/6
ZA2-18	2.5 YR 5/6 (red), 6/6 (light red), 5 YR 6/4 (light reddish brown)	5 YR 4/10, 5/10
ZA2-19	2.5 YR 6/3, 6/4 (light reddish brown), 6/6 (light red) white slip	7.5 GY 6/8, 5/8, 4/8 (from the lightest to the darkest)
ZA2-20	2.5 YR 6/4 (light reddish brown), 6/6, 7/8 (light red) cream slip	10 YR 5/8, 2.5 Y 6/10, 7/10
ZA2-21	5 YR 6/4 (light reddish brown), 2.5 YR 6/6 (light red)	7.5 YR 4/8, 2.5 Y 5/6
ZA2-22	5 YR 6/4 (light reddish brown), 5/4 (reddish brown), 6/6 (reddish yellow), white slip	7.5 Y 4/4, 4/6, 5/4 (darker green) 7.5 Y 8/2, 8/4 (lighter green)

Table B.1 (cont'd) Colors of the ceramic body, slip, glaze and paint parts examined by Munsell Color System

Sample code	**Body color**	**Glaze Color**
ZA2-23	2.5 YR 6/6, 6/8 (light red) cream slip	2.5 GY 5/6, 6/6
ZA2-24	5 YR 7/4 (pink), 7/6 (reddish yellow)	7.5 YR 5/10, 5/8, 4/8
ZA2-25	5 YR 6/4 (light reddish brown), 6/6, 6/8 (reddish yellow) white slip	7.5 YR 5/10, 10 YR 7/10
ZA2-26	5 YR 7/4 (pink), 7/6 (reddish yellow), 6/4 (light reddish brown) cream slip	10 YR 7/10, 6/0, 5/10 (from the lightest to the darkest)
ZA2-27	2.5 YR 7/6, 6/6 (light red)	10 Y 7/6 , 6/6
ZA2-28	2.5 YR 7/6, 7/8 6/8, 6/6 (light red) white slip	2.5 Y 7/10, 8/10
ZA2-29	5 YR 7/6, 6/6 (reddish yellow)	7.5 Y 3/4 7.5 GY 7/6, 6/6
ZA2-30	2.5 YR 7/6, 7/8 (light red), 6/4 (light reddish brown), 6/6 (light red) white slip	Yellow: 5 Y 9/4, 9/6 Honey brown stain: 10 YR 5/10
ZA2-31	2.5 YR 6/6, 6/8, 7/6 (light red), 5 YR 7/6 (reddish yellow) white slip	yellow: 5 Y 9/4, 8.5/4 brown stain: 2.5 Y 6/10, 5 Y 8/8
ZA2-32	5 YR 7/4 (pink), 7/6, 6/6 (reddish yellow) white slip	7.5 YR 5/10, 4/8, 10 YR 7/10
ZA2-33	5 YR 6/4 (light reddish brown), 7/6, 6/6, 6/8 (reddish yellow) white slip	7.5 YR 5/10, 4/8, 10 YR 7/10

APPENDIX C

PETROGRAPHY DIAGRAMS

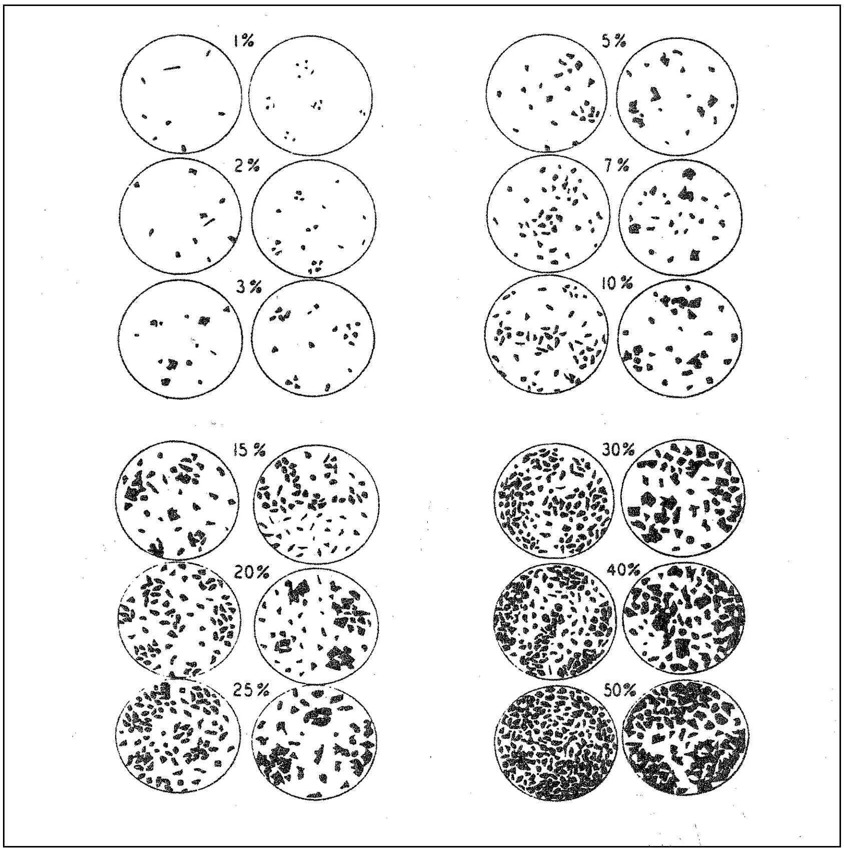


Figure C.1: Charts for the visual estimation of percentages of various components in thin sections (Terry and Chilingar 1955).

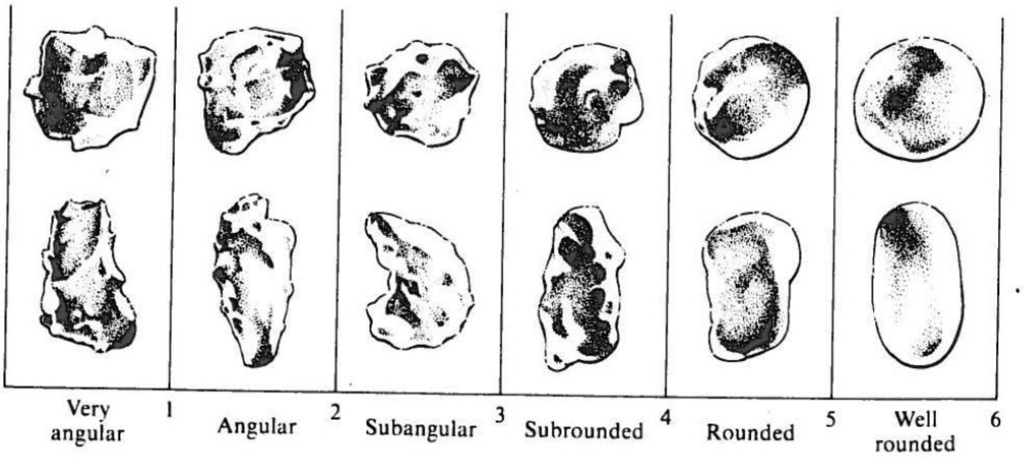


Figure C.2: Terminology for the degree of roundness of grains (Blatt 1982, p.111)

APPENDIX D

SEM-EDX TABLES

Table D.1: Compositions of the body parts analyzed by SEM-EDX (original data converted into oxides)

Sample code	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**Na_2O**	**TiO_2**
ZA1-1*	8.30	18.28	36.21	1.61	8.41	11.70	-	-
	2.77	26.10	46.52	6.22	5.92	6.33	1.14	-
ZA1-3	2.95	19.98	42.45	3.88	5.75	8.68	0.89	-
ZA1-4	4.05	19.19	43.30	2.85	8.21	8.82	-	-
ZA1-5	4.46	21.34	49.56	2.84	7.37	7.42	0.36	0.55
ZA2-8	3.68	23.12	54.70	4.13	11.45	11.17	-	-
ZA2-11	4.48	18.73	43.58	2.73	12.13	8.46	-	-
ZA2-15	4.93	21.59	49.71	2.67	12.08	8.34	-	-
ZA2-16	6.43	20.47	50.09	3.26	13.59	14.21	-	0.82
ZA2-22	4.06	21.21	55.56	3.84	12.39	9.59	-	0.98
ZA2-30	3.83	15.11	53.40	2.79	10.30	9.79	-	1.38
ZA2-31	4.46	14.97	37.47	2.04	13.51	7.19	0.44	0.72
ZFB1-42	4.76	19.72	46.33	2.81	11.08	8.25	-	0.73
ZFB1-47	3.75	17.69	39.40	2.18	9.30	6.67	-	0.45
ZFB1-51	3.80	14.90	40.96	1.93	7.81	7.49	0.70	0.53
ZFB2-59	4.06	16.79	45.00	2.43	11.16	6.05	-	0.58
ZFB3-64	3.73	21.04	47.87	2.98	10.25	8.32	0.24	0.82
ZFB4-65	3.81	13.83	52.87	1.32	10.30	8.16	0.58	1.43
ZFB5-67	4.24	12.84	40.41	2.30	21.45	12.99	0.19	0.88
ZFB6-76	4.34	12.43	40.57	1.88	8.88	4.57	1.14	0.52
ZFB6-78	1.74	12.62	44.57	2.53	4.35	10.29	-	-
ZFB6-81	6.45	18.83	43.78	2.08	13.12	12.87	-	3.32
ZFB6-84	2.80	18.39	52.53	2.92	7.01	10.21	1.74	1.28
ZS-89	4.01	17.77	45.43	2.46	13.64	13.59	-	-

Table D.2: Compositions of the slip parts analyzed by SEM-EDX (original data converted into oxides)

Sample code	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**Na_2O**	**PbO**	**TiO_2**
ZA1-3	-	18.90	34.60	2.77	0.71	4.42	-	15.58	-
ZA1-4	1.36	23.70	55.82	2.43	0.86	2.10	-	-	-
ZA1-5	0.70	19.94	56.67	2.82	-	2.00	0.49	8.15	1.42
ZA2-8	2.76	19.13	42.53	3.48	7.79	9.72	-	-	1.03
ZA2-11	0.88	26.48	55.95	3.48	-	2.28	-	-	1.56
ZA2-15	0.73	17.68	44.20	1.89	0.93	1.21	-	17.96	0.45
ZA2-30	1.16	29.54	45.07	1.37	1.19	1.83	-	4.93	-
ZFB1-47	1.06	25.35	63.36	2.71	1.23	3.25	-	-	-
ZFB3-64	1.56	18.42	46.09	4.26	1.24	4.26	0.78	19.27	1.16
ZFB4-65-in	0.85	9.69	74.18	1.60	1.03	0.63	0.43	9.32	0.60
ZFB4-65-out	1.23	11.22	78.88	2.05	1.94	1.06	0.39	5.66	0.86
ZFB6-76	1.57	22.49	43.91	3.77	2.63	0.68	0.59	0.81	0.35
ZFB6-81	-	18.51	67.83	4.22	-	2.43	-	13.58	1.33
ZFB6-84	1.72	18.53	51.44	4.01	2.28	3.72	1.39	19.74	0.40

Table D.3: Compositions of the glaze parts analyzed by SEM-EDX (original data converted into oxides).

Sample code	**Observed color**	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**Na_2O**	**PbO**	**TiO_2**	**NiO**	**Sb_2O_3**	**CoO**	**ZnO**	**MnO**	**CuO**
ZA1-1	Yellow	1.25	5.78	30.40	0.69	1.45	2.83	-	44.76	-	-	-	-	-	-	-
ZA1-3	Green	0.68	4.53	31.45	-	1.79	3.15	0.29	46.59	-	-	-	-	-	-	-
ZA1-4	Green	-	6.53	25.13	0.49	1.16	2.86	-	56.99	-	-	-	-	-	-	-
ZA1-5	Yellow	-	1.96	12.45	-	0.26	0.97	-	83.82	-	-	-	-	-	-	-
	Orange	-	5.59	35.31	0.73	0.43	1.04	-	41.60	-	-	-	-	-	-	-
ZA2-8	Honey brown	-	4.06	33.51	-	0.74	3.46	-	59.29	-	-	-	-	-	-	-
ZA2-11	Yellow	-	5.57	22.45	-	1.06	1.14	-	76.05	-	-	0.35	-	-	-	-
ZA2-15	Honey brown	0.75	7.93	40.88	-	-	1.42	-	48.01	-	-	-	-	-	-	-
ZA2-16	Brown	-	5.17	25.28	-	0.81	5.00	-	62.47	-	-	-	0.52	-	-	-
ZA2-22	Green-1	-	2.72	16.56	-	1.12	2.03	-	79.51	-	0.26	-	-	-	-	-
	Green-2	-	3.70	25.97	-	2.01	3.06	-	60.26	-	0.90	-	-	-	-	-
ZA2-30	Yellow	-	5.96	32.18	-	-	1.23	-	48.13	-	0.35	0.81	-	-	-	-
ZA2-31	Yellow-1	-	6.21	35.49	-	-	1.21	-	40.86	-	-	0.99	-	0.10	-	-
	Yellow-2	-	4.43	35.42	-	0.63	1.27	-	50.18	-	-	0.25	-	-	-	-
	Yellow-3	-	4.72	27.42	0.53	0.89	1.11	-	60.17	-	-	0.51	-	-	-	-
ZFB1-42	Honey brown	0.63	9.65	38.95	0.76	1.19	3.23	-	44.92	0.52	-	-	-	-	-	-
ZFB1-47	Honey brown	0.40	5.51	29.20	0.24	0.82	2.74	-	45.79	0.30	-	-	-	-	-	-
ZFB1-51	Yellow	0.40	7.46	28.79	0.59	0.24	1.03	-	45.08	0.28	-	-	-	-	-	-
ZFB2-59	Honey brown	0.71	5.06	32.81	0.49	0.57	2.94	0.21	55.47	0.28	-	-	-	-	0.07	-
ZFB3-64	Purple	-	5.02	34.82	0.81	0.98	1.30	-	61.63	-	-	-	-	-	1.25	-

Table D.3 (cont'd) Compositions of the glaze parts analyzed by SEM-EDX (original data converted into oxides).

Sample code	**observed color**	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**Na_2O**	**PbO**	**TiO_2**	**NiO**	**Sb_2O_3**	**CoO**	**ZnO**	**MnO**	**CuO**
ZFB4-65	Green	0.93	4.25	43.12	0.55	2.29	1.17	0.36	50.71	-	-	-	-	-	0.24	3.32
	Purple	0.53	3.44	35.40	0.58	0.96	0.88	0.28	64.46	0.62	-	-	-	-	2.37	0.34
ZFB5-67	Green-1	0.33	3.32	18.97	0.39	0.74	0.88	0.13	75.22	0.38	-	-	-	-	0.24	0.84
	Green-2	0.21	3.34	21.41	0.44	1.09	1.13	-	79.04	0.40	-	-	-	-	0.22	1.40
ZFB6-76	Light green	0.63	5.29	32.00	0.60	2.74	0.50	-	49.27	-	-	-	-	-	-	-
ZFB6-78	Purple	0.76	8.97	38.97	0.89	1.30	1.50	-	58.30	-	-	-	-	-	1.63	-
	Yellow	0.85	8.24	33.05	0.77	1.45	2.33	-	35.04	-	-	-	-	-	-	-
ZFB6-81	Green	-	4.44	36.87	-	2.31	1.28	-	65.04	-	-	-	-	-	-	1.90
ZFB6-84	Yellow	0.48	6.25	27.83	0.71	1.01	1.76	0.29	69.13	0.18	-	-	-	-	-	-
	Honey brown	1.41	7.99	40.11	1.55	3.17	3.77	0.70	51.84	0.47	-	-	-	-	-	-
ZS-89	Brown	-	5.85	30.99	-	1.07	8.24	-	53.98	-	-	-	-	-	-	-

Table D.4: Compositions of the interface crystals analyzed by SEM-EDX (original data converted into oxides)

Sample code	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**Na_2O**	**PbO**	**TiO_2**
ZFB1-42	0.46	16.07	34.82	2.30	1.43	2.08	-	49.07	0.47
	0.25	18.81	45.24	2.32	1.33	1.82	-	36.26	0.38
	0.56	19.09	45.37	2.34	1.07	1.57	-	29.51	0.42
ZFB1-47	0.36	15.90	32.17	2.46	0.58	1.11	-	18.94	0.43
	0.18	12.67	33.58	1.90	0.78	2.06	-	33.14	0.25
ZFB2-59	-	19.23	41.79	4.31	-	2.50	0.49	28.26	-
	-	16.68	47.53	5.20	-	1.63	-	31.47	0.30
	-	18.23	44.04	4.82	-	2.27	-	29.26	0.30
ZFB5-67	0.86	23.89	42.93	6.29	0.92	1.34	0.16	35.77	0.42
	0.99	23.65	44.43	6.19	0.79	1.07	0.35	32.09	0.45
ZFB6-84	1.11	17.60	39.91	1.38	10.37	4.47	1.12	30.26	-

APPENDIX E

RAMAN SPECTRA OF KUŞADASI KADIKALESİ/ANAIA GLAZES

Raman spectra recorded (baseline corrected) for each sample are listed in Figure E.1

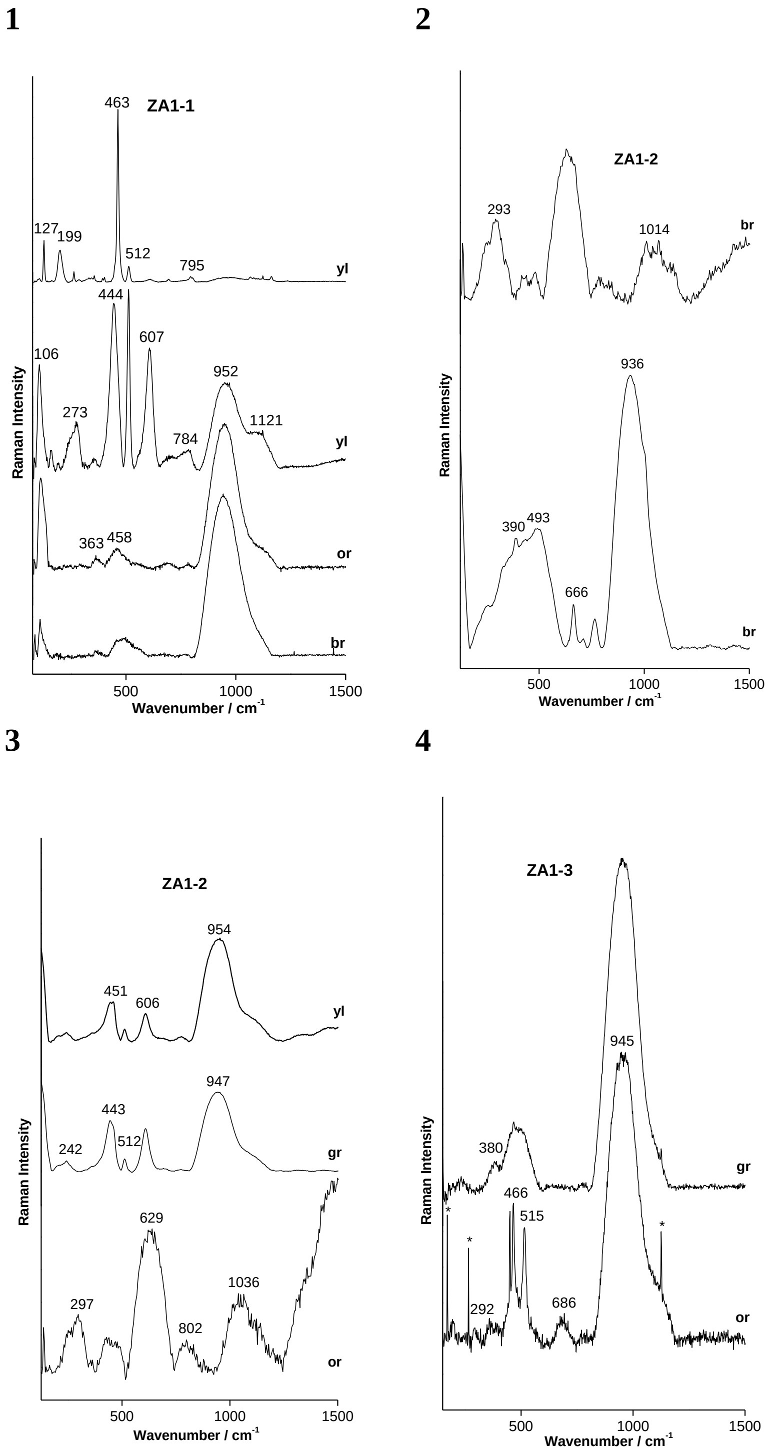


Figure E.1: Raman spectra after baseline subtraction 1) ZA1-1 by HR800, 2-3) ZA1-2 by HE532, 4) ZA1-3 by HR800 (the abbreviations refer to the colored regions on the glaze as br: brown (incised), or: orange, yl: yellow, gr: green)

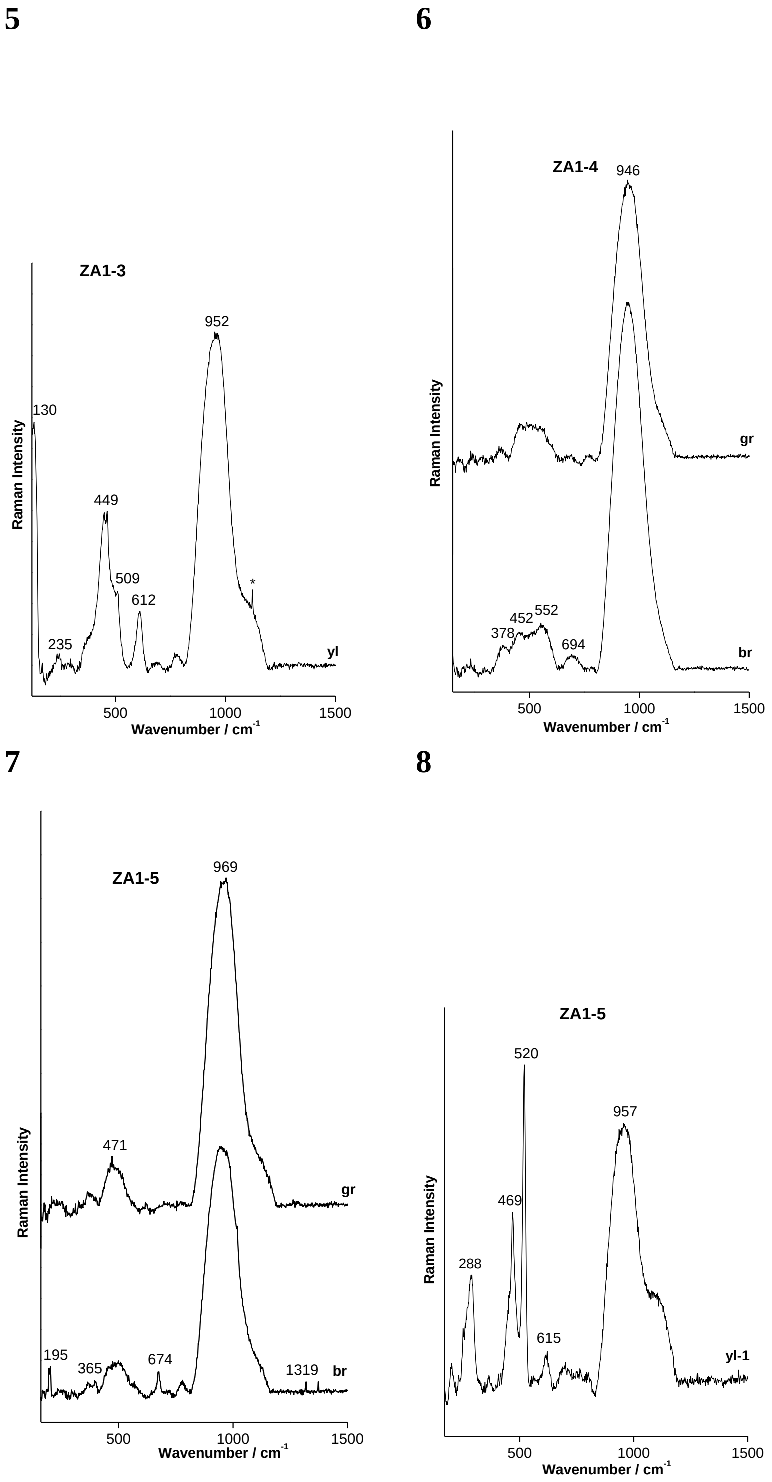


Figure E.1 (cont'd) Raman spectra after baseline subtraction 5) ZA1-3 by HR800, 6) ZA1-4 by HE532, 7-8) ZA1-5 by HR800 (br: brown (incised), yl: yellow, gr: green)

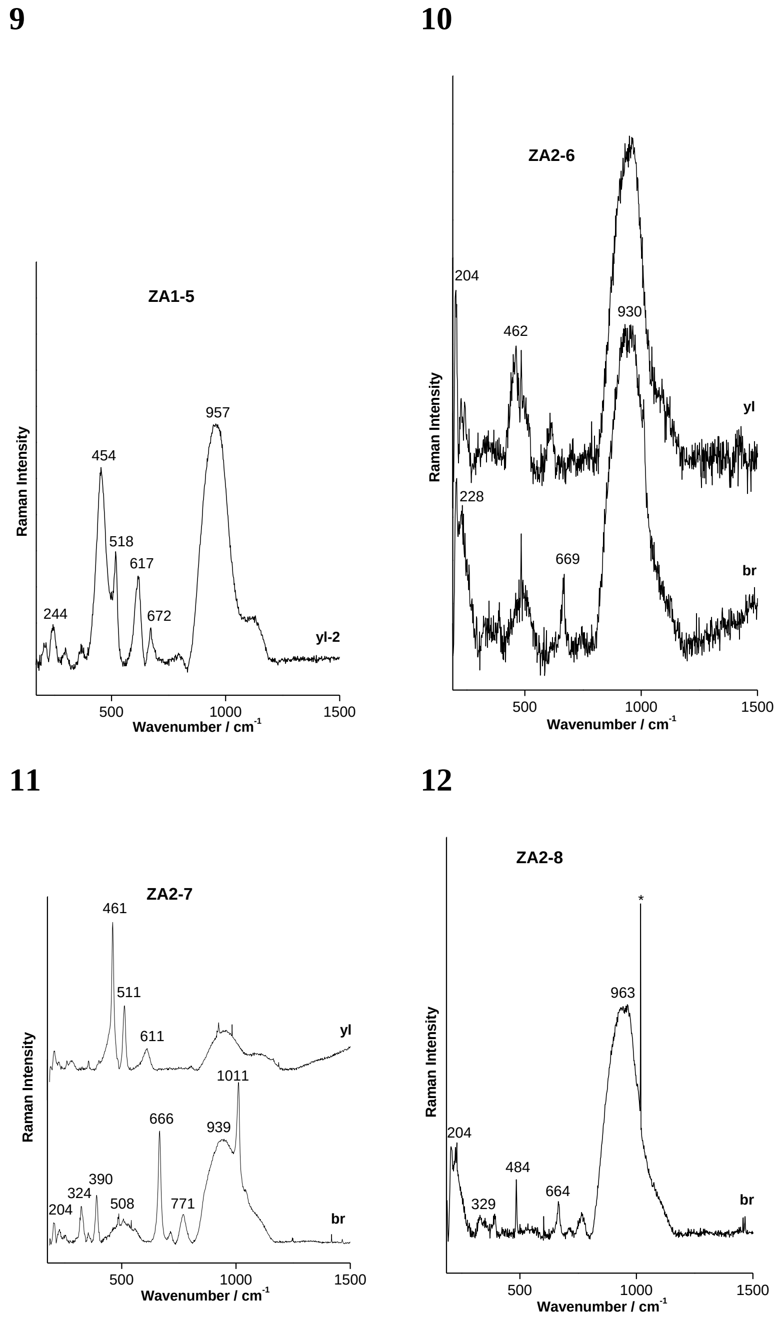


Figure E.1 (cont'd) Raman spectra after baseline subtraction 9) ZA1-5 by HR800, 10) ZA2-6 by LabRam Infinity, 11) ZA2-7 by LabRam Infinity, 12) ZA2-8 by LabRam Infinity (br: brown (incised), yl: yellow)

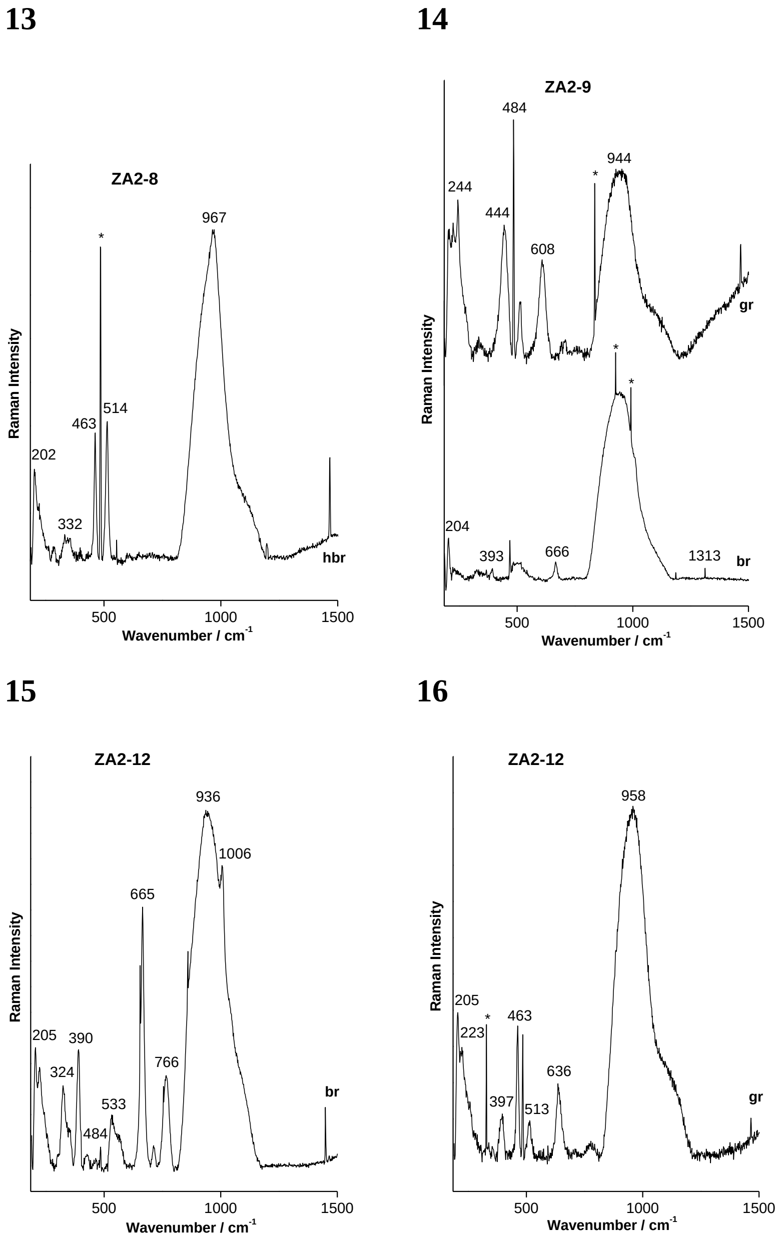


Figure E.1 (cont’d) Raman spectra after baseline subtraction 13) ZA2-8 by LabRam Infinity, 14) ZA2-9 by LabRam Infinity, 15-16) ZA2-12 by LabRam Infinity (br: brown (incised), gr: green, hbr: honey brown)

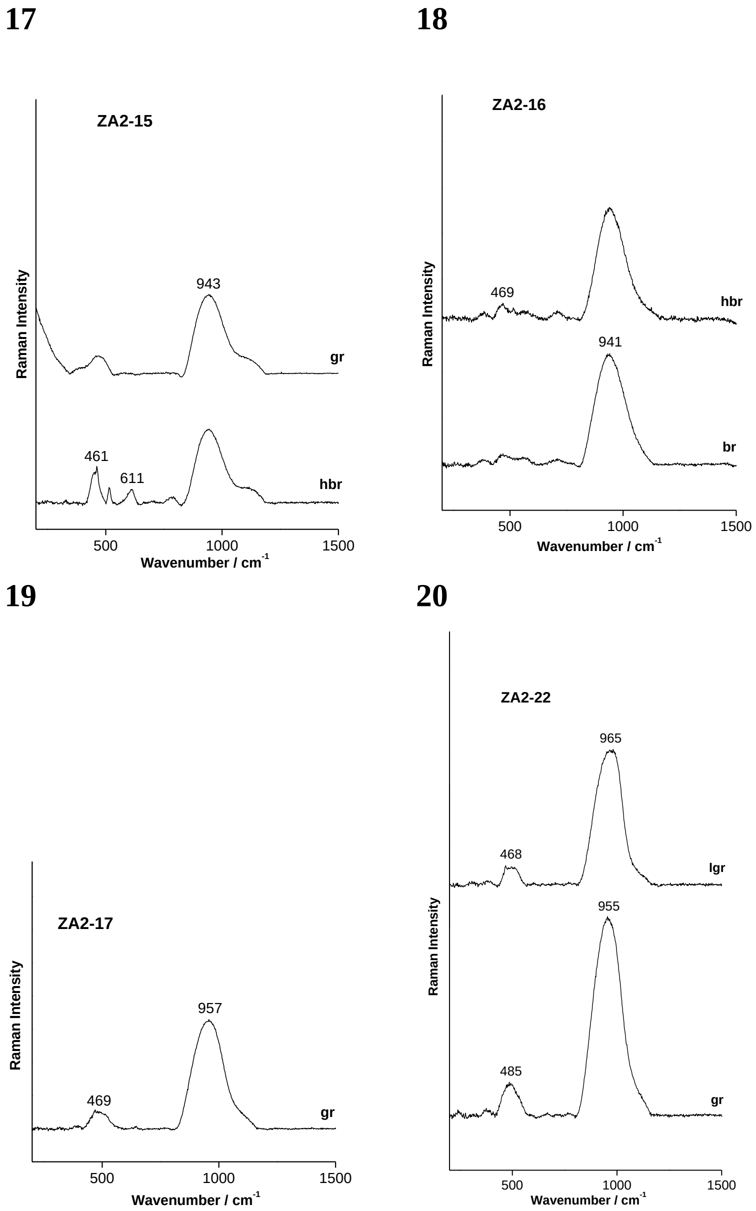


Figure E.1 (cont'd) Raman spectra after baseline subtraction 17) ZA2-15 by HR800, 18) ZA2-16 by HR800, 19) ZA2-17 by HR800, 20) ZA2-22 by HR800 (br: brown (incised), gr: green, hbr: honey brown, lgr: light green)

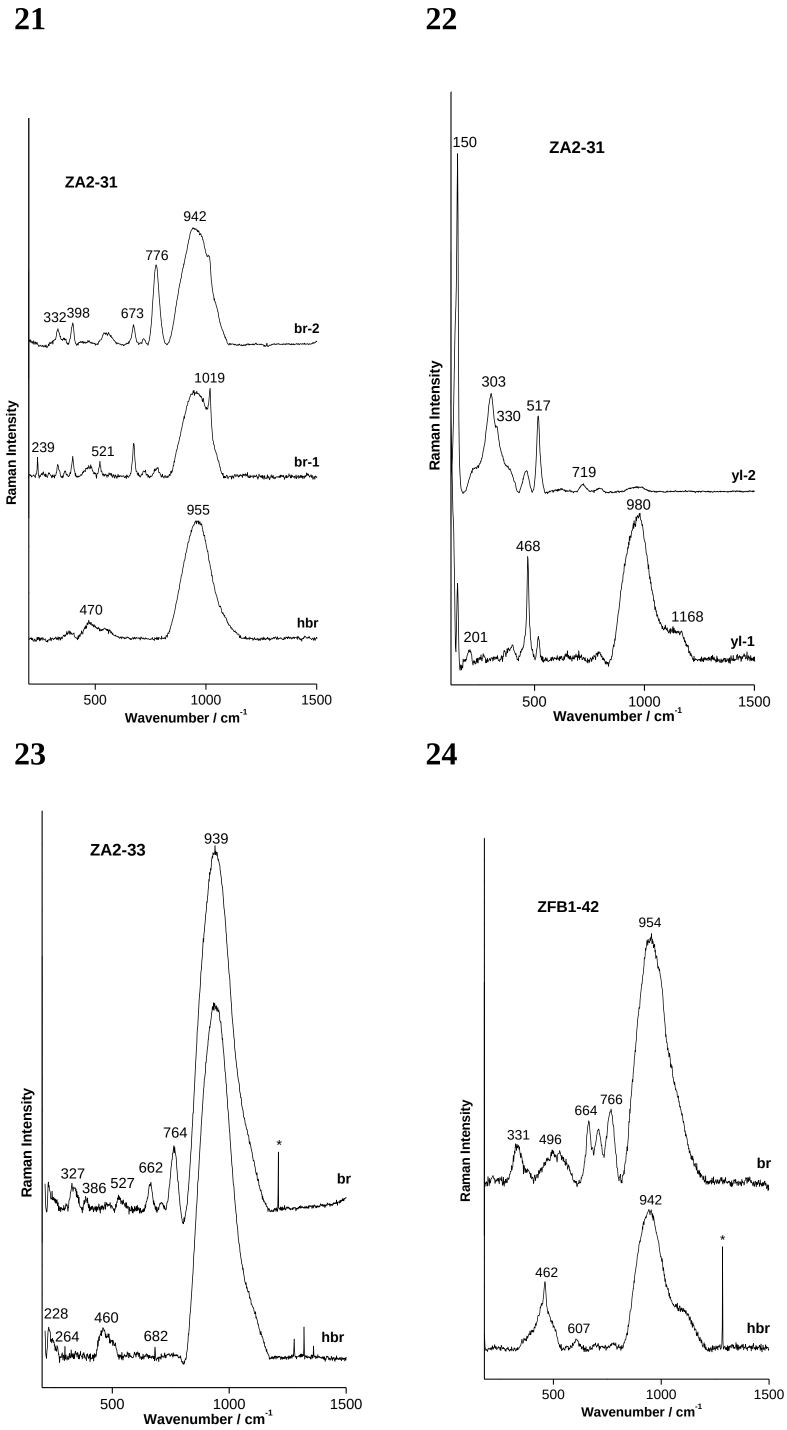


Figure E.1 (cont'd) Raman spectra after baseline subtraction 21-22) ZA2-31 by HR800, 23) ZA2-33 by LabRam Infinity, 24) ZFB1-42 by Renishaw (br: brown (incised), yl: yellow, hbr: honey brown)

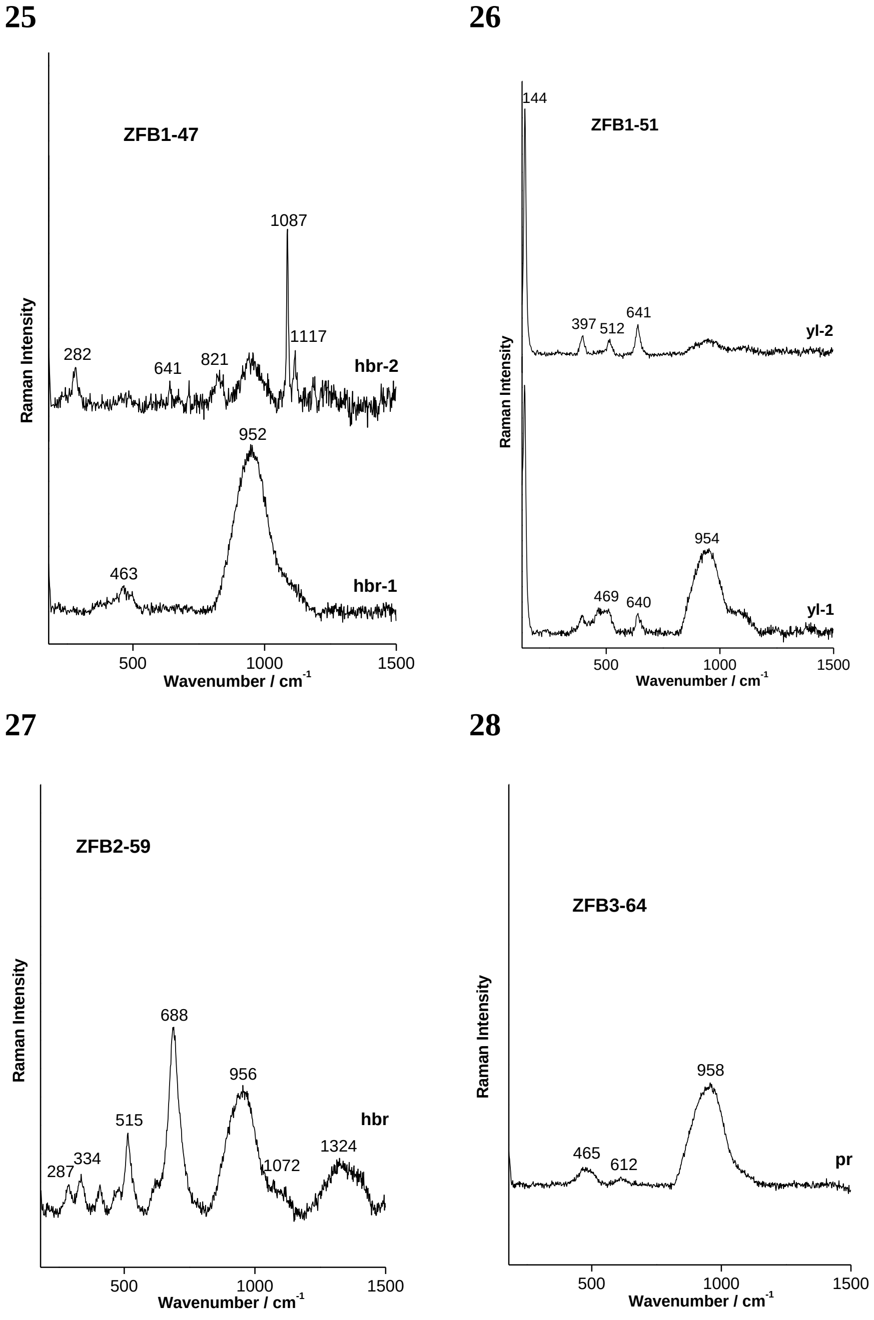


Figure E.1 (cont'd) Raman spectra after baseline subtraction 25) ZFB1-47 by Renishaw, 26) ZFB1-51 by Renishaw, 27) ZFB2-59 by Renishaw, 28) ZFB3-64 by Renishaw (hbr: honey brown, yl: yellow, pr: purple)

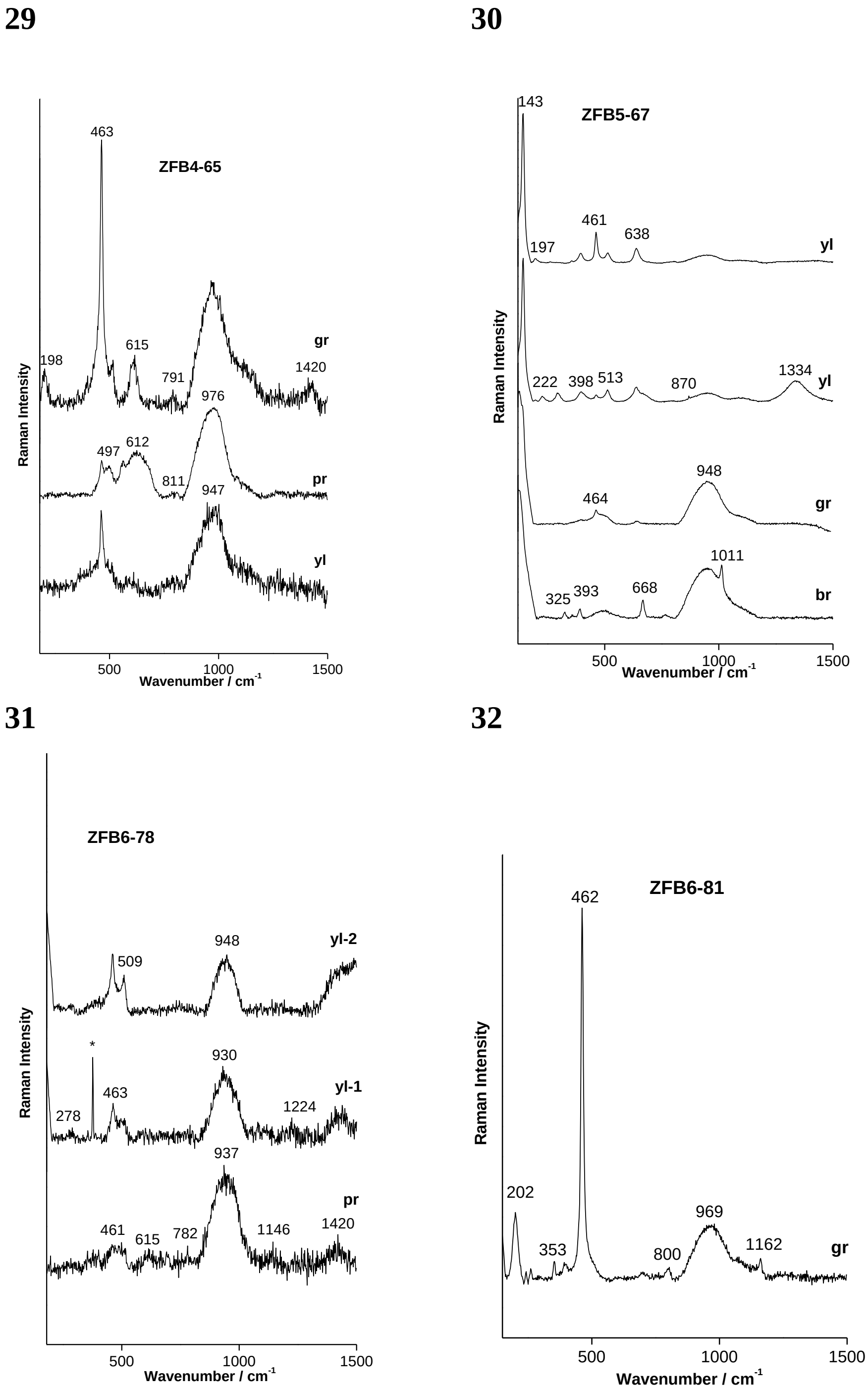


Figure E.1 (cont'd) Raman spectra after baseline subtraction 29) ZFB4-65 by Renishaw, 30) ZFB5-67 by Renishaw, 31) ZFB6-78 by Renishaw, 32) ZFB6-81 by Renishaw (br:brown, yl: yellow, pr: purple, gr: green)

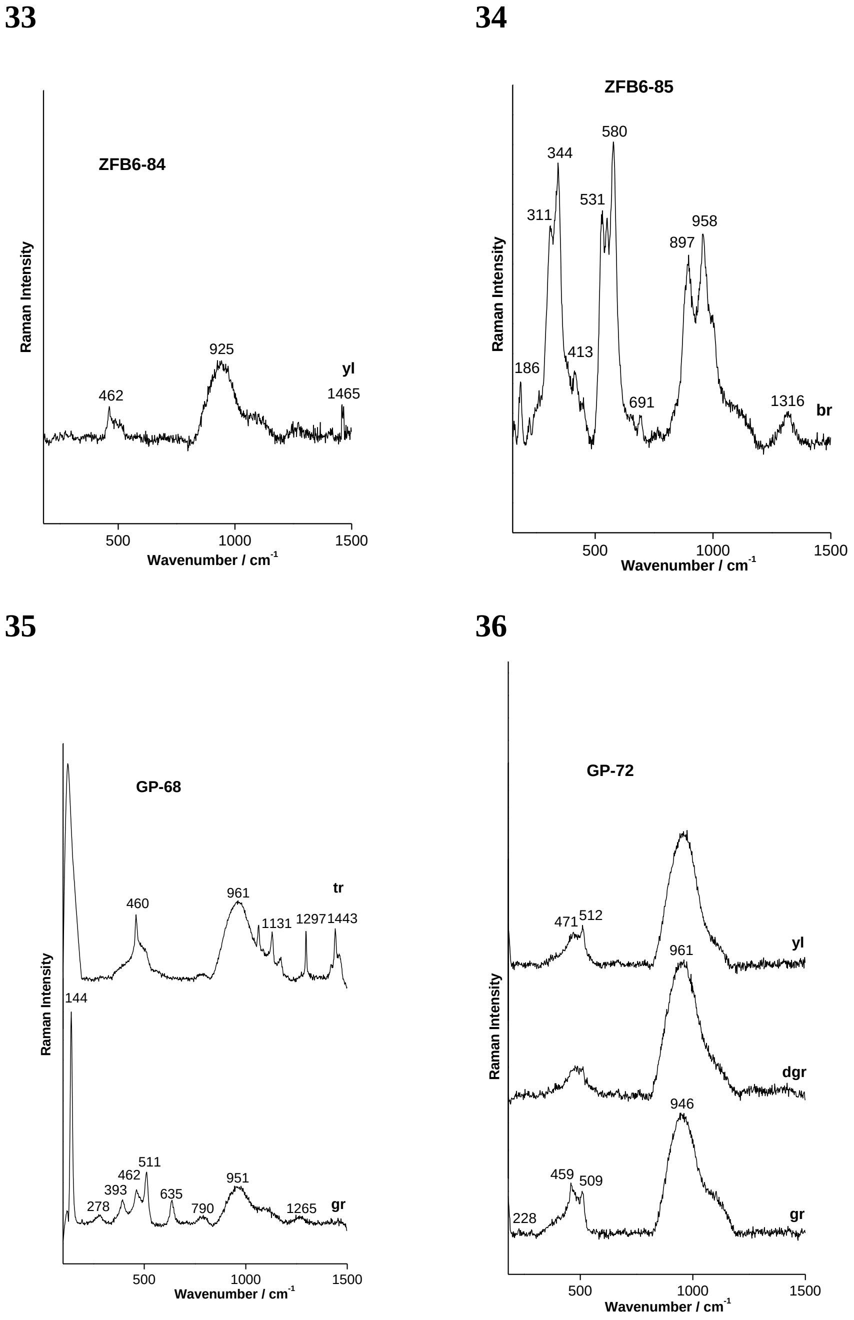


Figure E.1 (cont'd) Raman spectra after baseline subtraction 33) ZFB6-84 by Renishaw, 34) ZFB6-85 by Renishaw, 35) GP-68 by Renishaw, 36) GP-72 by Renishaw (br:brown, yl: yellow, tr: transparent, dgr: dark green, gr: green)

37

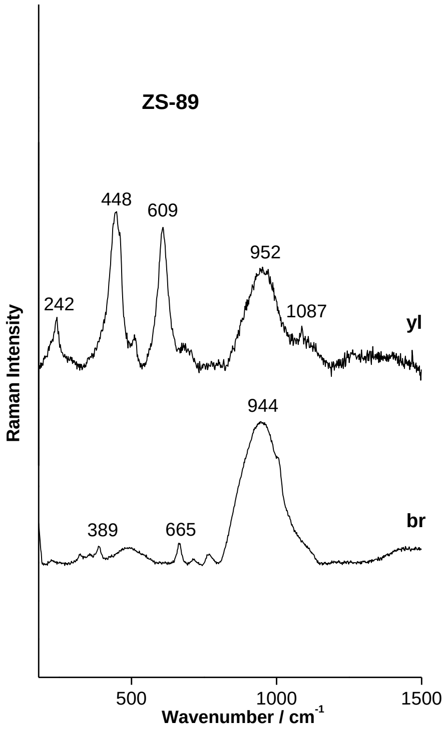


Figure E.1 (cont'd) Raman spectra after baseline subtraction 37) ZS-89 by Renishaw (br:brown, yl: yellow)

CURRICULUM VITAE

Miss Burcu Kırmızı holds a B.S. degree from İstanbul University Department of Chemical Engineering. In 2004, she gained her M.S. degree from the Archaeometry Program of Middle East Technical University (METU) Graduate School of Natural and Applied Sciences. Between 2006-2008, she has worked as a research assistant both in METU Graduate School of Natural and Applied Sciences and the Archaeometry Program. As a TÜBİTAK fellow, she has worked as a researcher in Laboratoire de Dynamique Interactions et Reactivite (LADIR) which is a mixed research unit of CNRS and University of Pierre and Marie Curie in France between October 2008– August 2009.

PUBLICATIONS:

Journal Publications:

Kırmızı B., Colomban Ph., Blanc M. (2010). On-site analysis of Limoges enamels from sixteenth to nineteenth centuries: an attempt to differentiate between genuine artefacts and copies. *Journal of Raman Spectroscopy*, **41**, 1240-1247

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