MINERALOGY AND PRODUCTION TECHNOLOGY OF DEĞİRMENTEPE (MALATYA) POTTERY

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MINERALOGY AND PRODUCTION TECHNOLOGY OF DEĞİRMENTEPE (MALATYA) POTTERY

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ABSTRACT

MINERALOGY AND PRODUCTION TECHNOLOGY OF DEĞİRMENTEPE (MALATYA) POTTERY

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A series of pottery samples provided from the survey investigations and excavations from Değirmentepe Mound (Malatya), belonging to Chalcolithic (Ubaid), Early Bronze and Iron Ages, were investigated by petrographic and X-ray diffraction (XRD) analyses to determine their textures, mineralogical compositions and microstructures. The sample microstructures and chemical (semiquantitative) compositions were also studied by scanning electron microscope with energy dispersive X-ray spectrometry (SEM - EDX). The chemical analyses of some samples were further investigated by inductively coupled plasma – optical emission spectrometry (ICP-OES). Almost all samples were observed to consist of rock fragments, originating from metamorphic and igneous rocks, although larger grain sizes and higher grain to matrix ratios are recorded for Chalcolithic Age samples compared to those samples belonging to Iron Age. XRD investigations on representative samples of the three periods, revealed high abundances of quartz, feldspar, and pyroxene group minerals in all samples, while the presence of hematite and mica minerals were observed both in Chalcolithic and Iron Age samples, but underlying the use of micaceous raw materials mostly in Iron Age. In the XRD traces of the investigated sherds of Chalcolithic and Iron Ages, the absence of clay fractions both in the bulk and oriented samples, supports a minimum firing temperature of around 800- 850 °C, while the presence of mullite phase both in XRD and SEM – EDX results showed the possible use of high firing temperatures, in the range of 950–1050° C, starting from Chalcolithic Age. Chemical compositions of major oxides obtained ICP – OES analyses exhibit similar compositions both for Chalcolithic and Iron Age samples. Few exceptions observed may indicate possible use of different raw material and/or different manufacturing technique.

Keywords: Chalcolithic, Ubaid Period, Pottery, Optical Microscope, XRD, SEM – EDX, ICP – OES

ÖZ

DEĞİRMENTEPE (MALATYA) SERAMİKLERİNİN MİNERALOJİSİ VE ÜRETİM TEKNOLOJİSİ

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Değirmentepe (Malatya) Höyüğünde yapılan yüzey araştırması ve kazı çalışmalarından elde edilen ve Kalkolitik (Obeyd) Çağ, İlk Tunç Çağı I ve Demir Çağına tarihlenen çanak – çömlek örneklerin dokusal, mineralojik ve mikro – yapısal özellikleri, petrografik, X-ışını Kırınımı teknikleri kullanılarak belirlenmiştir. Örneklerin mikro – yapıları ve yarı kantitatif kimyasal analizleri Taramalı Elektron Mikroskop (SEM) ve Enerji saçınımlı X – ışını (EDX) spektrometri teknikleri ile de çalışılmıştır. Daha sonra ise bazı örneklerin kimyasal analizleri Endüktif Eşleşmiş Plazma – Optik Emisyon Spektrometresi (ICP – OES) kullanılarak yapılmıştır. Hemen hemen bütün örneklerde gözlemlenen kayaç parçalarının, metamorfik ve volkanik kökenli olduğu ve bunun yanında Kalkolitik Dönem örneklerinin Demir Çağı örneklerine kıyasla daha kaba taneler içerdiği ve daha yüksek tane/ çimento oranına sahip olduğu belirlenmiştir. Bütün dönemlere ait çanak - çömleklerden seçilmiş temsili

örnekler üzerinde yapılan XRD analizleri sonucunda, kuvars, feldspat ile piroksen grubu minerallerin bütün örneklerde, hematite ve mika minerallerinin ise Kalkolitik ve Demir Çağı örneklerinde bulunduğu ortaya çıkarken, mikalı kilin daha çok Demir Çağında hammadde olarak kullanılmış olabileceği belirlenmiştir. Kalkolitik ve Demir Çağlarına ait hem tane boyu ayrılmamış hem de yönlendirilmiş örneklerde yapılan XRD analizlerinde herhangi bir kil mineraline rastlanmamış olması en düşük pişirme sıcaklığının 800 – 850 °C lerde olduğunu ortaya koymuştur. XRD ve SEM – EDX analizlerinde ise müllit fazının bulunması 950–1050°C arası yüksek bir pişirme sıcaklığına Kalkolitik Çağdan itibaren ulaşılmış olabileceğini göstermiştir. ICP – OES analizleri sonucunda elde edilen ana oksitlerin kimyasal kompozisyonları, Kalkolitik ve Demir Çağı örneklerinde benzer yapıdadır. Gözlenen birkaç farklı kompozisyon bu örnekler için farklı ham madde ve / veya farklı üretim teknolojisi kullanıldığına işaret edebilir.

Anahtar Kelimeler: Kalkolitik, Obeyd Dönemi, Çanak – Çömlek, Optik Mikroskop, XRD, SEM – EDX, ICP – OES

Dedicated to Prof. Dr. Ufuk Esin

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INTRODUCTION

1.1. Değirmentepe Mound

1.1.1. The Location

Değirmentepe Mound was located at 38° 28' north latitude and 38° 29' east longitude, and was 24 km away from Malatya city at the north east of Battalgazi county in Eastern Turkey (Figure 1.1). It was described physically as a middle sized mound covering 100x150 m² area with an 8 meters height, and lying 650 m above the sea level (Figure 1.2) (Özdoğan, 1977).

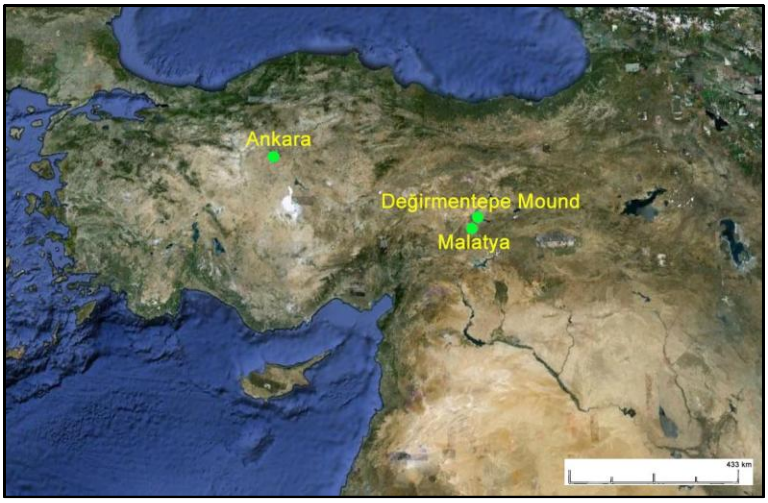


Figure1. 1. A map showing the location of Değirmentepe Mound

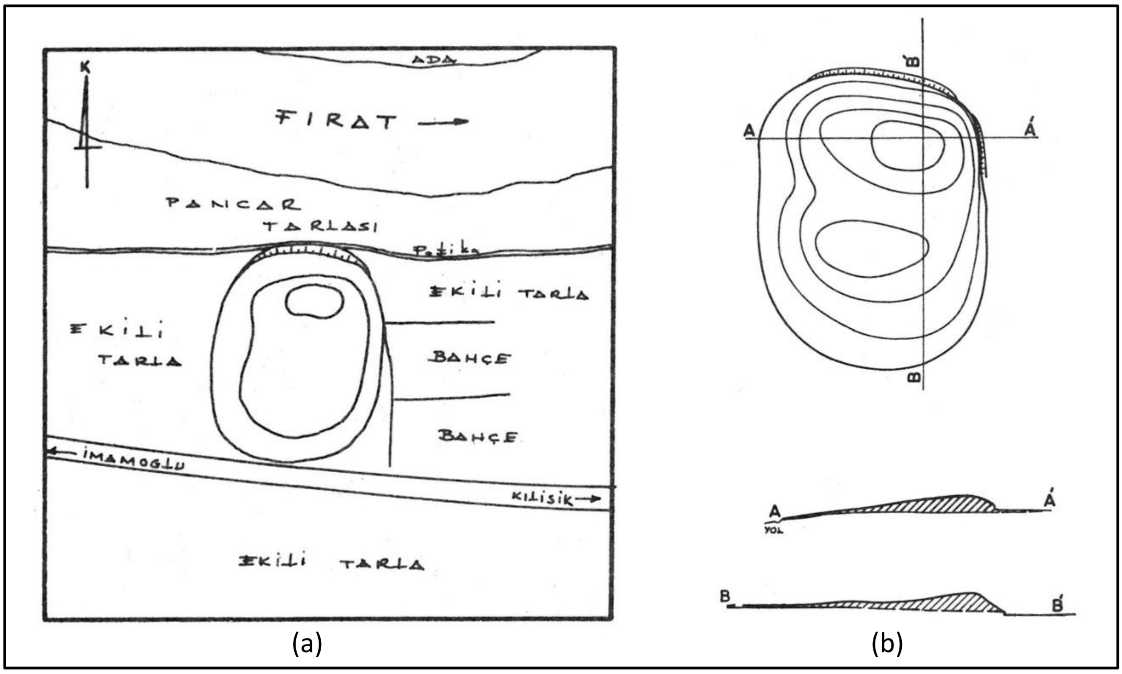


Figure1. 2. Drawings showing (a) the position of Değirmentepe Mound along the Euphrates River (b) physical features of the mound after Özdoğan, 1977.

The site has been completely submerged underwater due to the construction of Karakaya Dam in that area, since 1987. Archaeological investigations in Değirmentepe began with the surface survey performed in 1977 by Özdoğan and continued with eight successive excavation seasons during 1978 to 1986 directed by Ufuk Esin. The process was carried out within the framework of a regional salvation project, that is, "METU Lower Euphrates Project for Ancient Sites and Monuments".

Based on the excavation reports, eleven archaeological levels found at Değirmentepe site had been occupied from Chalcolithic period (5^{th} millennium BC) to Medieval Age (5^{th} to 15^{th} century AD). It presents divergent features in its settlement plan together with several architectural remains and wide range of archaeological finds (Table 1.1) (Esin and Harmankaya, 1987). Beside other phases, Değirmentepe gains its importance particularly with levels 6 to 11 all dated to the Chalcolithic period and revealing Ubaid characteristics. In fact, the levels of 6 and 7 were the most preserved ones presenting Ubaid tripartite/ multi-roomed plan and *aggluginated layout* with the additional material evidences such as kilns, altars etc., painted Ubaid pottery sherds, slag, flint pieces, *seals* and *bullea* (Harmankaya, et. al, 1998). Değirmentepe Mound is still one of few sites explored that had the elements of Chalcolithic Ubaid Culture in the large scale of evidences in the northern part of Taurus Mountains (Esin and Harmankaya, 1987).

Table 1. 1. Archaeological Stratigraphy of Değirmentepe settlement
After Esin and Harmankaya, 1987

Archaeological Stratigraphy	**Period**
Level 1	Iron Age (1000 BC) – Medieval Age
Level 2	Iron Age – Late Roman Period
Level 3 - 4	Iron Age
Level 5	Iron Age – Middle Bronze Age – Early Bronze Age – Chalcolithic Age, mixed level
Level 6 – 11	Chalcolithic Age (Ubaid Period)

1.2. Archaeological Investigations

1.2.1. Survey in 1977

Değirmentepe was first discovered by Ümit Serdaroğlu and his survey team, in 1975, and named as Adagören (Kilişik) Mound (Serdaroğlu, 1975). In 1977, Mehmet Özdoğan and his team carried out an extensive archaeological survey of the dam reservoir area which later would be flooded by Karakaya, Karababa and Gölköy Dams and the mound was renamed as Değirmentepe (Özdoğan, 1977). Later on, as a part of METU Lower Euphrates Project, excavations were carried out by the Prehistory Department of İstanbul University, directed by Prof. Dr. Ufuk Esin.

In 1977, a surface survey began in the Lower Euphrates Basin with the intent to record and document all the archaeological sites and remains within the reservoir area, and afterwards to gather primary information in order to assist further excavations to be carried out in the mentioned area. According to 1977 survey report, Değirmentepe mound was located within in the region of Atabey, İmamoğlu, Kilişik and surrounding area. The mound surface was cultivated. Northeastern slope was steep due to the removal of cultivated soil and erosion. During this survey, the wares collected were mostly belonging to the Late Chalcolithic Period. The site, therefore, was dated to Late Chalcolithic – transitional period in the published survey report (Table 1.2) (Özdoğan, 1977).

Table 1. 2. Classification of potteries which were collected during surface survey on Değirmentepe Mound after Özdoğan, 1977

Ware type*	**Description**	**Abundance**	**Note**
1.1	Dark faced burnished ware	few	-
1.2	Dark faced unburnished ware	few	coarse
1.4	Ubaid painted pottery	few	some with green paste
1.5	Chaff faced ware	many	-
1.6	Light colored fine ware	moderate quantity	-
1.8	Various coarse ware	many	-
1.9	Various painted ware	very few	-
1.11	Flint scraped ware	many	-
1.12	Beveled rim bowl	-	doubtful
1.13	Uruk like fine ware	-	doubtful
1.14	Uruk like coarse ware	many	-

*Ware types are given as specified in the publication

At the end of 1977 survey, 210 sites which take place in the survey area were systematically recorded together with the large number of wares gathered. According to final report of this survey (Özdoğan, 1977), collected wares were classified with respect to their periods by comparing them with the well known ware types from North Syria and Southeast Anatolia.

1.2.2. Excavations between 1978 and 1986

Later on starting from 1978, Değirmentepe Mound had been excavated by a team from Istanbul University Prehistory Department directed by Prof. Dr. Ufuk Esin. The excavation was carried out as a part of "METU Lower Euphrates Project for Ancient Sites and Monuments" with the cooperation of General Directorate of Museums and Ancient Monuments (Figure 1.3).

Figure1.3. Aerial view of Değirmentepe. To the north 50 m above the site, the meandering Euphrates River flows east after Gürdil, 2006

Based on these investigations it was believed that the initial Değirmentepe occupation was probably near the bank of river Euphrates, but later on, it was moved to a little far from river bank (Esin, et. al, 1978).

The excavations was carried out for eight successive summer seasons between 1978 to 1986, exhibited outstanding discoveries concerned with the culture, economy, architecture and religion of Değirmentepe within the last half of fifth millennium BC to the Medieval Age (5^{th} to 15^{th} century AD). As mentioned in Section 1.1.1, Değirmentepe Mound has eleven archaeological levels which dated from the Chalcolithic Age to Medieval – Late Roman Period (Esin and Harmankaya, 1986). One should note again that the most prominent layers were between 6 to 11 present the distinctive ware type and architecture of Ubaid Period with the additional evidences regarding the economy, metallurgical activities, flint production and social life during the Chalcolithic – Ubaid Period (Esin, 1981; Esin, 1981b; Esin, 1982; Esin and Arsebük, 1983; Esin 1984; Esin and Harmankaya, 1985; Esin and Harmankaya, 1986; Esin and Harmankaya, 1987, Esin et. al, 1987).

1.2.1.1. Chalcolithic Age in Değirmentepe (4500 BC)

Chalcolithic Age stratigraphy (levels 6 to 11) was determined by means of the trenches on the mound and considering the architectural and material-culture remains of these trenches. The presence of a step trench on the north of the mound also confirms the proposed sequence (Esin and Harmankaya, 1985). Dating method performed on Değirmentepe samples, such as thermoluminescence (TL) supports the presence of this stratigraphy (Esin and Harmankaya, 1985). Among these levels, level 7 is the most preserved one and it provides the main part of the information about the Ubaid Culture in the settlement. The Ubaid culture, which takes its name from Tell-al Ubaid, plays a important role in the urbanization of the Near East. Surviving for more than 1500 years (5500-3800 BC), it was characterized by important social, economic and political developments which influenced the development of urban polities both the Near East and the East and Southeastern Anatolia Regions (Erarslan, 2008). Ubaid culture has been principally characterized by its distinctive painted pottery and tripartite dwelling type, used during Chalcolithic Age, (Esin, 1982, Esin and Arsebük, 1983; Esin and Harmankaya, 1985; Esin and Harmankaya, 1986, Esin and Harmankaya, 1987).

In addition to excavation reports, detailed architectural and spatial analyses given in the dissertation research by Gürdil at 2005 support that there are two different types of Ubaid dwellings in the form of *agglutinated layout* (Gürdil, 2006). The first type is the tripartite buildings consist of a large rectangular room in the center which is surrounded with smaller ones at two or three side. The latter type is multi-room buildings which are irregularly attached to each other. The rooms are connected to each other by doorways but none of them has an outer door. The horizontal sequence of holes and bricks were considered as a second story of small rooms in tripartite buildings with the presence of staircase in some of buildings. A revealed mud brick wall built in the southeastern part of the mound probably surrounds the settlement, therefore plays a main defensive role with the thick exterior walls of the most dwellings (Gürdil, 2006; Esin and Harmankaya, 1986) (Figure 1.3).

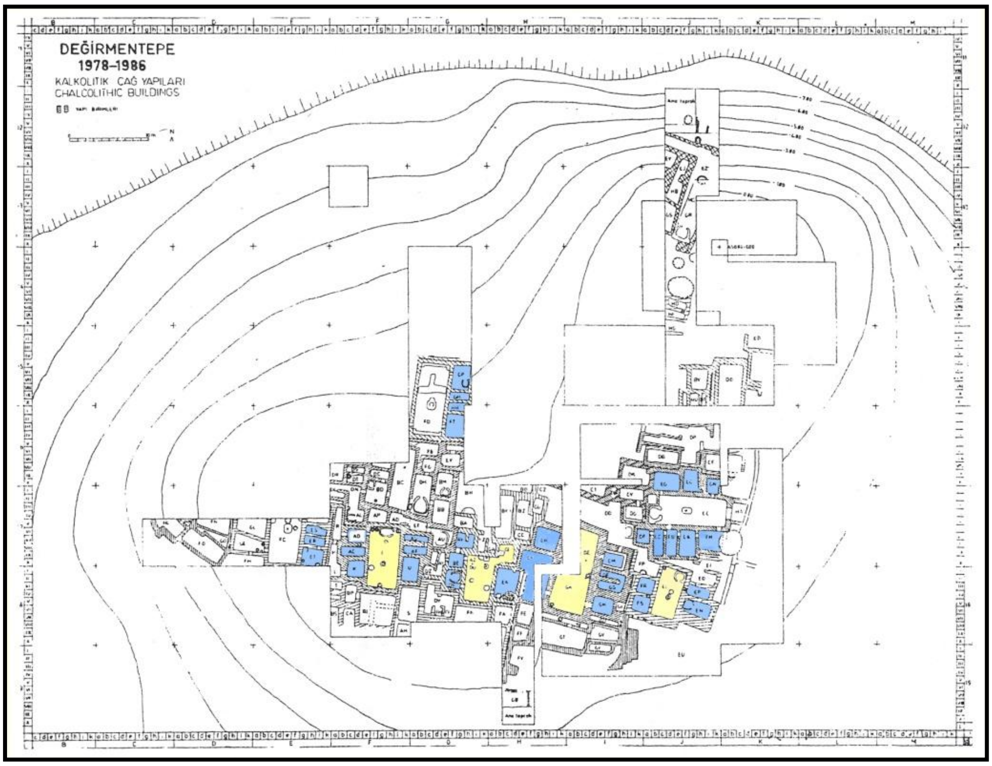


Figure1. 4. Settlement plan of Chalcolithic Age, tripartite dwellings; large room painted in the center painted in yellow and surrounding small rooms were painted in blue after Esin and Harmankaya, 1986.

The pottery group dated to Ubaid Period recovered from Chalcolithic Age levels in Değirmentepe Mound mainly consists of light colored wares which have greenish-gray or pink paste and slips, the painted Ubaid pottery and coarse dark colored cooking pots. Coba ware (flint-scraped bowls) is the main part of light colored wares which have irregular lines on the surface, those probably drawn by flint. Painted Ubaid pottery, on the other hand, has light color paste painted with red, black or brown color decorated with geometrical shapes, branch mesh or leafs. The next group is coarse and dark colored cooking pots which are handmade, dark colored such as brown or black and have some chaff and grit as temper material (Esin, 1982; Esin and Arsebük, 1983; Esin and Harmankaya, 1985; Esin and Harmankaya, 1986; Esin and Harmankaya, 1987; Harmankaya et. al, 1998).

One of the most important evidence is *bullea* that defines the trade or exchange during Ubaid Period in Değirmentepe (Esin and Harmankaya, 1986). It is a seal of safety and marked for the ownership of the traded materials. *Bullea* were found together with stone seals in some of Chalcolithic buildings provide valuable information in the sense of household emerged economy and social structure in Ubaid Period (Esin, 1986; Eraslan, 2008).

Flintstone fragments are another evidence for the local production in Değirmentepe and their large amount, as well, could be associated with trade habits and economy in that period (Esin, 1982).

There is a remarkable evidence for the copper production in Değirmentepe as well (Esin, 1986; Özbal, 1986). The copper slags were found near furnaces in some buildings. Their analyses showed that those wastes produced during copper smelting performed. From the technological point of view, copper production is already a significant activity taking place in Chalcolithic Age and it might play role as an export good traded to the southern Mesopotamia (Esin, 1986; Eraslan, 2008).

Chalcolithic levels of Değirmentepe Mound present proto – urban characteristics with Ubaid culture which is emerged in Southern Mesopotamia and expanded to regions nearby (Pollock, 1999). Based on archaeological evidences, Değirmentepe has both architectural and material remains which can be directly related to these proto-urban characteristics, the social life, political organization, economy and technology during the urbanization of these settlements. In this transformation, socially and economically dominant families might establish a central authority by taking control of economic activities, production and trade (Eraslan, 2008; Pollock, 1999). Controlling over the production of goods had probably brought the specialization of the craftsmanship and organized production resulted in production surplus. The most significant improvement in Ubaid pottery production is the use of *tournette* which is an important step in mass production and standardization of potteries (Harmankaya et. al, 1998; Rice, 1987). In addition to that, the kiln type used and the range of firing temperature applied play vital role in the improvement of the production technology of ceramics. On the other hand, metallurgical activities undoubtedly had a giant role in technological improvement in the sense of urbanization in Chalcolithic period (Esin and Harmankaya, 1986).

Therefore, changes in social structure and improvements in production led to a large quantity of standard products which are believed to be the main dynamics of long distance trade. In the light of all these information, Değirmentepe was a significant site where the copper and flint were produced and traded with lumber to the south Mesopotamia via Euphrates River (Esin, 1980; Esin 1981; Esin and Arsebük 1982; Esin, 1983; Esin and Harmankaya, 1984; Esin and Harmankaya, 1985; Esin and Harmankaya, 1986; Esin and Harmankaya, 1987).

1.2.2.1. Early Bronze Age I in Değirmentepe (3000 BC)

Early Bronze Age I were determined by a granary pit (No. 244) found at square 16 F. Inside the pit; sherds of Karaz bowls; bases for jugs and cups were found as well as the artifacts of barley and wheat (Esin, 1984).

1.2.2.2. Iron Age of Değirmentepe (1000 BC)

The small finds, potteries, features and architectural elements reflecting the Late Hittite, Phyrigian, Assyrian, Urartian cultural identities indicate the existence of the several occupations of Değirmentepe during Iron Age (Esin and Harmankaya, 1987). Iron Age pottery unearthed turns out to be one of the most prominent archaeological artifact excavated starting from the surface down to the level 5. The numerous kinds of characteristic pottery belong to various cultures reflect the devious political relations between those during Iron Age (Esin and Harmankaya, 1985).

A citadel with the bastion and the walls was present on the northern part of the mound. Its' circular architecture had similarities with the defensive structures in Persia in Iron Age (Esin, 1987). There were many burials placed in earthenware jars (tombs) at the southern side of citadel. However, houses having rectangular plans and stone baseline walls built on mud brick walls assigned as belonging to the earlier periods (Esin and Harmankaya, 1985).

1.3. Manufacturing Techniques of Archaeological Ceramics

Ceramic is the first material that produced synthetically by forming plastic raw materials (clay), then drying and/or firing it to give its permanent shape. Produced ceramics or dried clays have been widely used for many purposes; as containers for storing the foods in the houses or large vessels in trading, as building materials, as god figurines for sacred purposes. Consequently, they have been the most abundant material in archaeological records. Production technology of the ceramics has changed during thousands of years with the fire control (pyrotechnology) or inventions of new forming techniques (eg. Potters' wheel-tournette) with the considerable effects of cultural choices. Unspecialized type of production in villages began in houses and then turned into more organized production in workshops with social, cultural and technological changes during the Late Chalcolithic Period (Eraslan, 2008). Later on, plenty of ceramic materials have been produced in factories under specific standards which are manipulated by market and engineering requirements.

Production technology of ceramics was significantly influenced by technological level of the social, cultural, and environmental factors. These are all substantive factors that affect the stages of production and should be considered in order to understand the history of pottery production (Rice, 1987).

1.3.1. Raw Materials

The first stage of ceramic production begins with obtaining suitable clay which has satisfactory specifications such as plasticity, workability, drying shrinkage and color. Clay deposits usually have naturally existed inclusions which determine the raw material characteristics. Due to the desired specifications, clay may be processed by removing natural inclusions to increase plasticity, or by reverse of the process of modifying them by adding organic/inorganic temper to decrease the plasticity or to have desired visual characteristics. Moreover, mixing the fine clay with coarse clay is an opportunity to obtain desired plasticity and other characteristics such as color. On the other hand, aging clay in water improves its plasticity and workability by wetting surface of each clay particle (Rice, 1987; Velde and Druc, 1998). Addition of water to clay temper mixture creates its plastic characteristics and application of mechanical pressure to clay eliminates air bubbles and provides uniform particle structure and moisture distribution that increases the workability.

1.3.2. Pottery Forming Techniques

Plastic clay could be formed by various techniques with the help of some equipment or just by hands giving its final shape. These techniques explained with the examples in the leading publications of Rice (1987) and Henderson (2000);

i. Pinching and drawing are similar techniques which used to form the lump of clay by vertical movement of hands and fingers. Moreover, tools may be used to finalize the shaping by scraping the excess clay.

ii. Molding is an alternative technique performed by pressing or pouring clay into a mold. Mold could be the piece of broken vessel fragments or the form of a plaster. The important point is the separation of mold from the newly formed dried clay "green ware". It could be separated with the help of parting agents or the green ware can be separated from the concave molds by itself as a result of drying shrinkage.

iii. Another technique coiling is performed by mainly sticking the coils or rolls of clays one to the other. The technique has several variations; ring coiling, segmental coiling and spiral coiling differentiated due to the application of sticking and length of the coil.

iv. Clay can be also shaped by not only just with hands and small tools but with the aid of more improved type of "potter's wheel". Throwing technique is an important discovery (Ubaid Period) in the history of industrialization. Throwing should be performed by careful placing of clay on the center of the wheel to prevent the uneven thickness, then heightening the walls by lifting and drawing with both hands inside and outside of the lump aided by the centrifugal force.

In the production of a pottery, one of these techniques or the combination of them can be used.

1.3.3. Surface Treatments and Decoration

Formed pottery may be further processed by the surface treatments by smoothing, scraping, burnishing and other similar treatments which are considered as secondary forming techniques mainly affecting to the surface of the pottery but may change the vessel dimensions as well. These treatments performed by the help of some equipment, smooth or hard tools, leather or some textiles, or just by potters' hand.

The visual characteristics of the vessel are influenced by the cultural identity and potters choice. Pottery might be decorated by the applications of two main processes; displacement of surfaces and covering with different kinds of additives. Impressing, stamping, punctuation and cutting implemented with some sharp tools or dies to decorate the vessel surface cause to the displacement on the surface and penetration into the body. Joining the attachments on the surface, painting, slipping and covering with glaze was considered as adding material on the surface (Rice, 1987).

1.3.4. Drying / Firing

Pottery is strengthened and maintained its form at elevated temperatures however the original mineral structure will be lost. Firing causes irreversible physical and chemical changes in the material. There are three main variables in pottery firing which have high influence on the final product; firing atmosphere, maximum firing temperature and soaking time (firing duration). Those should be considered together when discussing the production technology (Velde and Druc, 1998). The atmosphere has an influence on the physical properties of pottery such as color, hardness and porosity. Firing temperature and its duration determines the changes of mineral structure and physicochemical reactions. Oxidizing atmosphere created by free gas circulation during firing provides the bonding of oxygen molecules in gaseous state to various elements. Firing temperature and its duration period strongly depend on kiln type (open and close firing), its design and type of fuel used. Pottery and other ceramic materials have been fired in kilns in Europe, Asia and Africa for thousands of years. However its use in firing was rare in New World before European influence in America (Rice, 1987). The open and close firing techniques both have advantages and disadvantages; still it is not a mistake to tell that the development in kiln technology is based on increasing the ability of reaching and keeping the maximum temperature for a certain period of time.

Investigations on production technology of ancient ceramics by using various techniques mainly aim to reconstructing the manufacturing technology in the past. The studies of production technology reveals the type of raw materials, forming techniques that utilize to shape the clay, surface treatments, painting procedure, the kind of pigments, and firing conditions. On the other hand, the choices on production process should be also considered in order to understand ceramic production. These are material choices such as raw material, temper, forming technique, decoration and cultural choices such as impressions of social stratification on decoration (Tite, 2008).

Archaeometric approach to the entire process of production provides a wide range of information about production history of pottery (Rice, 1987). The physical, chemical and mineralogical properties of clay, natural inclusions and/or temper restrict the physical and mechanical properties of final product. The investigation of raw material characteristics provides valuable information for choice of raw materials, intentionally added materials and provenience of ceramics. Nevertheless, the following steps of production have various signs on physical condition of final product. Hereby, archaeometrical study investigates and describes the chemical, mineralogical, microscopical and physical properties of final product and raw materials as well.

1.4. Mineralogical Characterization

Mineralogical characterization provides useful information about fabrication and raw material source of the ancient pottery. Depending on research objectives, the characterization techniques allow to analyze the crystalline substances in ceramic body and sometimes in slip and glaze. The starting point of analysis entirely depends on the question to be answered which could be several different depending on the archaeological problems (Rice, 1987).

Optical microscopy (petrography), X-ray diffraction and various kinds of thermal analyses (Rice, 1987) with the help of scanning electron microscopy (SEM) as well are primary techniques for investigating mineralogical characterization. By using them, natural and intentionally added inclusions, particular types of constituents and the crystalline substances may be formed during firing process can be identified. The coarser particulates in clay matrix can be investigated not only by the mineralogical approach but also by examining their physical orientations, associations and quantities. Combination of these techniques provides more powerful and reliable information than their individual applications.

1.5. Previous Archaeometric Investigations on Değirmentepe Pottery

Değirmentepe together with İkiztepe and Tülintepe archaeological sites were assigned as selected pilot sites that would provide the archaeological materials for the first and foremost archaeometric research in Turkey. These pioneer studies were initiated by The Scientific and Technological Research Council of Turkey (TÜBİTAK) at 1980. Thereafter, the archaeological materials found belonging to various periods in Değirmentepe, have been extensively studied by several researchers in the fields of anthropology, zooarchaeology, archaeobotany and geomorphology (Esin, 1983). Değirmentepe pottery was investigated in detail and discussed in the sense of provenance and production technology by using several techniques like X-ray Fluorescence (XRF), Neutron Activation Analysis (NAA), X-ray Diffraction (XRD), Optical Microscope and Scanning Electron Microscopy – Energy Dispersive X-ray Spectrometry (SEM – EDX).

Birgül, Esin and her colleagues performed trace element analyses on Değirmentepe samples by using NAA and XRF techniques (Birgül, 1981; Esin et. Al, 1985; Esin et. al, 1989), and evaluated their results by multivariate statistical methods for possible classification of potteries belonging to Chalcolithic, Early Bronze and Iron Ages. The results of their study indicated three different pottery groups which were found to be in good agreement with the archaeological estimation of these samples carried out by Esin (Esin et. al, 1985). According to these results; Potteries in Group A corresponds to Early Bronze Age I, potteries of Group B corresponds to Chalcolithic Age and Group D samples were from a mixture of Chalcolithic and Iron Ages (Table 1.3).

Based on their mineralogical and petrographic characteristics, Türkmenoğlu et al., (1985), classified the ceramics from Değirmentepe into three groups (Group 1, 2 and 3) by means of thin section study (Table 1.3). They also investigated the clay material, collected from some clay deposits nearby Değirmentepe site and stated that some of these deposits were probably used as the raw material source for particularly Group 1 and Group 2 ceramics. Relationships of groupings done by Esin et al., (Esin et. al, 1985) and Türkmenoğlu et al., (Türkmenoğlu et al., 1985) are given in the Table below:

Table 1. 3. Relationships of Değirmentepe sample groupings by Esin et al., and Türkmenoğlu et al., together with corresponding archaeological periods

Esin et al., 1985	**Türkmenoğlu et al., 1985**	**Archaeological Period**
Group A	Group 3	Early Bronze
Group B	Group 1	Chalcolithic
Group D	Group 2	Chalcolithic and Iron Age

As a continuation of her previous study described above, Türkmenoğlu performed X-ray Powder diffraction analysis on the samples studied and on their clay fractions (Türkmenoğlu, 1989; Türkmenoğlu and Göktürk, 1996). The study of clay fractions revealed the presence of only amorphous material indicating the minimum firing temperature in the range of 800˚C - 850˚C. Presence of α-crystobalite, α- quartz, calcite assemblage in Group 1 and Group 2 showed a maximum temperature of lower than 1000˚C. Different results obtained in the analysis of Group 3 indicate the use of a different manufacturing technology and a different firing temperature, probably higher than 1000˚C.

1.6. Aim of The Study

The present study is an attempt to explore the potential of more advanced techniques such as SEM- EDX and ICP- OES, along with additional, intensive petrographical studies and XRD investigations, for characterizing the potteries belonging to Chalcolithic, Early Bronze and Iron Ages found at Değirmentepe Mound (Malatya), in order to assist the understanding of technological characteristics of ceramic production in Değirmentepe.

CHAPTER 2

MATERIALS AND METHODS

2.1. Samples and Sampling Locations

Pottery samples examined in this research were provided from Değirmentepe collection of Prehistory Department of Istanbul University by the assistance of Prof. Dr. Mihriban Özbaşaran. Part of the samples was collected during the surface survey in 1977, while the rest were obtained in the excavations carried out during the period of 1978-1986. Twenty two of them belong to Late Chalcolithic, two of them from Early Bronze Age and seventeen of them from Iron Age. More detailed information of each period is presented in following sections.

2.1.1. Chalcolithic Age (Late Ubaid Period)

Late Chalcolithic Age pottery samples consist of 22 sherds dated to Ubaid Period. One group of samples (Sample No: 156, 157, 160, 165, 176, 177, 205, 209, 210, N1, N2, N3) were already present in the collection of a previous studies in METU (Birgül, 1981; Birgül, 1985; Esin, Birgül, Yaffe, 1985; Esin, Birgül, Yaffe, Marshall, 1989), and the rest (Sample No: E1, E2, E3, S1, S2, S3, S4, S5, S6 and S7) were obtained from the collection of Istanbul University, Prehistory Department.

The list of these samples together with their excavation year, trench information that they belonged to and their specific location if remarked are given in

Table 2.1 and marked on the plan of the Chalcolithic settlement (Figure 2.1). Their photographs are given in Figures 2.2.

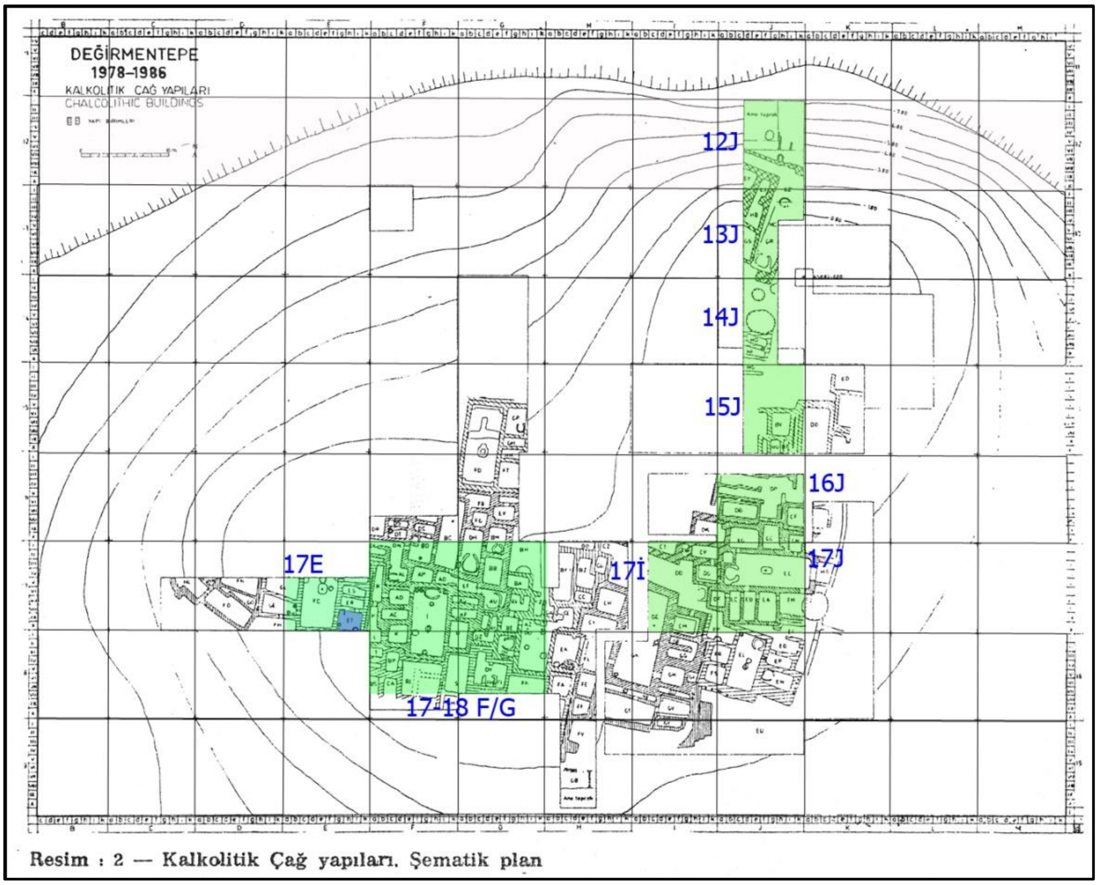


Figure 2. 1. Location of Chalcolithic Age samples on settlement plan of level 7

Table 2. 1. Chalcolithic Age (Ubaid) Samples

Sample No	Year of Excavation	Trench	Location
157	1982	16j	-
160	1982	16j	-
165	1982	16j	-
176	1982	17i	401
177	1982	17j	CI
205	1984	17i	-
209	1984	17-18 F,G	-
210	1984	16j	BP
E1	1986	13-14j	I-90
E2	1986	17E	ET
E3	1986	14J	64.8
N1	1987	17i	CM
N2	1985	12j	v/d
N3	1985	12j	v/d
S1	1977	Survey	-
S2	1977	Survey	-
S3	1977	Survey	-
S4	1977	Survey	-
S5	1977	Survey	-
S6	1977	Survey	-
S7	1977	Survey	-

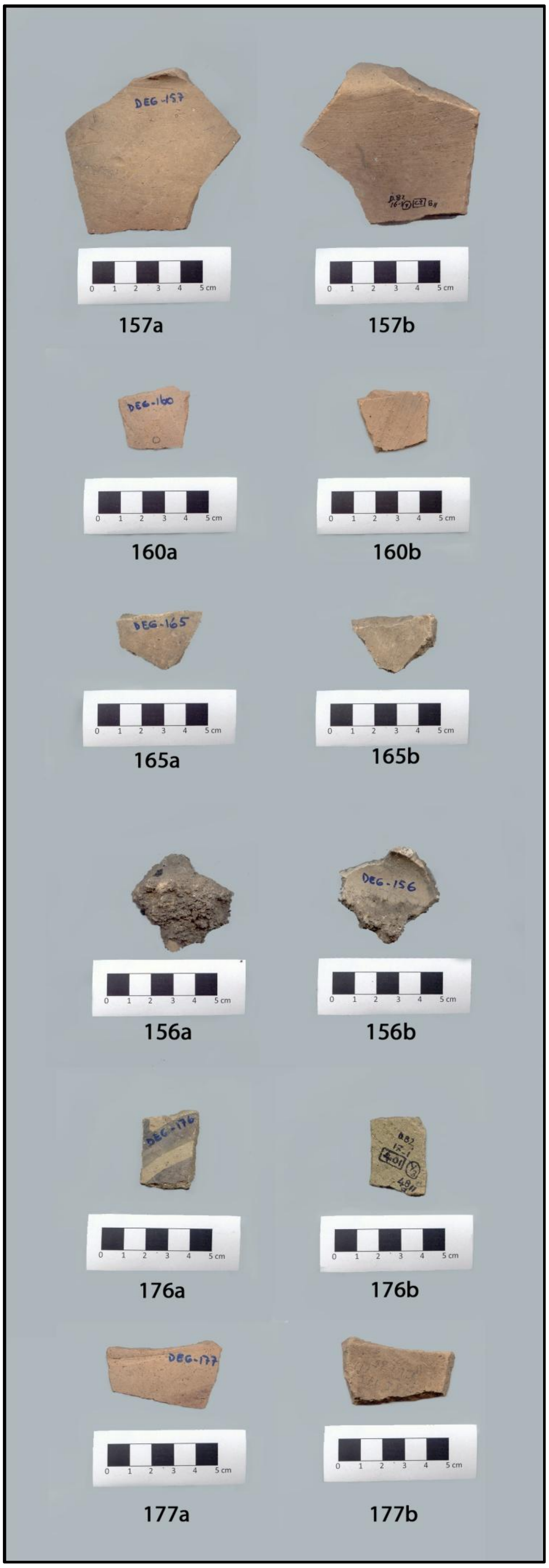


Figure 2. 2. Photographs of Chalcolithic Age Samples (X**a** represents outer face; X**b**, inner face).

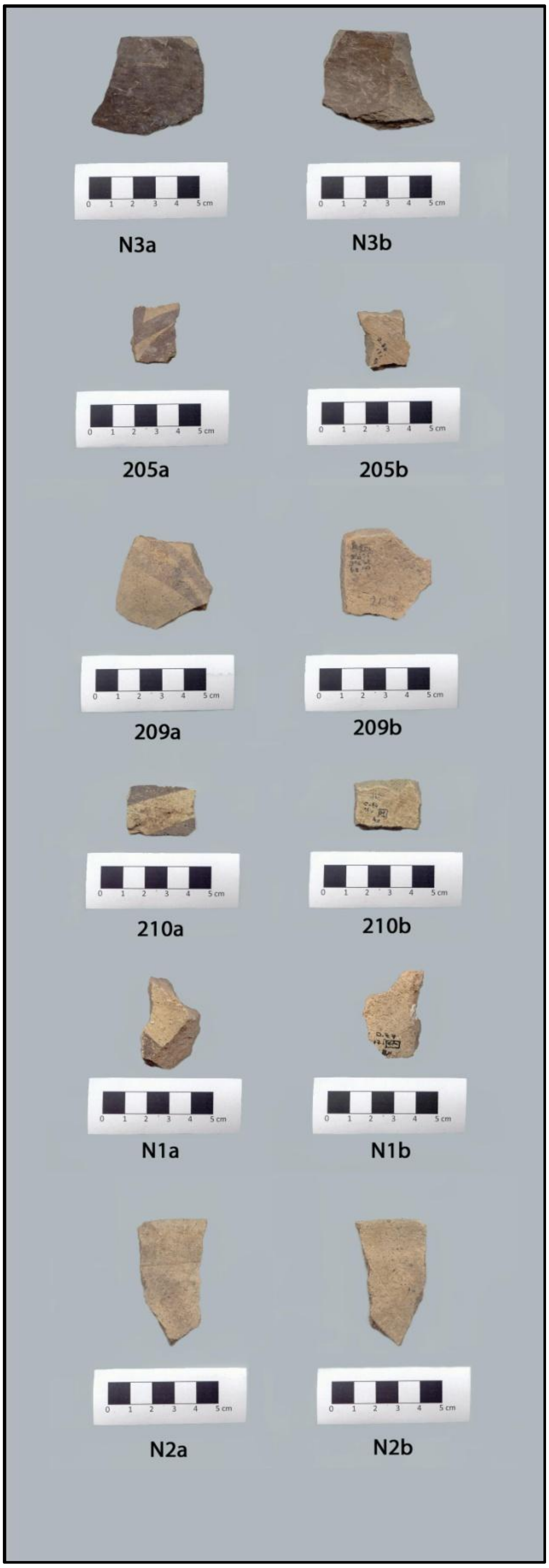


Figure 2. 2 (continued)

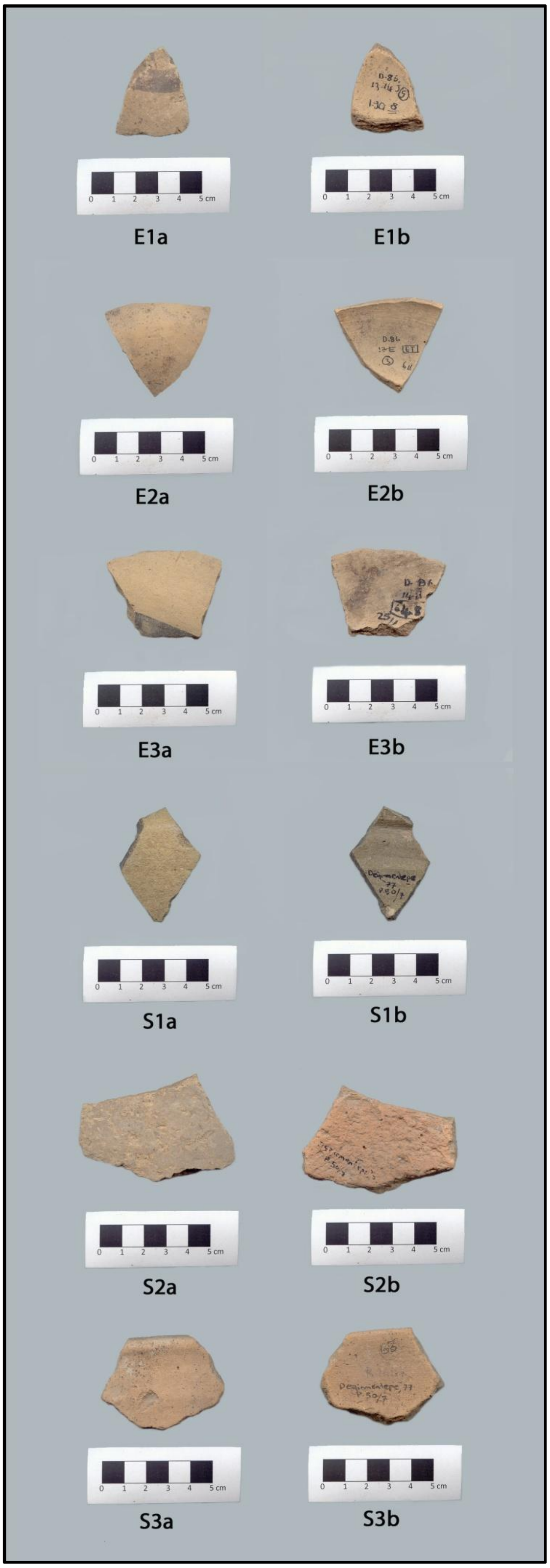


Figure 2. 2 (continued)

Figure 2. 2 (continued)

2.1.2. Early Bronze Age

Two sherds examined in this group, which were dated to Early Bronze Age, have dark grey color and burnished surface (Figure 2.4). Similarities in color, thickness and the texture between these two sherds which gathered from the same location in grid 16F, can be associated with they are in fact the different pieces of the same pottery (Figure 2.3, Table 2.2). Their locations related information and photographs are given in Figure 2.3, Table 2.2 and 2.4 respectively.

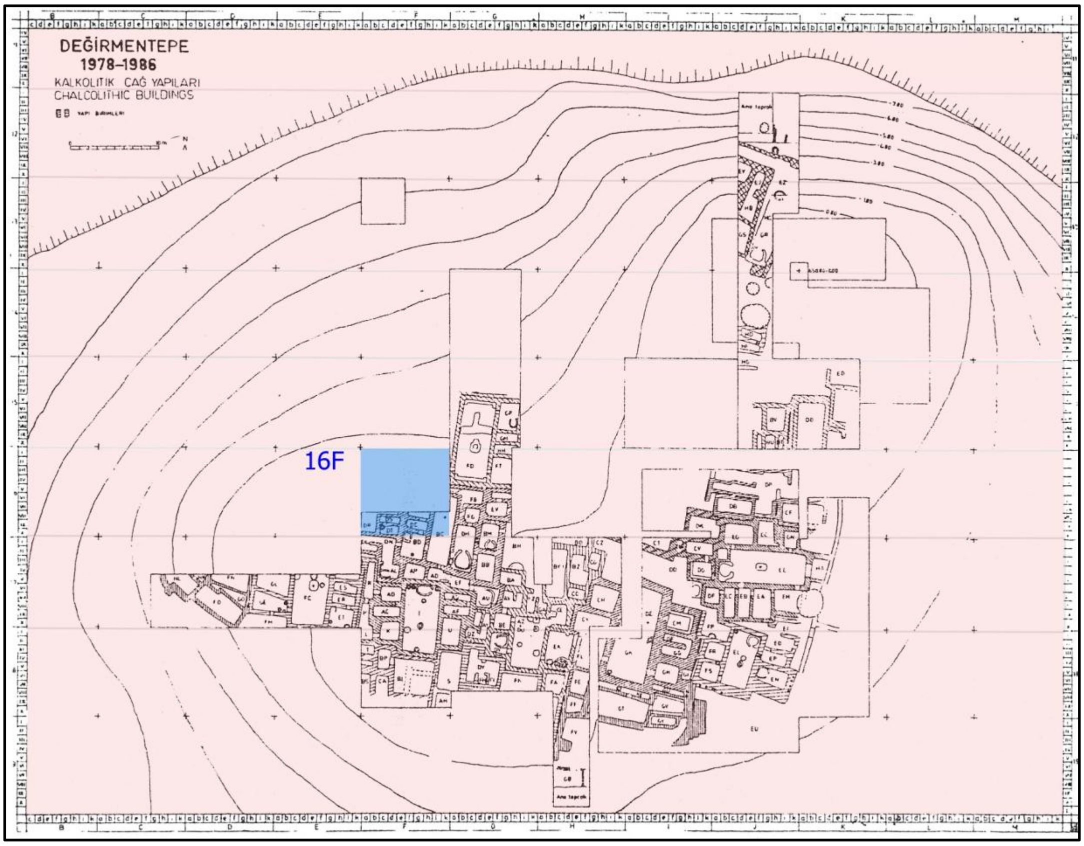


Figure 2. 3. Location of Early Bronze Age I samples on the settlement plan of Chalcolithic level 7

Table 2. 2. Early Bronze Age Samples

Sample No	Year of Excavation	Trench	Location
150	1982	16F	244
151	1982	16F	244

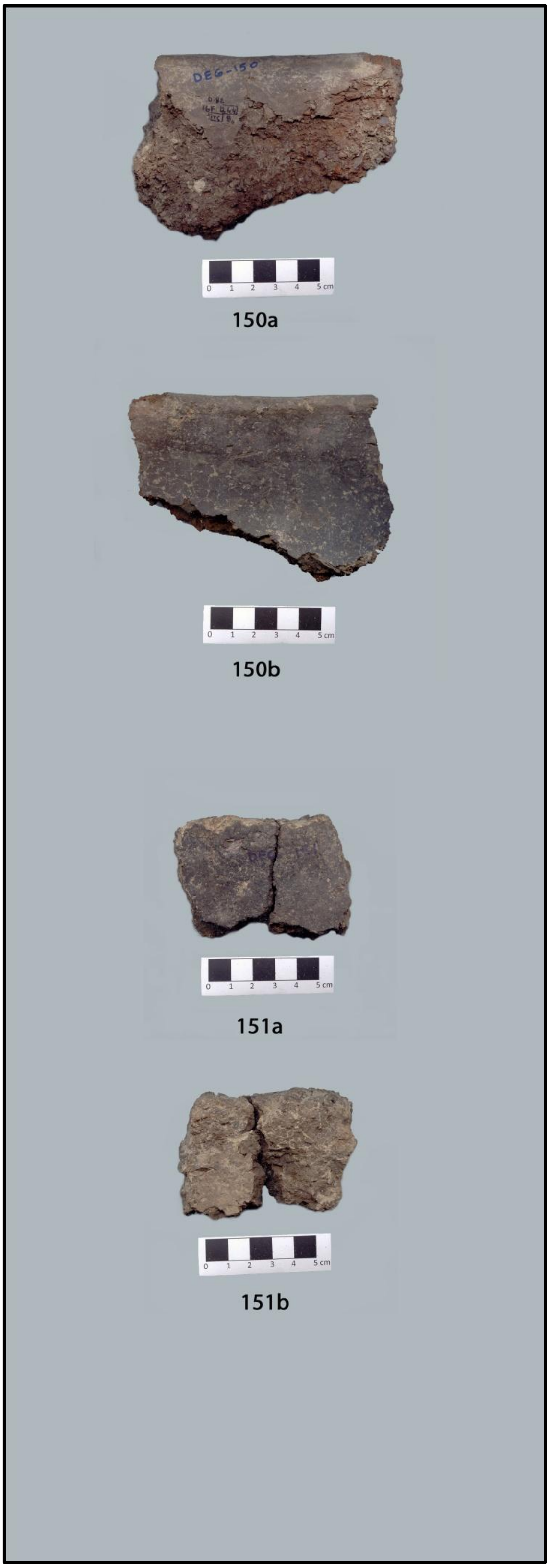


Figure 2. 4. Photograph of Early Bronze Age Samples (X**a** represents outer face; X**b** inner face)

2.1.3. Iron Age

The Iron Age pottery group consists of 17 sherds. They were collected from 3 different grids (16J, 16I and 17I) and Samples 189 and 187 were from structure CI which is a specific location in grid 16J (Figure 2.5, Table 2.3 and Figure 2.6).

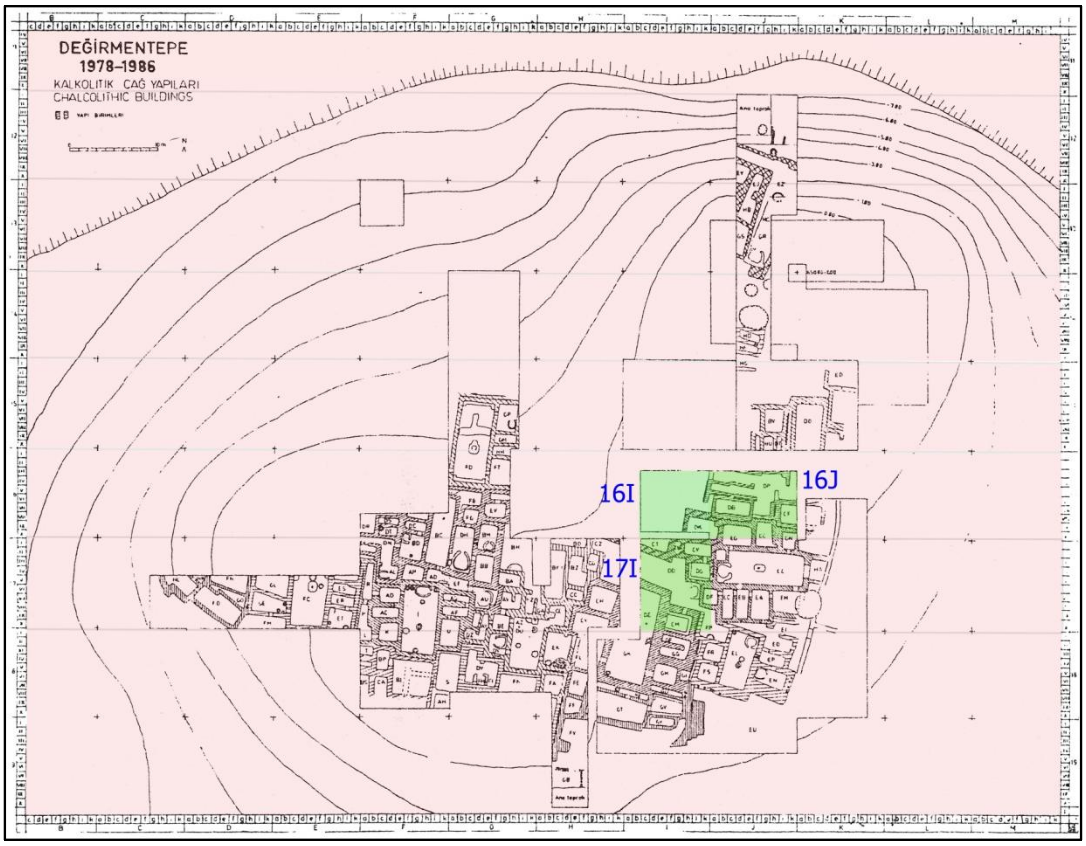


Figure 2. 5. Location of Iron Age samples on the settlement plan

Table 2. 3. Iron Age Samples

Sample No	Year of Excavation	Trench	Location
187	1982	16J	CI
189	1982	16J	CI
223	1984	16I	-
224	1984	17I	-
227	1984	16I	-
228	1984	16I	-
230	1984	16I	-
231	1984	16I	-
233	1984	16I	-
235	1984	16I	-
237	1984	16I	-
238	1984	16I	-
239	1984	16I	-
244	1984	16I	-
246	1984	16I	-
248	1984	16I	-
249	1984	16I	-

Figure 2. 6. Photograph of Iron Age Samples (X**a** represents outer face; X**b** inner face).

Figure 2. 6 (continued)

Figure 2. 6 (continued)

2.2. Visual Classification and Dating

Visual classification and archaeological dating were already carried out by Değirmentepe Excavation Team of İstanbul University, Prehistory Department, and used as such in the following sections (Private communication with Mihriban Özbaşaran).

2.3. Thin Section Analysis

Thin section analyses of all the samples were carried out as follows: A slab of pottery is cut from the ceramic fragment 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 microscope slide and ground away with abrasives to a uniform thickness of 0.03 mm. The slide is covered with a thin glass. The correct layer of thickness is achieved at 0.03 mm where the proper interference colors of minerals are obtained in the polarizing microscope (Rice, 1987).

Thin section preparation was carried out at the Thin Section Laboratory of the Geological Engineering Department in METU. The optical examination was carried out in the laboratories of Geological Engineering Department of METU by using Olympus CX31 model petrographic (polarizing) microscope occupied with photo attachement.

2.4. Stereo Microscopy

Following the thin section investigations carried out by using polarizing microscope in Geological Engineering Department, further examination for all thin sections were carried out with the aid of a Leica model stereo microscope in the Materials Conservation Laboratory – Department of Architecture, METU. The aim was to get favorable overview of size, shape and distribution of particles and pores in ceramic thin sections.

2.5. X-ray Diffraction Analysis (XRD)

X-Ray powder diffraction analyses of all the samples were carried out at the METU Central Laboratory by using “Phillips PW 3710” X-ray diffractometer with CuKα radiation with a Ni filter at a scan speed of 2°/min.

Two types of analysis were performed:

a. First, bulk XRD analyses were performed on 9 unoriented powdered samples
b. Then, 3 samples (which appeared to contain some clay fractions in the bulk analysis) were treated by using procedure given below (Jackson, 1975):

- Pottery sherds were powdered in order to reduce the particle size
- Powdered samples were sieved through the 2 mm sieve to obtain 10 grams of sample
- 10 grams of sample were placed in a 600 ml beaker and filled with deionized water
- 0.02 N sodium pyrophosphate was added to enhance the dispersion
- Sample was poured into a plastic container and stirred with mechanical blender to achieve a good dispersion
- Sample was returned to the beaker and allowed to stay still long enough (around 4 hours) to sediment sand sized material.
- Dispersed suspension is allowed for the settlement of 2 μm particles may settle. At 20˚C, 2 μm sized particles are moved down one centimeter during 45 minutes. Equivalent settling of 5 cm distance can be obtained by centrifugation for 2.9 minutes at 750 rpm in a 100 ml tube at the international centrifuge.

- Centrifuged sample (residue) was transferred onto a petrographic slide with the help of a slice.
- After drying in the atmospheric condition, oriented sample on petrographic slide was obtained.

2.6. Scanning Electron Microscopy Coupled with Energy Dispersive X-ray Spectrometry (SEM - EDX)

Scanning Electron Microscope analyses were performed on six samples from Chalcolithic Age (Sample No: 210, N1 and S1) and from Iron Age (Sample No: 230, 246 and 248).

Targets prepared using fresh fracture surfaces of pottery samples (approx. 1x1x2 cm) were coated with Au-Pd film to provide the electrical conducting layer to prevent the surface charging. SEM coupled with EDX analyses were performed at the METU Central Laboratory. A QUANTA 400F Field Emission SEM (FE- SEM) coupled with EDX was used in the measurements.

2.7. Inductively Coupled Plasma Optical Emission Spectrometry (ICP - OES)

10 samples were selected for ICP-OES analysis which was performed in Central Laboratory of METU. Samples investigated were cut to fragments, ground in an agate mortar and transferred to the Central Laboratory for the analysis. There, they were first digested using Anton Paar Multiwave digestion system. ICP-OES investigations for Fe, Al, Na, Mg, K, Ca, Si, Ti, P and Mn were carried out using Perkin Elmer Optima 4300 DV ICP-OES spectrometer.

CHAPTER 3

RESULTS AND DISCUSSION

3.1.Visual Examination and Archaeological Dating

Archaeological dating of the forty one samples to be examined in this study was previously carried out by Değirmentepe Excavation Team from İstanbul University, Prehistory Department. Their visual classifications were also done based on their physical appearances by the same team. These investigations were resulted in three different groups of different periods: Chalcolithic – Ubaid, Early Bronze and Iron Age (Private communication with Prof. Dr. Mihriban Özbaşaran). The details of these classifications are given in the following Tables 3.1 - 3.3.

Table 3. 1. Visual description of samples from Chalcolithic Age

Sample No	Description	Color	Decoration	Visible features
157	body piece	light brown-beige	non decorated	burnished, wheel made
160	body piece	pink-beige	non decorated	burnished, wheel made
165	body piece	light brown-beige	non decorated	burnished, wheel made
176	body piece	greenish-beige	purplish black painted	burnished, wheel made
177	body piece	pink-beige	red painted	burnished, wheel made
205	body piece	light brown-beige	purplish black painted	burnished, wheel made
209	body piece	light brown-beige	purplish black painted	burnished, wheel made
210	body piece	greenish-beige	purplish black painted	burnished, wheel made
E1	body piece	light brown-beige	purplish black painted	burnished, wheel made
E2	body piece	light brown-beige	non decorated	burnished, wheel made
E3	body piece	light brown-beige	purplish black painted	burnished, wheel made
N1	body piece	light brown-beige	purplish black painted	burnished, wheel made
N2	body piece	light brown-beige	non decorated	burnished, wheel made
N3	body piece	dark grey	non decorated	burnished
S1	body piece	greenish-beige	non decorated	burnished, wheel made, slipped
S2	body piece	pink-beige	non decorated	burnished, wheel made, slipped
S3	body piece	pink-beige	non decorated	burnished, wheel made, slipped
S4	body piece	greenish-beige	non decorated	burnished, wheel made, red slipped
S5	body piece	pink-beige	non decorated	burnished, wheel made, dark brown slipped
S6	body piece	light brown-beige	non decorated	burnished, wheel made
S7	body piece	dark brown – grey	non decorated	burnished, wheel made, dark brown slipped

Table 3. 2. Visual descriptions of samples from Early Bronze Age I

Sample No	Description	Color	Decoration	Visible features
150	Rim	Dark grey	Non decorated	Burnished
151	body piece	Dark grey	Non decorated	Burnished

Table 3. 3. Visual descriptions of samples from Iron Age

Sample No	Description	Color	Decoration	Visible features
187	body piece	light brown-beige	Non decorated	wheel made
189	body piece	light brown-beige	Non decorated	wheel made
223	body piece	light brown-beige	Non decorated	wheel made
224	body piece	light brown-beige	Non decorated	wheel made
227	body piece	light brown-beige	Non decorated	wheel made
228	body piece	light brown-beige	Non decorated	wheel made
230	body piece	light brown-beige	Non decorated	wheel made
231	body piece	light brown-beige	Non decorated	wheel made
233	body piece	light brown-beige	Non decorated	wheel made
235	body piece	light brown-beige	Non decorated	wheel made
237	body piece	light brown-beige	Non decorated	wheel made
238	body piece	light brown-beige	Non decorated	wheel made
239	body piece	light brown-beige	Non decorated	wheel made
244	body piece	light brown-beige	Non decorated	wheel made
246	body piece	light brown-beige	Non decorated	wheel made
248	body piece	light brown-beige	Non decorated	wheel made
249	body piece	light brown-beige	Non decorated	wheel made

3.2.Mineralogical Analysis

This part of the study mainly focuses on the examination and identification of minerals, rock fragments, clay minerals, grain size, shape and particle distribution in the clay matrix. Thin section analysis was the first technique applied. Then, XRD analyses were performed which provided an opportunity for the identification of crystalline phases in the bulk specimens. The observations are further checked and confirmed by SEM- EDX analyses.

3.2.1. Mineral Identification

In general feldspar, quartz, plagioclase, pyroxene, hornblende, are found in almost all of the samples investigated via thin section analyses (Table 3.4).

Table 3. 4. Common and less common minerals detected in thin section analyses. Px= Pyroxene, Hbl= Hornblende, Mca= Mica, Bt= Biotite, Pl= Plagioclase, Fsp= Feldspar, Asf= Alkali Feldspar, Qzt= Quartz.

Sample No	Dating	Px	Hbl	Mca	Bt	Pl	Fsp	Afs	Qzt
187	Iron Age	+				+	+		
189	Iron Age	+	+	+			+		
223	Iron Age					+			
224	Iron Age		+		+		+		
227	Iron Age						+		
228	Iron Age	+					+		
230	Iron Age	+				+	+		
231	Iron Age	+			+	+			
233	Iron Age					+	+	+	+
235	Iron Age	+		+	+	+		+	
237	Iron Age	+		+	+	+	+		
238	Iron Age		+	+	+	+	+		
239	Iron Age	+	+	+	+		+		
244	Iron Age			+			+		+
246	Iron Age	+		+	+			+	
248	Iron Age					+	+		
249	Iron Age	+				+	+		
156	Chalcolithic Age					+	+		+
157	Chalcolithic Age	+				+			
160	Chalcolithic Age	+		+			+		+
165	Chalcolithic Age	+					+		
176	Chalcolithic Age	+				+			
177	Chalcolithic Age								+
205	Chalcolithic Age				+		+		
209	Chalcolithic Age	+	+			+			+
210	Chalcolithic Age	+				+	+		+
E1	Chalcolithic Age		+				+		
E2	Chalcolithic Age				+	+	+		
E3	Chalcolithic Age	+	+			+	+		
N1	Chalcolithic Age		+			+	+	+	
N2	Chalcolithic Age	+	+			+	+		
N3	Chalcolithic Age	+					+		
S1	Chalcolithic Age			+		+	+		+
S2	Chalcolithic Age					+	+		+

(Table 3.4 continued)

Sample No	Dating	Px	Hbl	Mca	Bt	Pl	Fsp	Afs	Qzt
S3	Chalcolithic Age	+					+		
S4	Chalcolithic Age			+			+		
S5	Chalcolithic Age						+	+	
S6	Chalcolithic Age	+					+		
S7	Chalcolithic Age						+	+	

Summary of the minerals identified in thin section analyses are given in Figure 3.1.

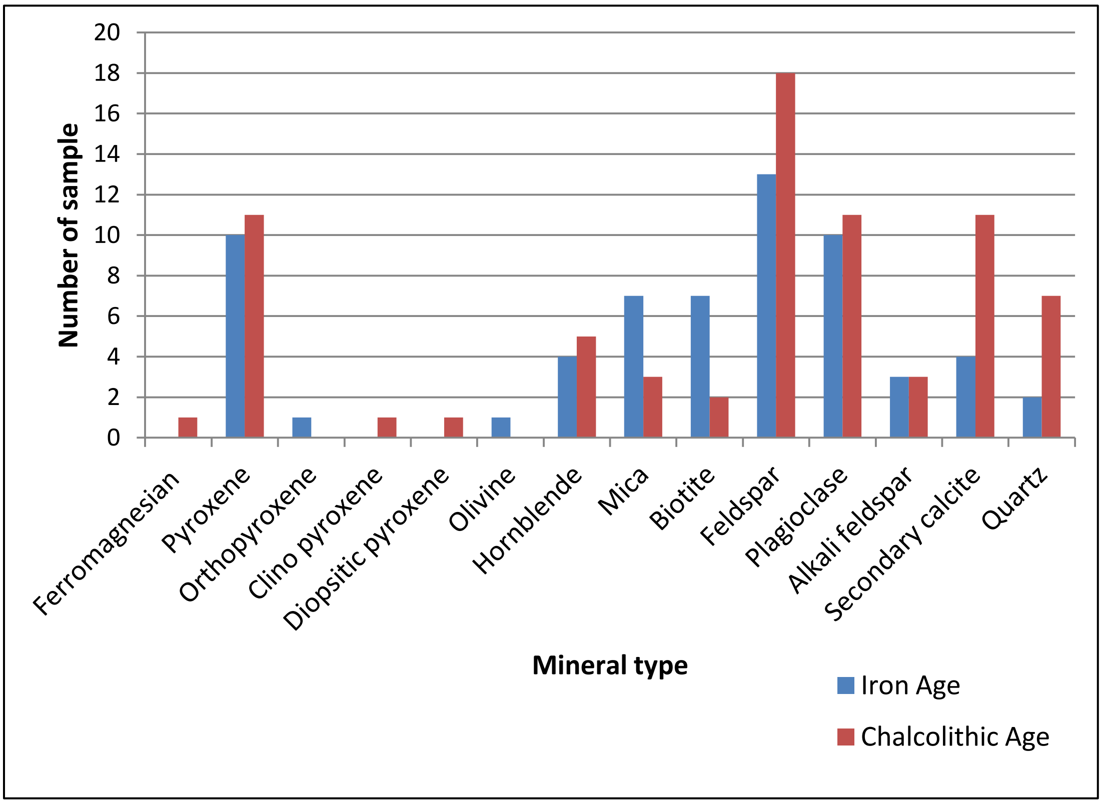


Figure 3. 1. Summary of the minerals identified in thin sections

Three most intense d –spacings (Å) used in the identifications are given in Table 3.5.

Table 3. 5. Three most intense d – spacings* of the minerals used in XRD analysis. Qzt= Quartz, Fsp= Feldspar, Pl= Plagioclase, Di= Diopside, Hem= Hematite, Mca= Mica, Mul= Mullite, Mc= Microcline.

	Qzt	Fsp	Pl	Di	Hem	Mca	Mul	Mc
d-spacing (Å)	3.34	3.74-3.78	4.03	2.98	2.7	10.01-9.96	3.39	3.24
	4.25	6.60-6.30	3.17-3.21	2.51-2.52	2.51	5.00-4.98	3.42	4.22
	1.81	3.45-3.49	2.92-2.95	2.88	3.68	4.48-4.45	5.39	3.37

*In the order of decreasing intensity

Characteristic peaks observed in XRD traces of the pottery samples investigated confirm the observations of thin section analyses and are given in Table 3.6.

Table 3. 6. Major crystalline phases detected in XRD analyses. Qzt= Quartz, Fsp= Feldspar, Pl= Plagioclase, Px= Pyroxene, Hem= Hematite, Mca= Mica, Mul= Mullite, Mc= Microcline.

Sample No	Age	Qzt	Fsp	Pl	Px	Hem	Mca	Mul	Mc
151	EBA	+	+	+	+		+		
210	Chal.	+	+	+	+	+		+	
E1	Chal.	+	+	+	+	+	+ (?)		
N3	Chal.	+	+	+	+	+ (?)	+		
S1	Chal.	+	+	+	+			+	
S4	Chal.	+				+ (?)	+		+
230	Iron	+	+	+	+	+		+	
246	Iron	+	+	+	+	+		+	
248	Iron	+	+	+	+	+		+	

Detailed discussion for the observed minerals in pottery samples investigated by thin section, XRD and SEM – EDX analyses are given in below:

Quartz: can be detected with its distinctive features such as low relief and birefringence, lack of cleavage or twinning under optical microscope. In addition to that, quartz grains have fresh surfaces due to its high stability in weathering environments (Nesse, 2004). It is observed in samples of Chalcolithic Age (Sample No: 156, 160, 177, 209, 210, S1, S2) and Iron Age (Sample No: 233, 244). The shape of crystals appeared to be sub – angular with the sizes varying between 100 – 200 μm. The presence of quartz also confirmed by XRD and SEM – EDX analyses. XRD traces contain three most intensive peaks belong to quartz at 3.34, 4.25 and 1.81 Å (Table 3.6, Appendices B1 – 9). The micro – chemical investigation present fresh crystals have pure silicon and oxygen content (Figure 3.2 and 3.3).

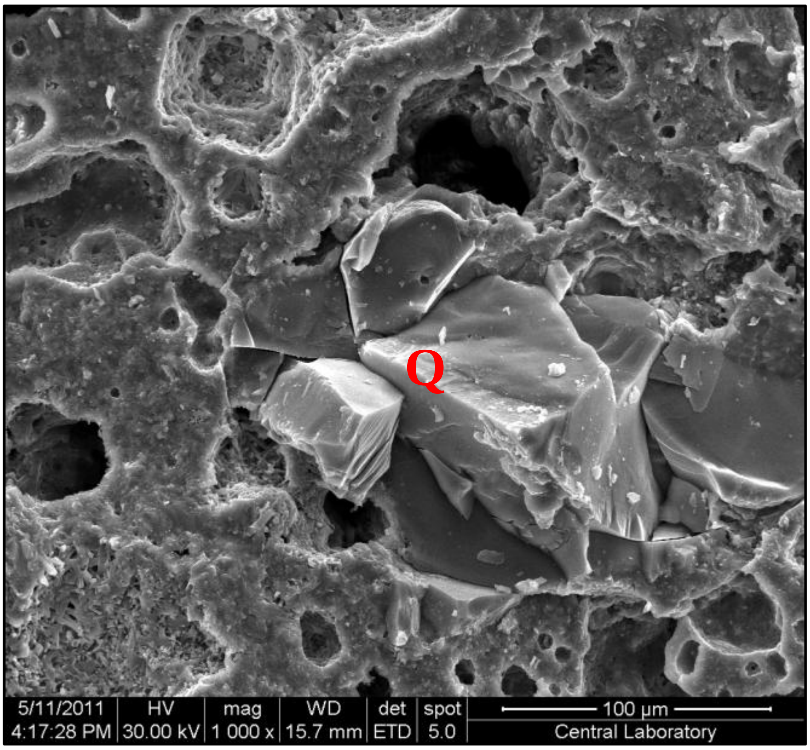


Figure 3. 2. SEM micrograph of fractured quartz grain (Q), Sample S1, Chalcolithic Age.

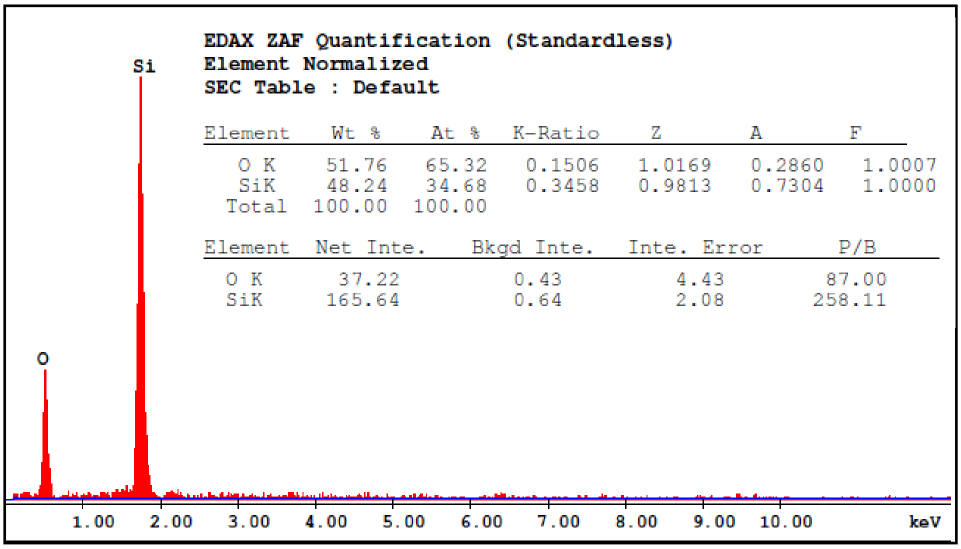


Figure 3. 3. Semi quantitative EDX analysis of quartz grain (Figure 3.2) of Sample S1, Chalcolithic Age.

<u>Feldspar group minerals</u> are the most abundant mineral group in the earth's crust, and so as expected, they were also identified with different grain sizes in almost all of the samples during thin section analyses of Chalcolithic Age (Sample No: 156, 160 165, 205, 210, E1, E2, E3, N1, N2, N3, S1, S2, S3, S4, S5, S6, S7), and Iron Age (Sample No: 187, 189, 224, 227, 228, 230, 233, 237, 238, 239, 244, 248, 249). Feldspar grains were identified as natural inclusions which were probably weathered and originated from metamorphic and igneous rocks (Table 3.4, Figure 3.4).

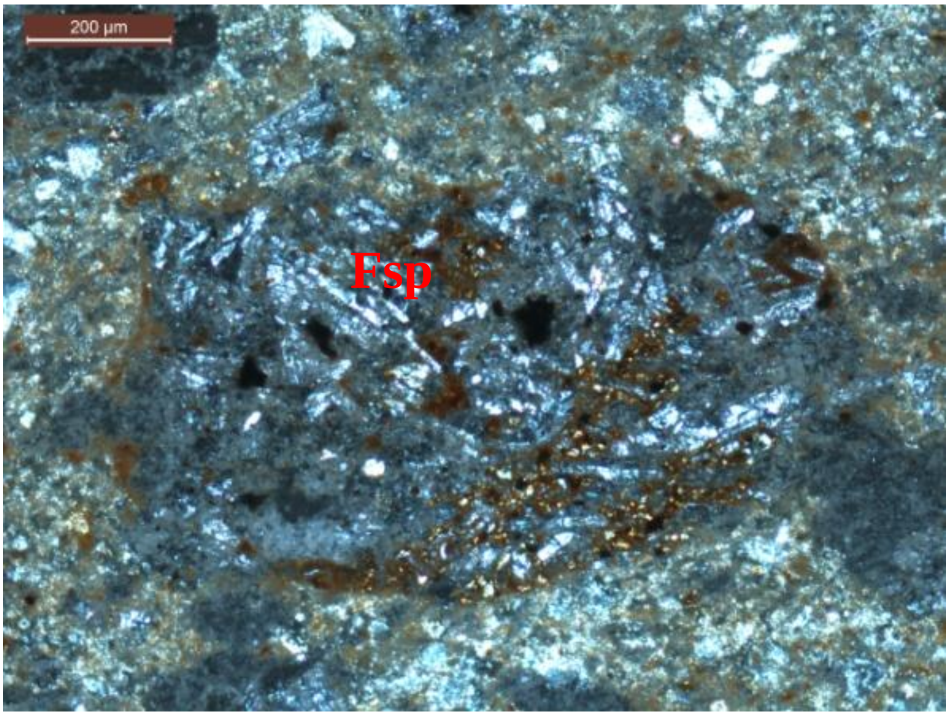


Figure 3. 4. Photomicrograph of feldspar (Fsp) grains in igneous rock fragment, Sample E1, Chalcolithic Age (Ubaid)

Feldspar group minerals fall into two different groups (Plagioclases and K-feldspars) due to the compositional change in three end members; Albite ($NaAlSi_3O_8$), anorthite ($CaAl_2Si_2O_8$) and K feldspars ($KAlSi_3O_8$)

However, these two different types of feldspar minerals are separately detected during thin section analysis and with XRD. Plagioclase series (calcium sodium feldspars) have compositions between albite and anorthite, and having triclinic crystal system. Next, polysynthetic twinning is a characteristic of plagioclase minerals. These minerals are widely detected during thin section analysis of Chalcolithic Age (Sample No: 156, 157, 176, 209, 210, E2, E3, N1, N2, S1, S2, N2, N1), and Iron Age samples (Sample No: 187, 223, 230, 231, 233, 235, 237, 238, 248, 249) (Figure 3.5). On the other hand, the presence of plagioclase minerals were confirmed by their two most intense XRD peaks at 3.19 and 4.03 Å in their XRD traces of samples 151 of Early Bronze Age I and 210, E1, N3 and S1 of Chalcolithic

Age and 230, 246, 248 of Iron Age samples (See Appendices B1, B2, B3, B4, B5, B6, B7, B8, B9).

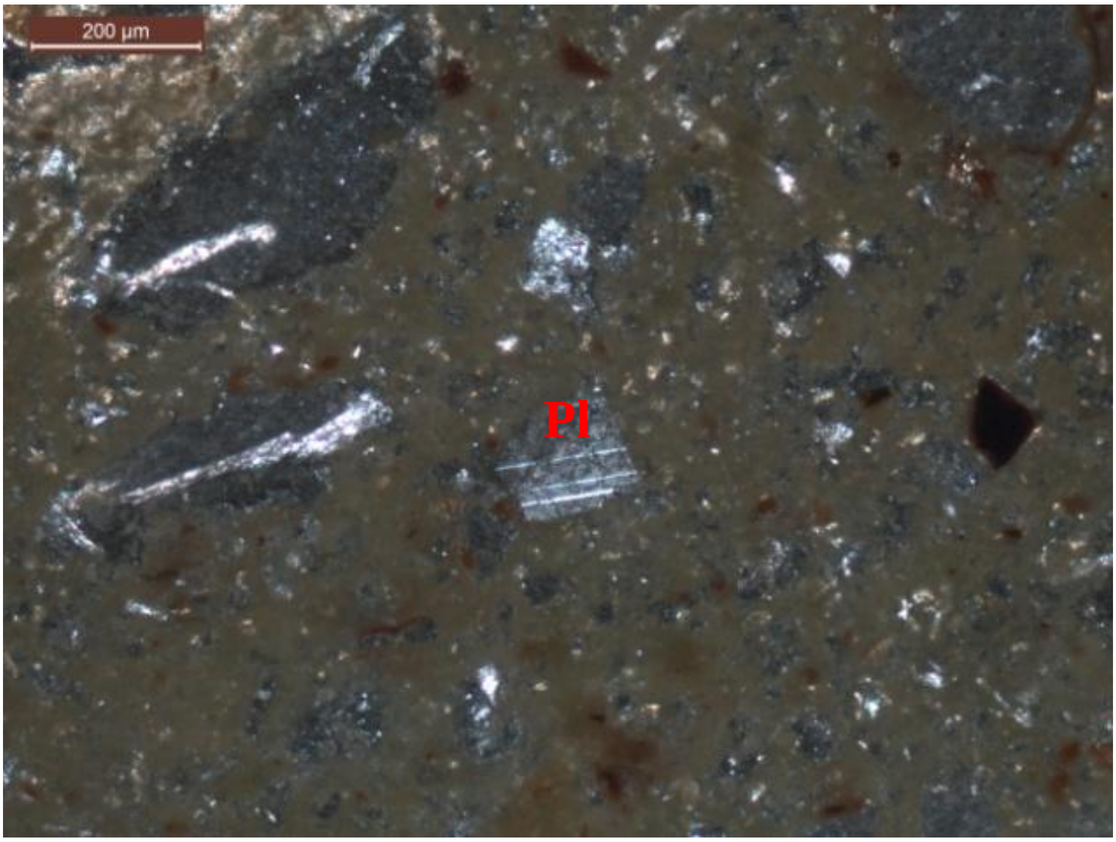


Figure 3. 5. Photomicrograph of plagioclase (Pl) grain presenting polysynthetic twinning, Sample 249 of Iron Age

Alkali Feldspars series include compositions between K – feldspars and albite. Alkali feldspars are microcline, orthoclase, sanide and anorthoclase minerals, have different features such as crystal system and optical properties. While, microcline has triclinic – pinacodial crystals system and has characteristic polysynthetic crosshatched twinning, orthoclase has monoclinic – prismatic crystal system and shows complex twinning. Sanidine has monoclinic – prismatic crystal sytem and shows Carlsbad twins with a compositional plane parallel to (010) divide crystals into two segments. Anorthoclase has monoclinic – prismatic crystal system and shows zoning and polysynthetic crosshatched twinning similar to microcline (Pichler and Schmitt – Riegraf, 1997). Alkali feldspars were detected in Iron Age samples (Sample No: 233, 235, 246) and Chalcolithic Age samples (Sample No: N1, S5 and S7) in thin section analyses, but not distinguished into mineral types.

Pyroxene group minerals: are chain silicates (inosilicates) constructed of single chains of silicon tetrahedra that extend parallel to c – axis. Their main formula is $XYSi_2O_6$ (X and Y are cations).

Pyroxene group minerals are mainly formed in igneous and metamorphic rocks. Those minerals were observed in thin sections of almost all of the samples of Chalcolithic Age (Sample No: 157, 160, 165, 176, 209, E3, N2, N3, S3, S6), and Iron Age (Sample No: 187, 189, 210, 228, 230, 231, 235, 237, 239, 246, 249). Orthopyroxene minerals were distinguished from clinopyroxenes during thin section analyses with their lower birefringence, parallel extinction and the common pale pink to green plaeochroism (Nesse, 2004). Pigeonite which is a clinopyroxene group mineral is seen in thin sections with colorless, pale brownish green, or pale yellowish green and it is not pleochroic. Augite from same group is also not paleochroic and is usually colorless, pale green, pale brown or brownish green in thin sections.

Unclassified orthopyroxene mineral was detected in also a thin section of Iron Age sample (Sample No 237). However, diopside which is a clinopyroxene detected in thin section of Iron Age sample (Sample No: 235

Monoclinic Pyroxene was detected in just one Chalcolithic Age sample (Sample No: N2).

In addition to that, XRD traces revealed the congregated d-spacings between 2.86 and 2.98 Å, possibly belonging to pyroxene group minerals (except samples of S4 and N3) (Figure 3.6).

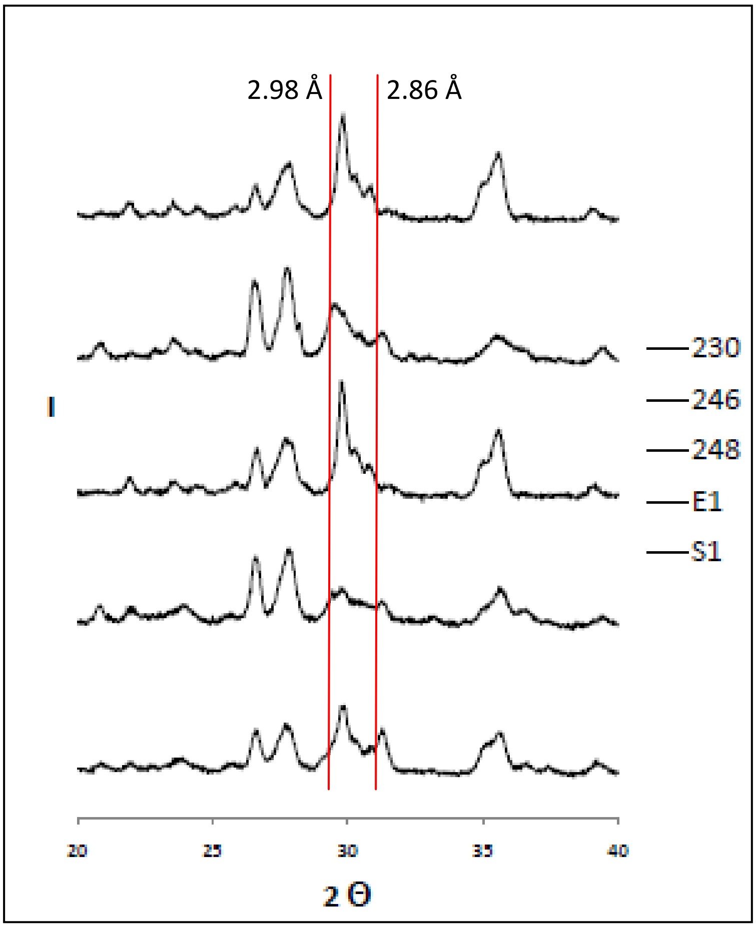


Figure 3. 6. XRD traces of samples 230, 246, 248 of Iron Age (three spectra at the top, respectively) and E1, S1 of Chalcolithic Age (last two spectra at the bottom); red lines showing the range of d – spacing between 2.86 and 2.98 Å.

Hematite:, (Fe_2O_3) is a fully oxidized form of iron oxide. It has hexagonal crystal system and a red or reddish brown color in thin sections. It was identified in all the samples of Chalcolithic Age (except samples N3 and S4) and Iron Age in thin section analyses (Figures 3.7). Samples N3 and S4 have grayish and dark colors, which can be explained by a reducing atmosphere during firing (Rice, 1987).

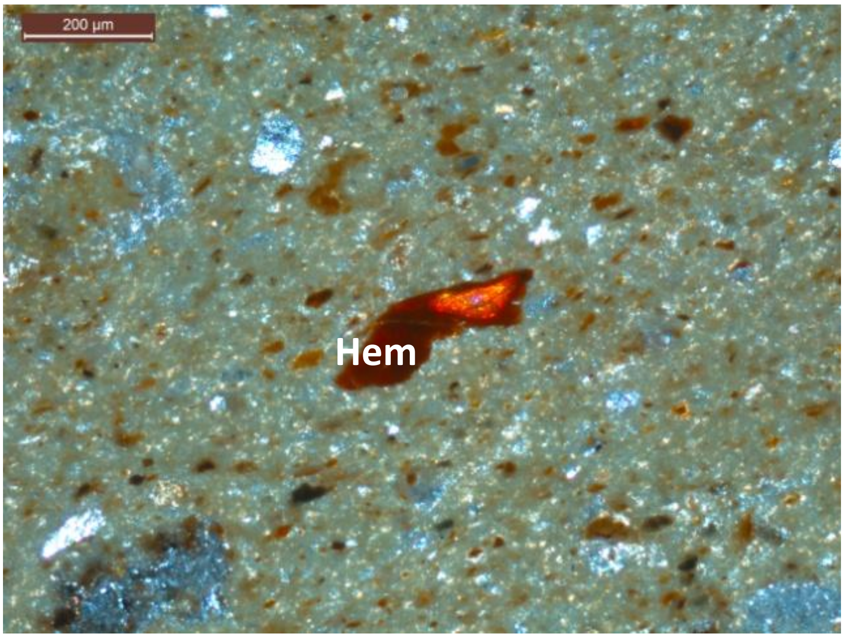


Figure 3. 7. Photomicrograph of hematite grains (Hem), Sample 230, Iron Age

Mica minerals: belong to phyllosilicate group (sheet silicates) and all have a monoclinic crystal system. Micas are divided into two subgroups due to the occupation of octahedral lattice spaces by cations (Pichler and Schmitt – Riegraf, 1997). In white micas (muscovite, phengite, paragonite,and glauconite), which are dioctahedral sheet silicates, two or three octahedral lattice spaces are occupied with trivalent cations. In all other micas (dark micas) such as biotite series, trioctahedral sheet silicates have three octahedral positions occupied by bivalent cations.

Mica group minerals both white and black micas were identified with their perfect basal cleavage in most Iron Age samples (Sample No: 189, 235, 237, 238, 239, 244 and 246) and some of Chalcolithic Age samples (Sample No: 160, S1 and S4) in thin section analyses. Biotite was also mostly identified with its strong paleochroic characteristic and brown, yellow – brown, red – brown, olive – green or green colors in thin sections of Iron Age samples (Sample No: 224, 231, 235, 237, 238, 239 and 246) and of several Chalcolithic Age samples (Sample No: 205, E2).

Mica group mineral, possibly muscovite was detected in two samples belonging to Chalcolithic (Sample No: N3) and Early Bronze Age (Sample No: 151).

On the other hand, a grain showing the typical grain flaky shape of mica type minerals observed with SEM in Iron Age sample 246; is identified as mica (Figure 3.8 and 3.9).

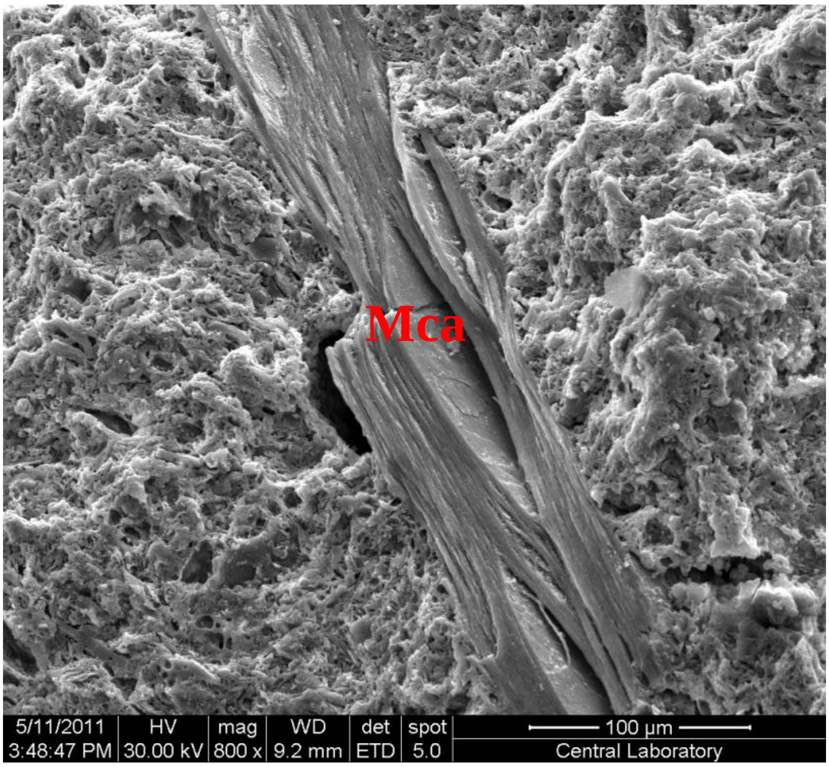
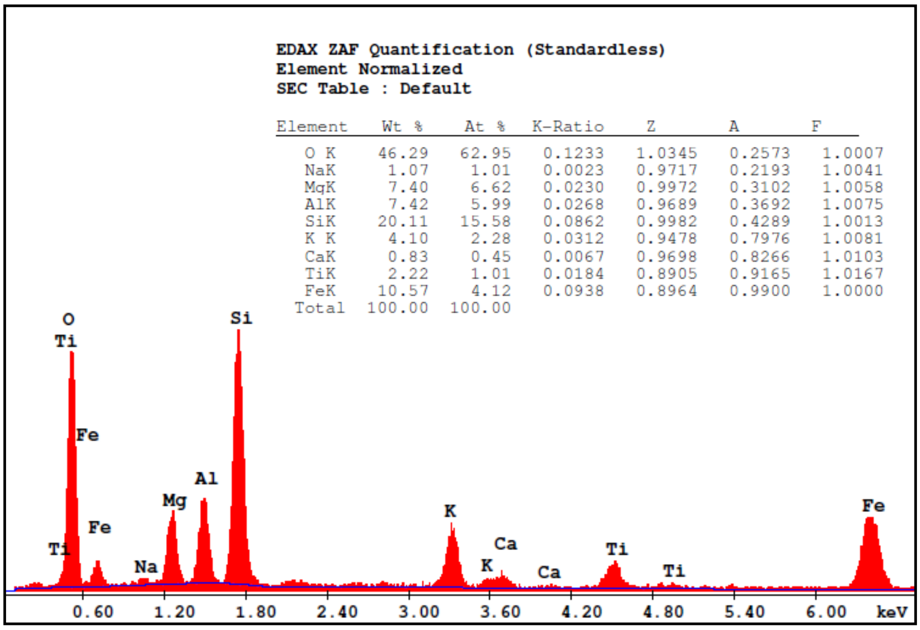


Figure 3. 8. SEM micrograph of mica grain (Mca), Sample 246, Iron Age



Element	Wt %	At %	K-Ratio	Z	A	F
O K	46.29	62.95	0.1233	1.0345	0.2573	1.0007
NaK	1.07	1.01	0.0023	0.9717	0.2193	1.0041
MgK	7.40	6.62	0.0230	0.9972	0.3102	1.0058
AlK	7.42	5.99	0.0268	0.9689	0.3692	1.0075
SiK	20.11	15.58	0.0862	0.9982	0.4289	1.0013
K K	4.10	2.28	0.0312	0.9478	0.7976	1.0081
CaK	0.83	0.45	0.0067	0.9698	0.8266	1.0103
TiK	2.22	1.01	0.0184	0.8905	0.9165	1.0167
FeK	10.57	4.12	0.0938	0.8964	0.9900	1.0000
Total	100.00	100.00				

Figure 3. 9. Semi quantitative chemical analysis of mica grain in Figure 3.8 with EDX anaylsis

<u>Hornblende</u> has monoclinic crystal system and is a series of minerals (ferromagnesians) in the amphibole group. The shape of green hornblende is short to long fibrous shape and color is always strong green but can vary between greenish – yellow and bluish – green. Its cleavage is perfect on [110] with cleavage intersection angles of 124˚ and 56˚. Extinction is oblique but basal sections show symmetric extinction. The extinction angle is 14˚ - 22˚. Brown hornblende is called oxyhornblende and it has euhedral to subhedral crystals short to long prismatic habit. It has perfect cleavage on [110]. Color changes strong brown to reddish brown and having strong paleochroism (Pichler and Schmitt – Riegraf, 1997).

Hornblende crystals were detected in several Iron Age samples (Sample No: 189, 224, 238, 239), and Chalcolithic Age samples (209, E1, E3, N1 and N2) in thin section analyses with its optical properties mentioned above.

Olivine: is a magnesium iron silicate; has orthorhombic – dipyramidal crystal structure. Olivine group minerals mostly have a composition in complete solid solution has end members between forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). Even though optical characteristics of olivine strongly depend on its composition, it can be distinguish by its high birefringence, distinctive fracturing, lack of cleavage and its alteration products. Its color is usually colorless to pale yellow in thin sections but darker colors correspond to higher iron content.

Olivine grain was detected only in a thin section of Iron Age sample (Sample No 223).

Mullite: is an alumina silicate mineral. Its natural form is rare, occurring on the Isle of Mull close to the west coast of Scotland (William E. Lee, W.Mark Rainforth, 1994). It can synthetically form in two stoichiometric forms: primary mullite, $2Al_2O_3.SiO_2$, or secondary mullite $3Al_2O_3.2SiO_2$. They form at different temperature ranges (950 – 1000, 1050 – 1150°C respectively) and have different formation mechanisms during the firing of the clay. Crystalline structure of mullite is given in Figure 3.10.

Crystalline structure of mullite can be identified by two characteristic d-spacings at 3.40 and 5.39 Å. In addition, if it is a well crystallized mullite, two split lines at 3.38 and 3.41 Å can also be observed (Chakraborty and Ghosh, 1978).

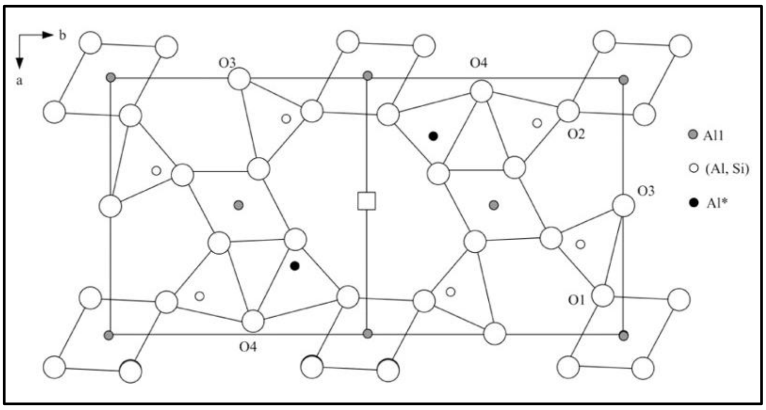


Figure 3. 10. Orthorhombic crystal structure of mullite, projected in the (001) plane (Chuin-Shan Chen et. al, 2010)

In this study, 3.40 and 5.39 Å d - lines belonging to mullite formation are observed in XRD analysis of 5 samples belonging to Chalcolithic Age (S1, 210) and Iron Age (Samples No: 230, 246, and 248) (Appendices B). Although the two split lines expected at 3.38 and 3.41 Å are not observed in their spectra (Figure 3.11), it has been already reported that those lines may be merged when mullite is newly formed at high temperatures which make their identification difficult (Chakraborty and Ghosh, 1978).

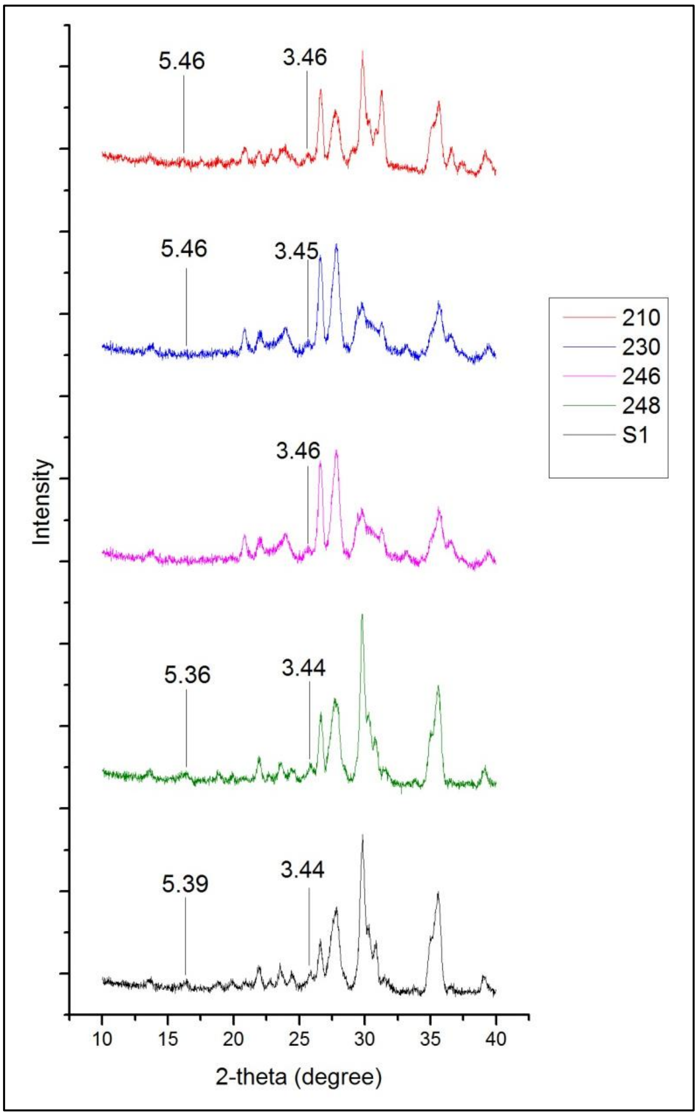


Figure 3. 11. XRD traces of samples S1, 210 (Chalcolithic Age), 230, 246, 248 (Iron Age) indicating the presence of mullite

Supporting these XRD observations, mullite crystals with a distinct needle like shape were also clearly detected in SEM analyses of sample S1 (Figure 3.12). The result of micro-chemical investigations on those crystals indicating the presence of calcium, magnesium, and iron contents, do not support the expectations for the typical stoichiometric 3:2 aluminum-silicon ratios which is not unexpected situation (Figure 3.13). This contradiction was already stated in a previous study with a probable cause of the overlapping of the glass and crystal phases (W.E. Lee, et. al, 2008).

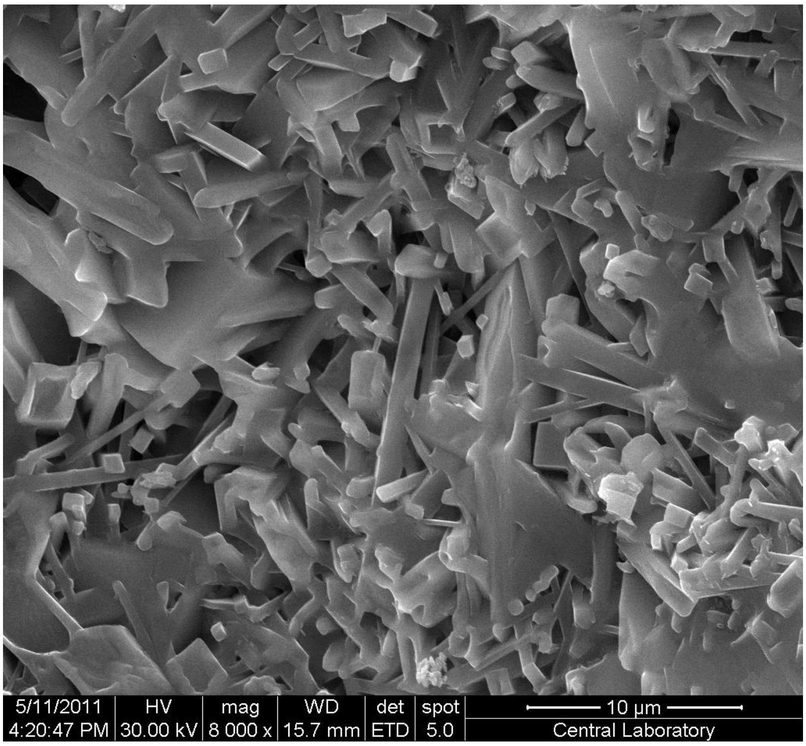


Figure 3. 12. Needle like mullite crystals in glassy matrix in Sample S1 (Chalcolithic Age)

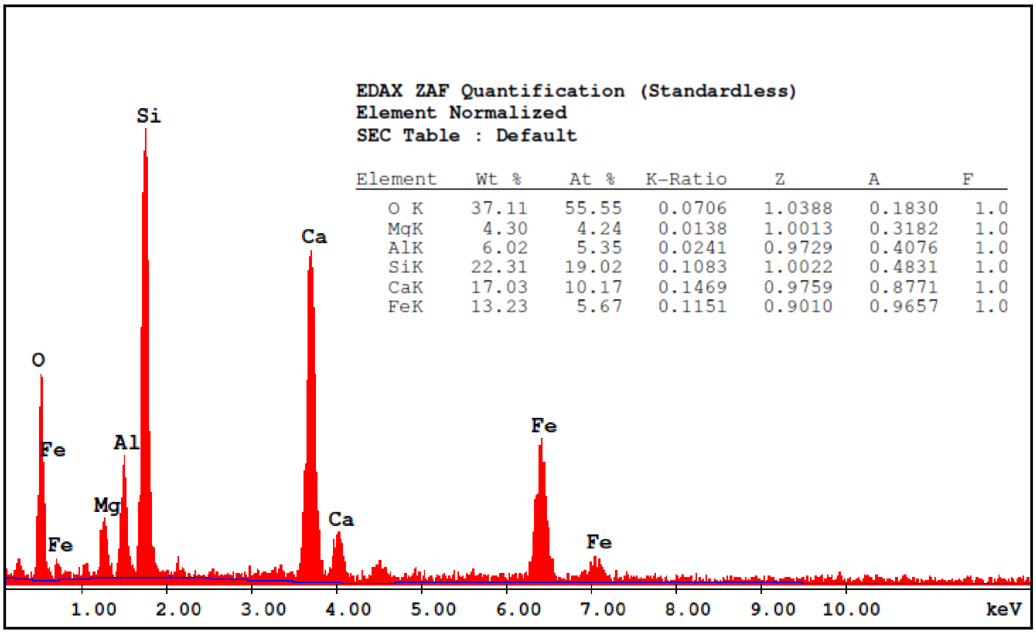


Figure 3. 13. EDX analysis of mullite crystals in Figure 3.12, Sample S1 (Chalcolithic Age)

The identification of mullite in mineralogical and micro-structural analyses of pottery samples provides valuable information for the estimation of firing temperatures. The presence of mullite crystals, especially in Chalcolithic Age samples indicates that they might have been fired at temperatures above 1050˚C (Grim, 1968, Table 3.7; Tite and Maniatis, 1975).

Table 3. 7. Initial temperatures for the formation of mineral phases from clay minerals at high temperatures after Grim, 1968, M –Kln=Meta Kaoline, Kln= Kaoline, Sme= Smectite, Ill= Illite, Chl=Chlorite, All=Allophane, Ol= Olivine, Spl=Spinel, Crs=Cristobalite, Mul=Mullite, β-q=β-quartz, α- q=α- quartz, An=Anorthite, En=Enstatite, Per=Periclase, Crd=Cordierite.

Clay mineral Group	600˚C	850˚C	900˚C	950˚C	1000˚C	1100˚C	1200˚C	1250 - 1300 ˚C
Kln	M-Kln			Spl	Mul			Crs
Sme			Spl		β-q	β-q	Crd	Per
					Crs			
					α- q			
					Mul			
					An			
					En			
Ill			Spl			Mul		
Chl		Ol				En		
		Spl						
All			Crs					

<u>Clay Minerals:</u>

Bulk samples of two potteries belonging to Chalcolithic Age (N3, S4) and one pottery sample belonging to Early Bronze Age (Sample No: 151), revealed diffraction lines at d values of 14 – 8 Å proposing a possible presence of some clay fragments in their structure (Figure 3.14). For that reason, oriented clay fractions of those pottery samples were prepared as described in Section 2.5) and again analyzed by XRD for further investigations. However, all the XRD traces revealed totally amorphous structures which indicate minimum firing temperatures in the range of 800 – 850˚C. This observation has already been stated by Türkmenoğlu (Türkmenoğlu, 1989) in a previous study. Therefore the lines observed in bulk samples of N3, S4 and 151 may be attributed to the presence of mica minerals.

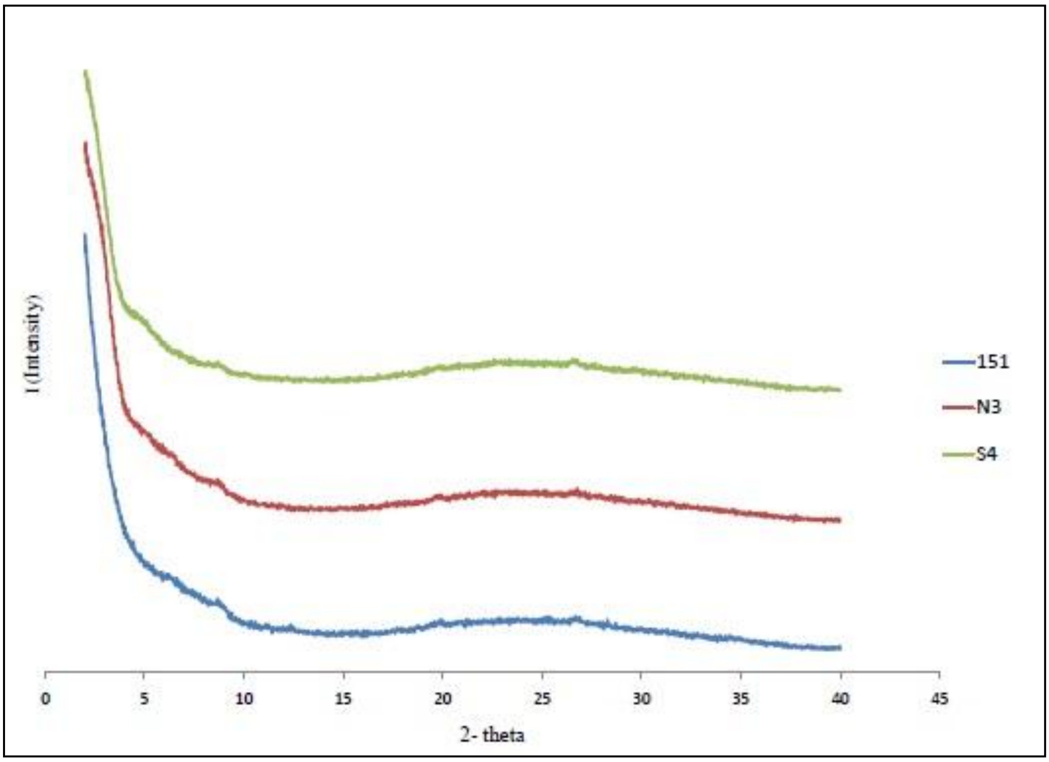


Figure 3. 14. XRD traces belonging to Samples 151, N3 and S4, after clay fraction separations showing their amorphous structure

3.2.2. Rock Fragments

Fragments of metamorphic, volcanic, and sedimentary rocks were identified in thin section analyses of all samples (Table 3.8). Their presence and identification may help to determine possible provenance of pottery samples.

Schist, polycrystalline quartz, and phyllite fragments, which are metamorphic rock fragments, were observed under polarized microscope.

Igneous rocks were identified in thin section analyses. The fragments of igneous rock are mostly of volcanic (extrusive igneous) origin, but some intrusive igneous rock fragments were also observed.

Limestone and chert fragments were encountered in thin section analysis. The observation of limestone fragments is notable for its calcium carbonate content which decomposes in the 650 – 900 ˚C temperature range (Rice, 1987).

Table 3. 8. Types of rock fragments identified in thin section analyses.

Rock Class	**Rock Type**	**Sample No and Age**	
		Chalcolithic Age	**Iron Age**
Metamorphic	Schist	S4, S5	244
	Polycrystalline quartz	160, 165, 176, 210, N3	
	Phyllite	205	
	Unclassified	157, 160, 165, 177, 187, 189, 205, 209, 210, E3, N1, N3, S4, S5	223, 224, 230, 231, 233, 235, 237, 238, 244, 246, 249
Igneous	Intrusive igneous	189, E1	
	Volcanic igneous	189, 156, 157, 165, 176, 177, 210 , E1, N1, N2, S1, S2	223, 224, 228, 231, 235, 237, 238, 239
	Unclassified	209, E3, S7	
Sedimentary	Chert	165	231
	Limestone	156, 160, 205, N3, S5	233

3.2.3. Texture

The texture, porosity, degree of vitrification and the types of cement material were the main parameters which were also determined by thin section analysis. The degree of vitrification, an important indicator for estimating the firing temperature, was visually determined under polarizing microscope and SEM. 9 of 41 samples; of Chalcolithic age (Sample No: 160, 176, 210, N3, S1), and Iron Age (Sample No: 228, 230 239, 244) were characterized as having well vitrified bodies regarding their fine texture and glassy matrix (Figure 3.15 and 3.16). These vitrified samples have greenish color and low grain/ matrix ratios. The scanning electron microscopy provides higher magnifications (up to X10000) and the opportunity to examine the morphology even at the nanometer scale. According to Tite and Maniatis (1975), the degree of vitrification can be determined by the formation of a network of glassy phase and isolated pores or absence of flaky clay particles in the ceramic matrix. Considering these parameters, 9 samples (Sample No: 160, 176, 210, N3, S1 of Chalcolithic Age and 228, 230, 239, 244 of Iron Age) have well vitrified body/ matrix and small grain size characteristics when compared to the rest. The developments of glassy phases and glass networks which surrounded the boundaries of mineral grains were clearly observed in SEM analysis (Figure 3.17).

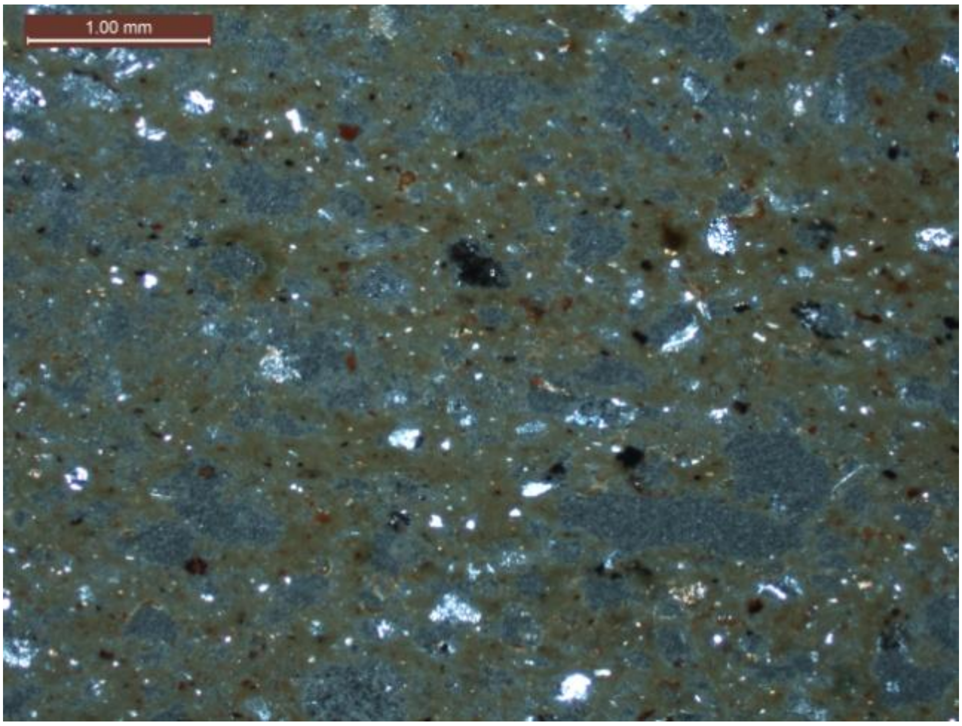


Figure 3. 15. Photomicrograph of well vitrified body, Sample 210 (Chalcolithic Age)

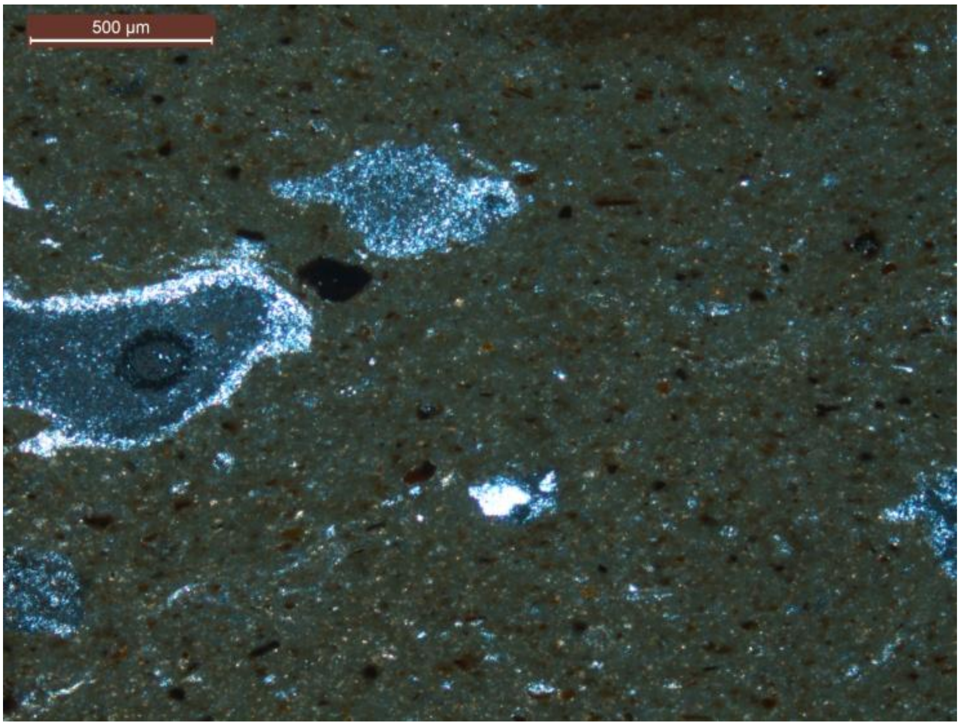


Figure 3. 16. Photomicrograph of well vitrified body, Sample 230 (Iron Age)

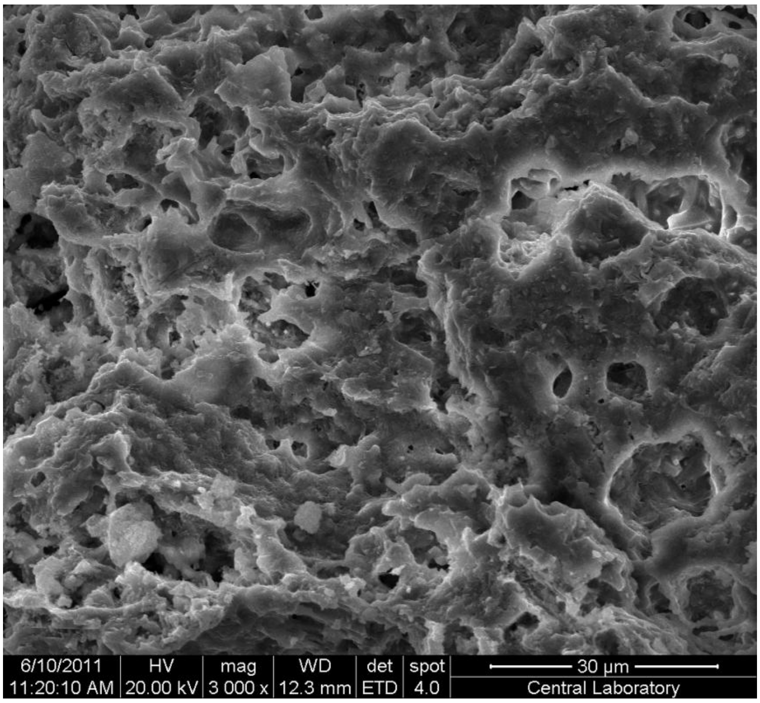


Figure 3. 17. SEM micrograph of vitrified body, Sample 210 (Chalcolithic Age)

Considering the matrix color; samples display wide range of colors under cross-polarized light, changing from mostly reddish brown to greenish – beige and occasionally darker colors. A reddish color indicates the use of oxidizing atmosphere due to the formation of ferric oxide (Fe^{3+}) during firing, while a darker color indicates the application of a reducing atmosphere or insufficient air circulation and the presence of ferrous oxide (Fe^{2+}) (Rice, 1987). Considering these facts, samples N3, S1, S4 and S7 of Chalcolithic Age with dark colors were probably fired under the reducing atmosphere conditions, while most of the samples have reddish color indicating the use of oxidizing atmosphere.

Distributions of non-plastic grains (mineral grains and rock fragments) in the studied samples were investigated by examining the thin sections with optical and stereo microscopes. These investigations suggest that the rock fragments consist of larger particle sizes which change from coarse to fine sand sizes (1.00 to 0.1 mm). On the other hand, sizes of mineral grains are found to have very fine sand sizes (0.5-0.1 mm) (Figure 3.18 and 3.19). Based on these observations, it can be said that Chalcolithic Ubaid samples have larger grain sizes and a higher grain/ matrix ratio than those of Iron Age. That may indicate the use of different raw material sources or a different method of raw material processing for the elimination of courser particles during ceramic production in Iron Age.

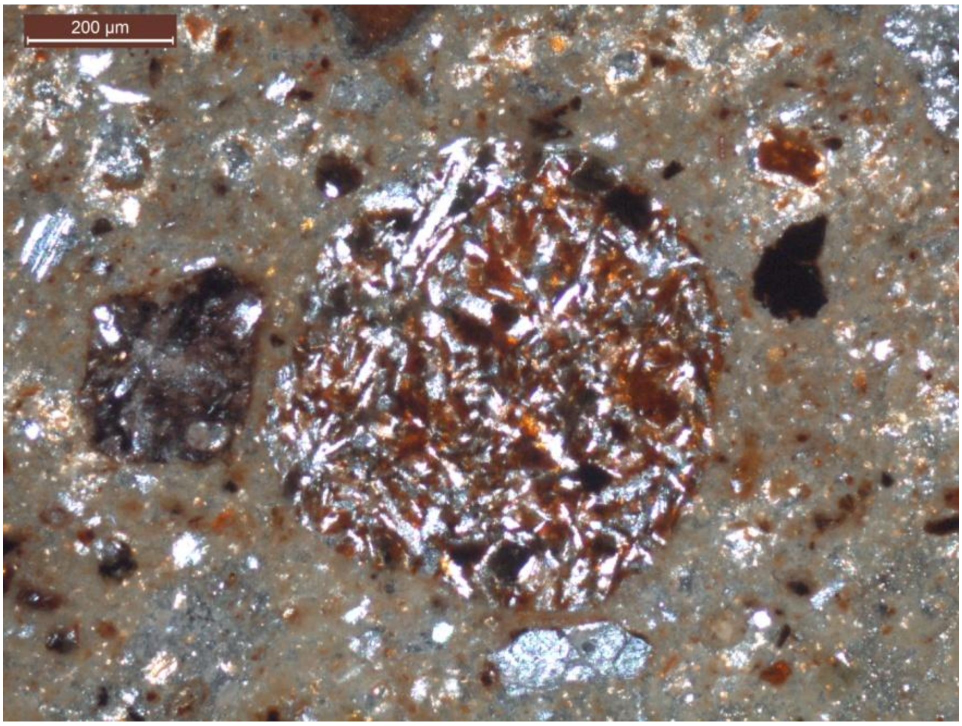


Figure 3. 18. Photomicrograph of grain distribution in the matrix of Sample 210 (Chalcolithic Age)

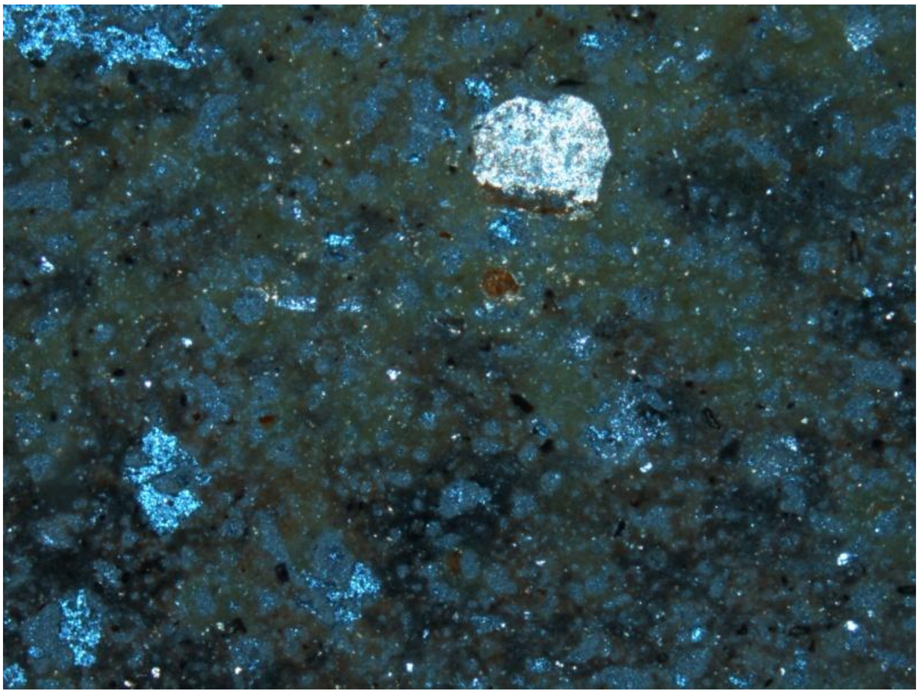


Figure 3. 19. Photomicrograph of grain distribution in the matrix of Sample 248 (Iron Age)

As far as pore size and pore size distribution are concerned, there is a significant difference in the pore size of the investigated samples. In some of the samples (Figure 3.20 and 3.21), the pore size is as large as 2 mm. while some others (Figures 3.22 and 3.23) have very dense body.

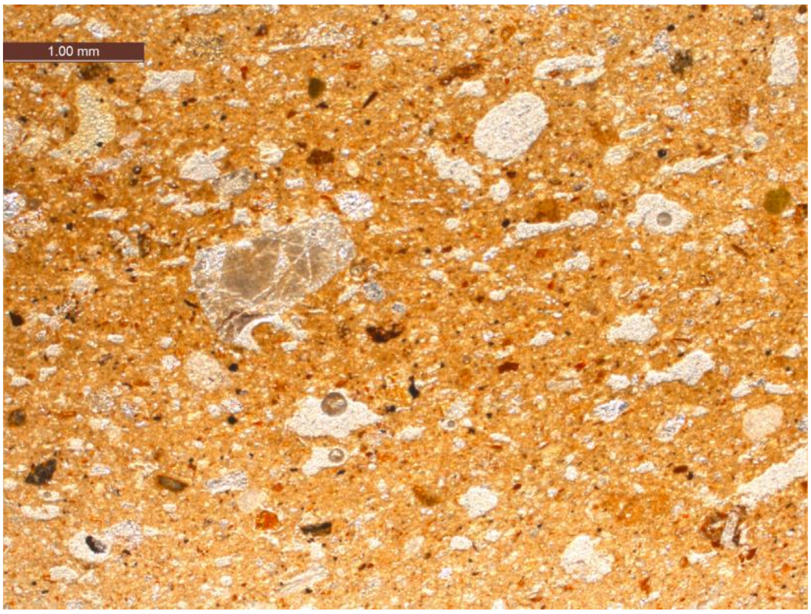


Figure 3. 20. Stereo microscope image of Sample 157 (Chalcolithic Age)

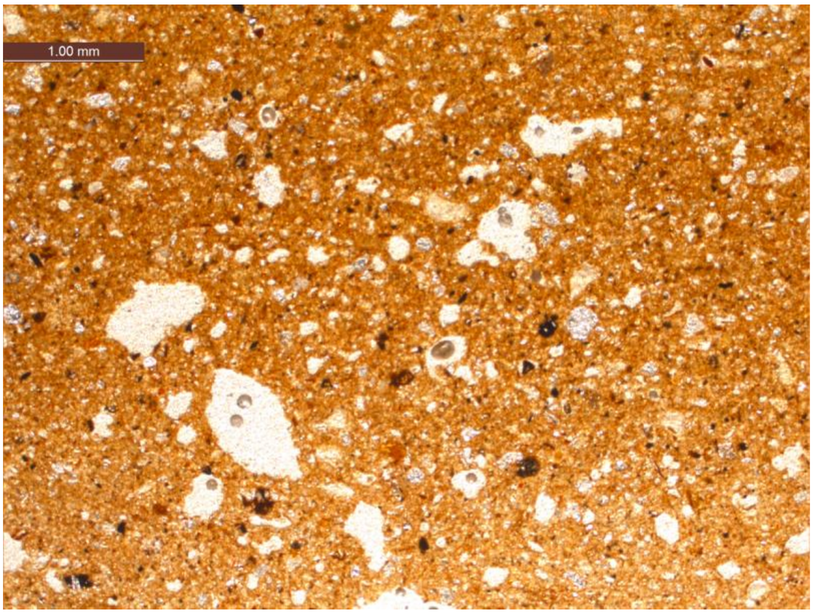


Figure 3. 21. Stereo microscope image of Sample S6 (Chalcolithic Age)

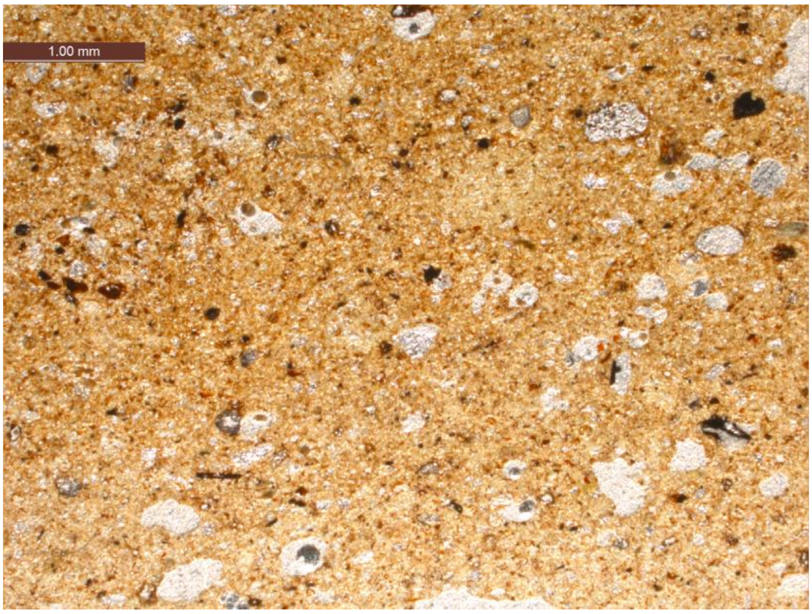


Figure 3. 22. Stereo microscope image of Sample 228 (Iron Age)

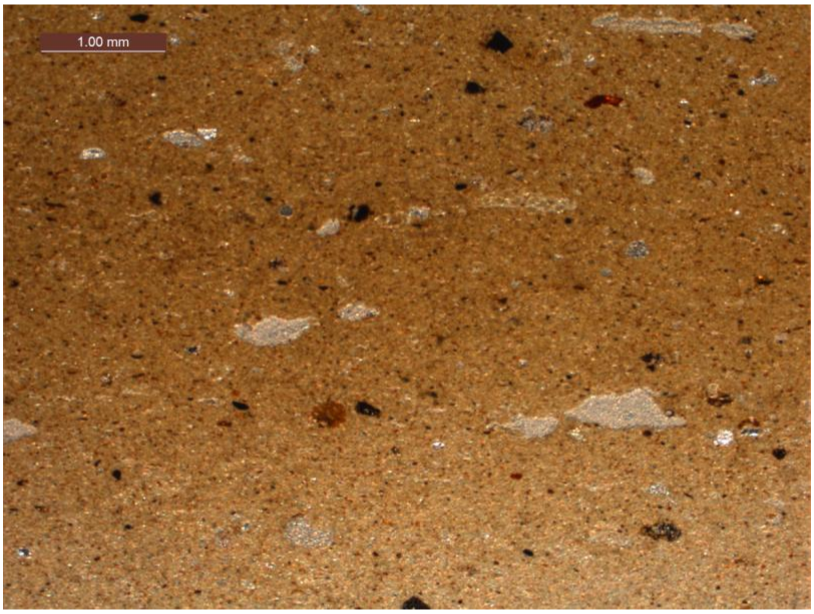


Figure 3. 23. Stereo microscope image of Sample 228 (Iron Age)

It can be noted that Iron Age samples have more compact and amorphous bodies when compared to those of Chalcolithic Age samples. Studies at higher magnifications with scanning electron microscope (X5000 – X8000) revealed the presence of spherical pores in Chalcolithic Age samples which are very similar to those seen in Iron Age samples (Figure 3.24). These spherical pores were probably developed because of the compaction of the ceramic body during firing.

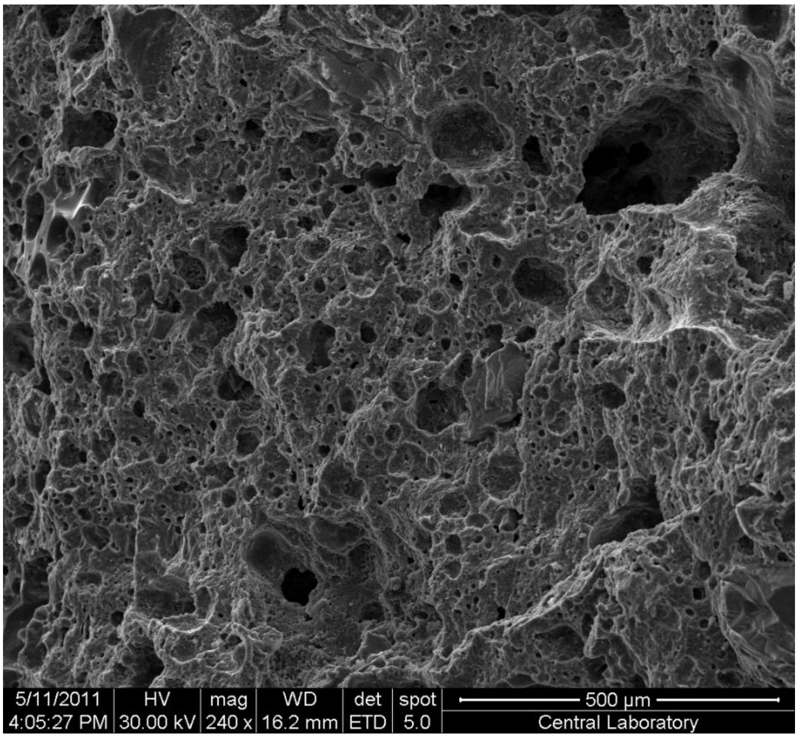


Figure 3. 24. SEM micrograph of spherical pores, Sample S1 (Chalcolithic Age)

Some elongated pores were also identified in Chalcolithic sample N3, which can be easily distinguished from others (Figure 3.25).

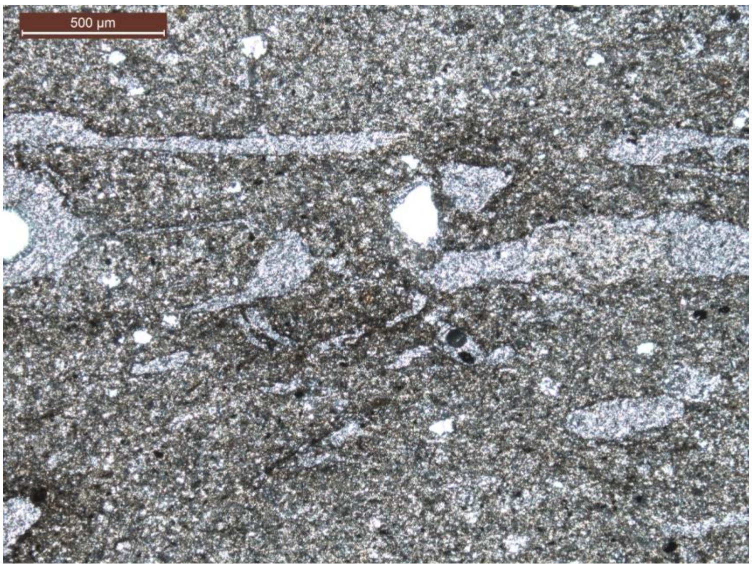
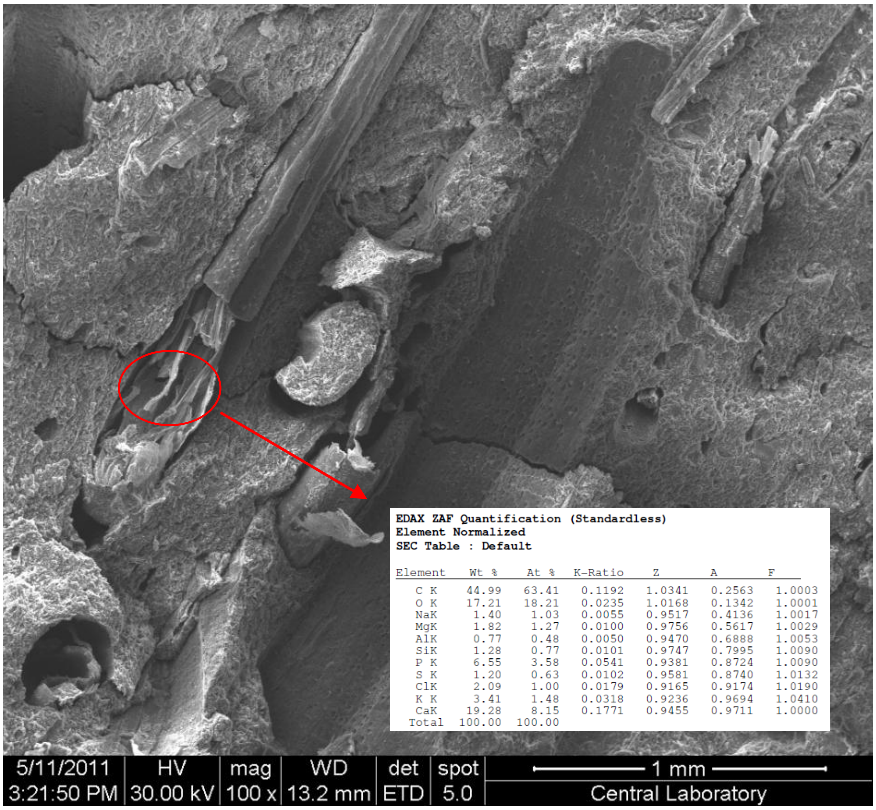


Figure 3. 25. Photomicrograph of elongated pores, Sample N3 (Chalcolithic Age)

The existence of elongated pores in N3 of Chalcolithic Age indicates the possible presence of chaff as an additive. The EDX analyses of these additives indicate the presence of phosphorus (P) and chlorine (Cl) that confirms the results of morphological investigations of these pores and plant traces (Figure 3.26). similar observation were recorded for some other samples such as sample 248 of Iron Age (Figure 3.27).



Element	Wt %	At %	K-Ratio	Z	A	F
C K	44.99	63.41	0.1192	1.0341	0.2563	1.0003
O K	17.21	18.21	0.0235	1.0168	0.1342	1.0001
NaK	1.40	1.03	0.0055	0.9517	0.4136	1.0017
MgK	1.82	1.27	0.0100	0.9756	0.5617	1.0029
AlK	0.77	0.48	0.0050	0.9470	0.6888	1.0053
SiK	1.28	0.77	0.0101	0.9747	0.7995	1.0090
P K	6.55	3.58	0.0541	0.9381	0.8724	1.0090
S K	1.20	0.63	0.0102	0.9581	0.8740	1.0132
ClK	2.09	1.00	0.0179	0.9165	0.9174	1.0190
K K	3.41	1.48	0.0318	0.9236	0.9694	1.0410
CaK	19.28	8.15	0.1771	0.9455	0.9711	1.0000
Total	100.00	100.00				

Figure 3. 26. SEM micrograph and EDX analysis of chaff is a possible organic additive in Sample N3 (Chalcolithic Age)

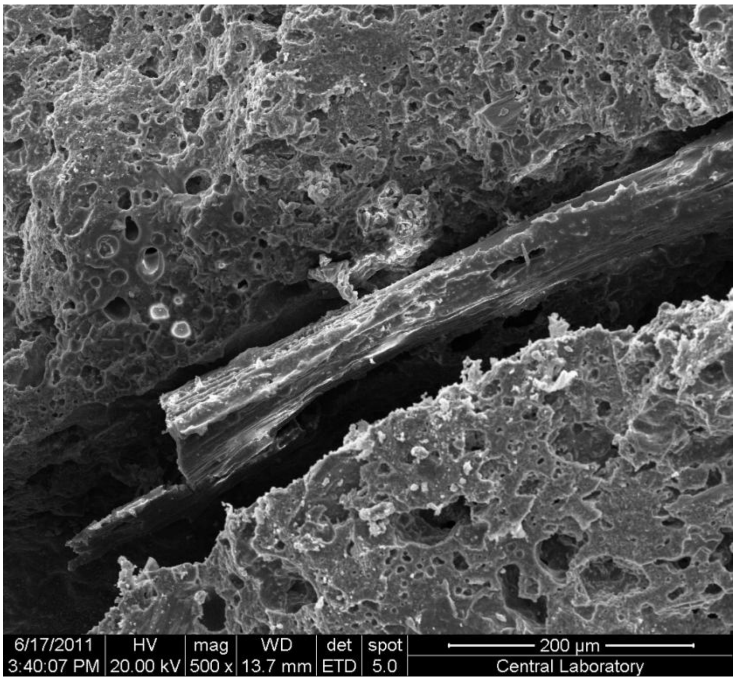


Figure 3. 27. SEM micrograph of chaff in Sample 248 (Iron Age)

Calcite was observed in samples of Chalcolithic Age (Sample Code: 157, 165, 177, 205, 209, E2, E3, N2, S1, S3, S4) and, Iron Age (Sample Code: 224, 233, 237, 246) during thin section analyses and also confirmed with SEM investigations. These occurrences observed on the pore walls in the form of pore linings are interpreted as micritic (secondary) calcite and are believed to arise from the deposition during burial conditions (Velde and Druc, 1998). This conclusion mainly depends on the small crystal shapes cumulated on the surface of the pottery (Figures 3.28 and 3.29), related EDX analysis given in Figure 3.30 and also minimum firing temperature (> 800 ˚C) ensued in Section 3.2.1.

Unfortunately, nothing much could be said about Early Bronze Age period as there were only two samples available for reliable comments.

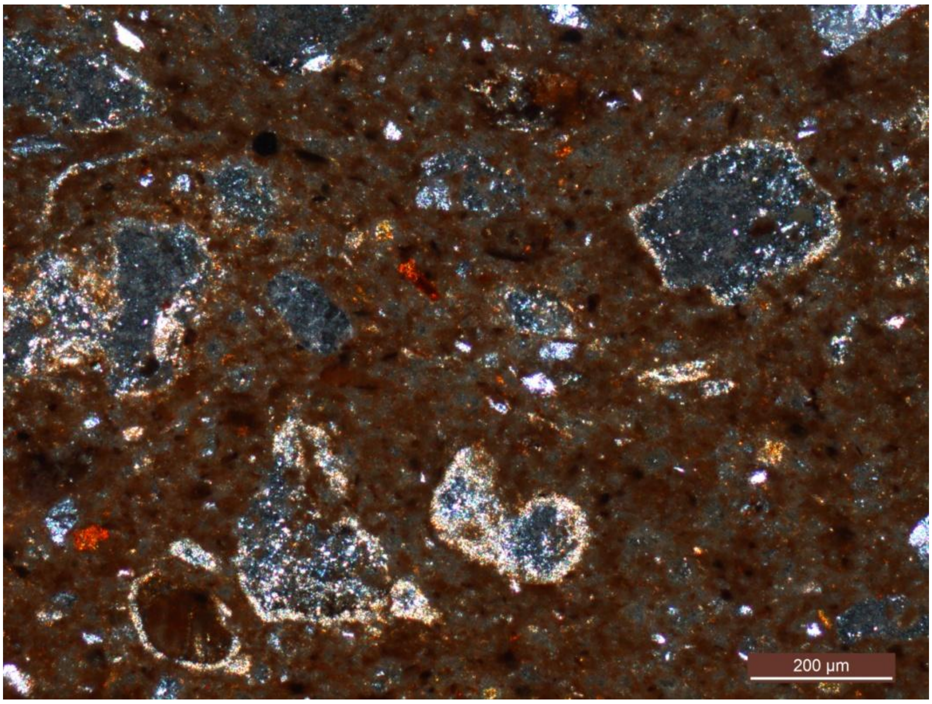


Figure 3. 28. Photomicrograph of secondary calcite formation, Sample 246 (Iron Age)

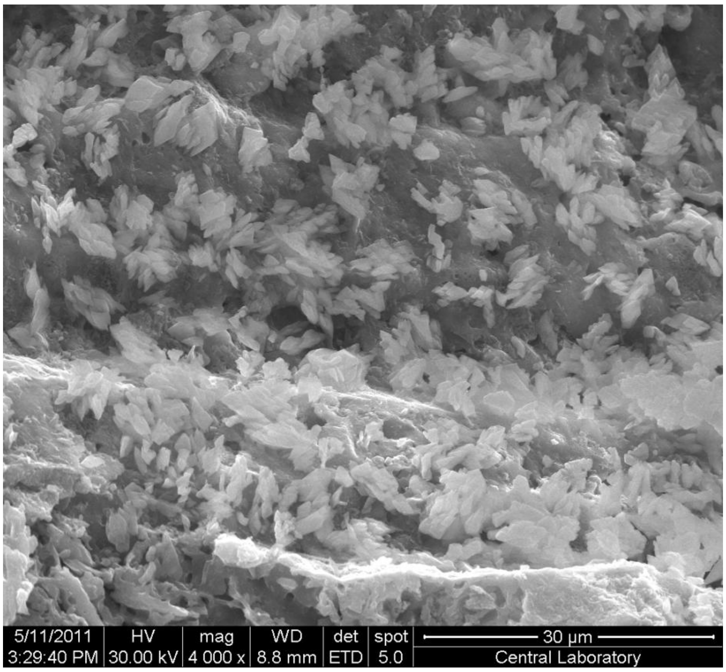


Figure 3. 29. SEM micrograph of micritic calcite formation, Sample 246 (Iron Age)

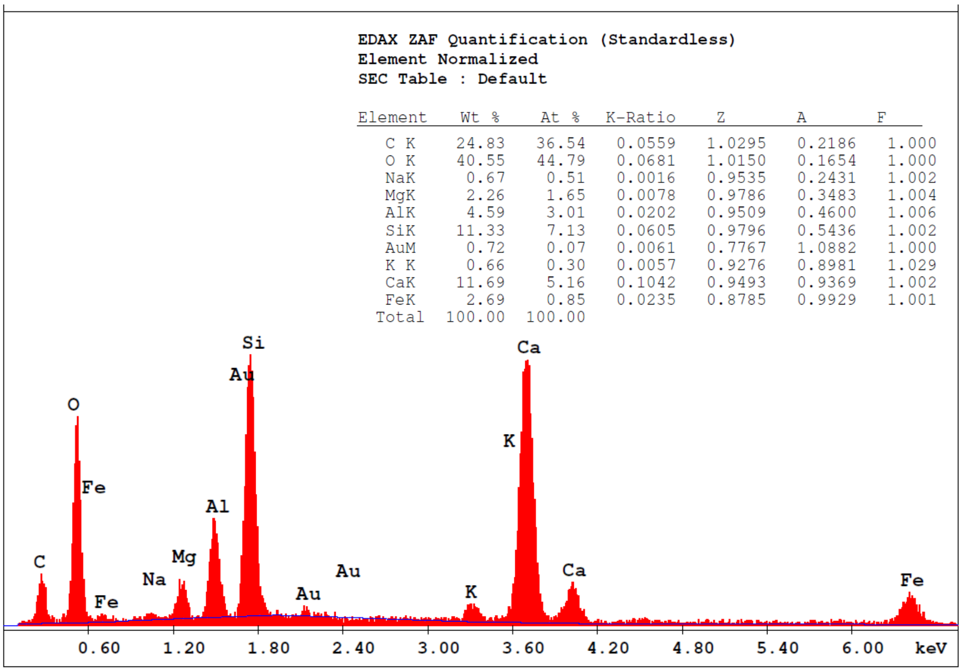


Figure 3. 30. EDX analysis of micritic calcite formation in Sample 246 (Iron Age)

3.3.Chemical Analysis

Sample No.: E1, E2, N3, S1, S4, 205, 210 belonging to Chalcolithic Age and Sample No.: 230, 246, 248 of the Iron Age were analyzed by ICP-OES for their Si, Al, Ca, Mg, Fe, Na, K, Ti, Mn and P contents at the Central Laboratory of METU. The results obtained are given in their oxide forms (in weight percent) together with their ages, year of excavations and trench descriptions in Table 3.9.

Table 3. 9. Chemical compositions of the major oxides of pottery samples in weight percent.

Sample Code	E1	E2	N3	S1	S4	205	210	230	246
Age	Chal.	Chal.	Chal.	Chal.	Chal.	Chal.	Chal.	Iron	Iron
Year of Excavation	1986	1986	1985	1977	1977	1984	1984	1984	1984
Trench	13-14j	17E	12j	Survey	Survey	17i	16j	16I	16I
SiO_2	41.50	36.79	46.63	45.77	53.9	45.99	45.56	42.14	43.42
Al_2O_3	9.96	8.12	14.6	12.47	17.23	11.24	10.98	11.9	14.85
CaO	14.27	17.21	5.04	14.97	1.18	12.09	15.39	16.23	11.36
MgO	4.56	5.5	4.19	5.59	1.08	4.63	5.57	4.79	4.49
Fe_2O_3	6.18	6.06	8.61	7.34	10.93	6.84	6.51	7.15	8.58
Na_2O	1.24	0.69	1.75	1.35	0.75	1.39	1.52	0.88	1.39
K_2O	1.87	2.28	2.28	1.75	1.82	2.06	1.58	1.63	1.9
TiO_2	0.92	0.73	0.95	0.82	1.48	0.78	0.73	0.71	0.95
MnO	0.08	0.1	0.11	0.15	0.15	0.12	0.12	0.14	0.16
P_2O_5	0.21	0.35	0.35	0.27	0.31	0.17	0.34	0.18	0.38

Related Variation diagrams of the oxides for Chalcolithic and Iron Age samples are given in Figures 3.31 and 3.32 respectively.

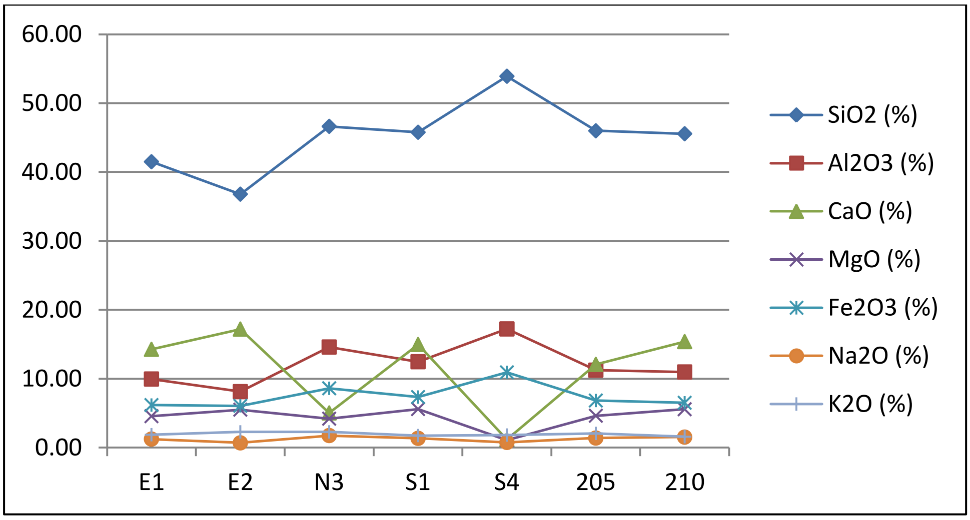


Figure 3. 31. Variation Diagram of chemical compositions of Chalcolithic Age samples

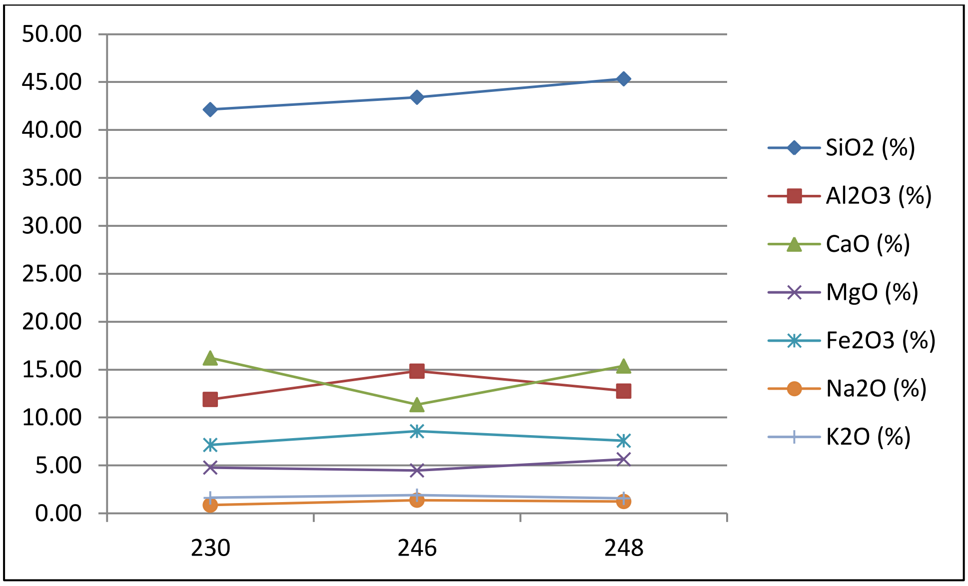


Figure 3. 32. Variation Diagram of chemical compositions of Iron Age samples

As seen from these figures, the chemical compositions of raw materials used both in Chalcolithic and Iron Ages resemble each other with SiO_2 contents lying within 35 to 55% and the rest of the oxides range within 0.1 – 18 % (Table 3.9). Therefore, a significant deviation for any of the sample could not be observed by using these Variation Diagrams. However, this may be an indication for the use of rather similar raw materials and/ or similar manufacturing technologies in both ages in general.

For more compulsive investigations of chemical analysis carried out, ternary phase diagrams of CaO – Al_2O_3 – SiO_2; CaO – MgO – SiO_2 and MgO – Al_2O_3 – Fe_2O_3 are plotted and given in Figures 3.33 to 3.35.

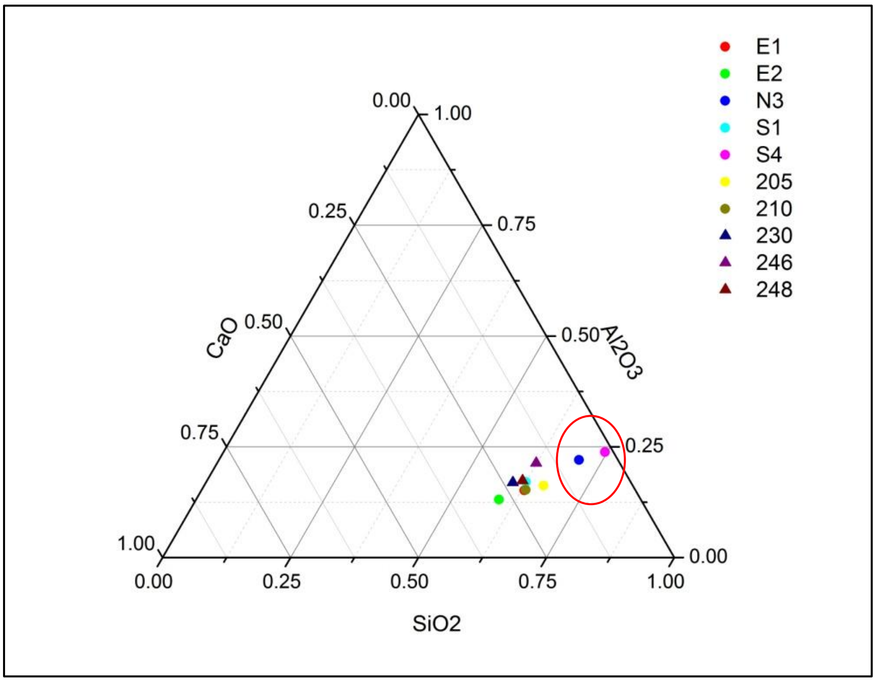


Figure 3. 33. Ternary diagram of CaO –Al_2O_3 – SiO_2 system (Full dots represent Chalcolithic Age Samples, triangles represent Iron Age Samples).

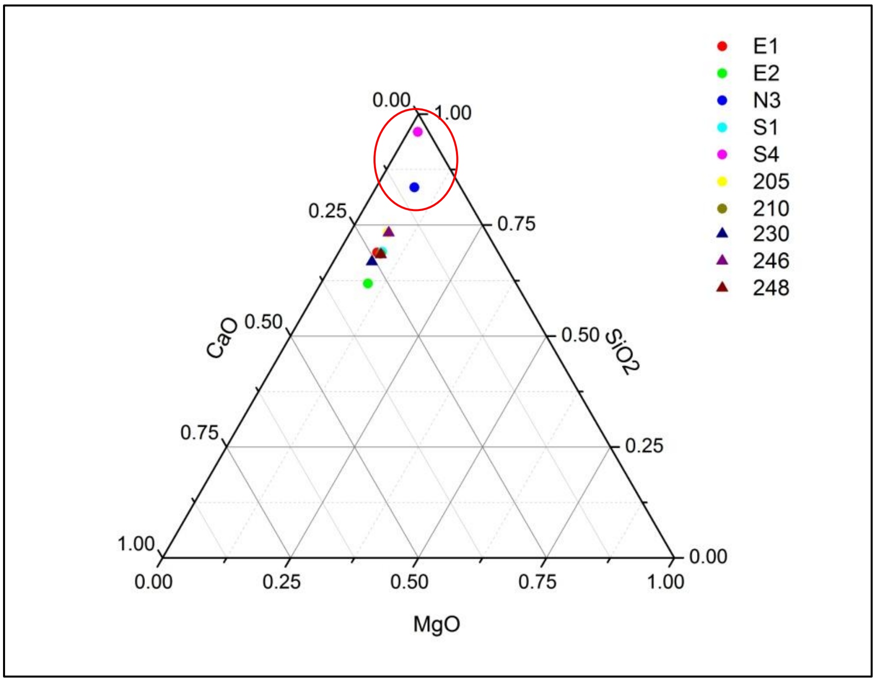


Figure 3. 34. Ternary diagram of CaO – MgO – SiO_2 system (Full dots represent Chalcolithic Age Samples, triangles represent Iron Age Samples).

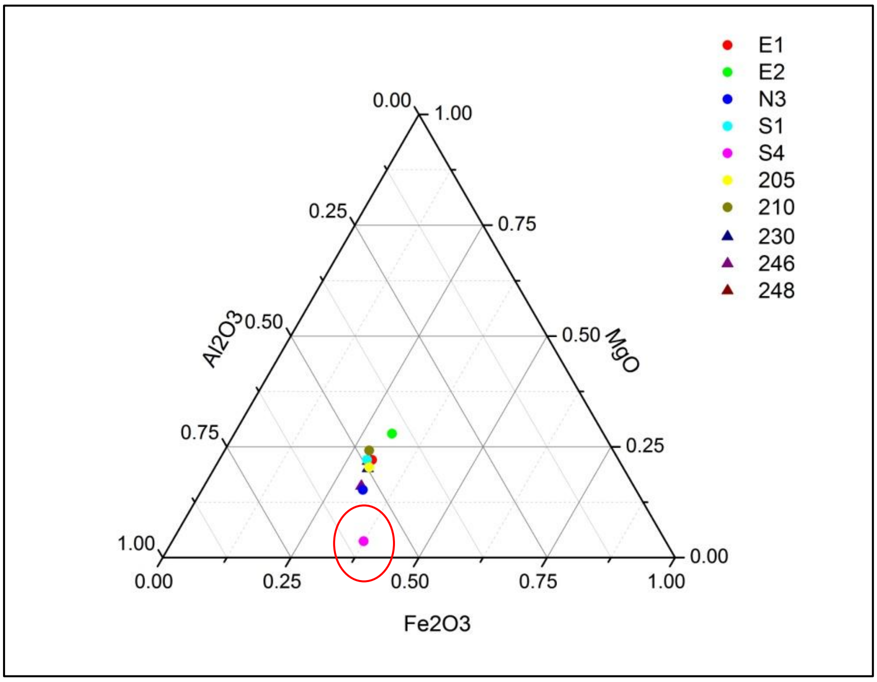


Figure 3. 35. Ternary diagram of MgO – Al_2O_3 – Fe_2O_3 system (Full dots represent Chalcolithic Age Samples, triangles represent Iron Age Samples).

Investigation of ternary diagrams given in Figures 3.33 - 3.35 clearly shows that the samples N3 and S4 of Chalcolithic Age significantly fall apart from the rest of the clusters by their high SiO_2, Fe_2O_3 and Al_2O_3 concentrations (see also Table 3.9). The optical and XRD investigations discussed in Section 3.2 indicate the presence of unclassified metamorphic and schist fragments in S4, and unclassified metamorphic rock, polycrystalline quartz and limestone fragments in N3 while both of them also include mica in their bodies. These facts may indicate the use of different raw materials and/ manufacturing techniques (import?) for these two samples compared to the others, which reflect itself in the ternary diagrams plotted.

The presence of phosphorus (0.2 – 0.4% P_2O_5, Table 3.9), in several samples may indicate the presence of organic inclusions such as chaff as it is also supported in SEM – EDX analyses. See SEM micrographs of sample N3 of Chalcolithic Age (Figure 3.26) and sample 248 of Iron Age (Figure 3.27).

CHAPTER 4

CONCLUSION

Mineralogical analyses along with micro – structural studies and chemical analyses of Değirmentepe (Malatya) pottery belonging to Chalcolithic (Late Ubaid Period), Early Bronze and Iron Ages showed that almost all samples investigated were observed to contain rock fragments, originating from metamorphic and igneous rocks. However, larger grain sizes and higher grain to matrix ratios are recorded for Chalcolithic Age samples compared to those samples belonging to Iron Age. This indicates the use of different raw material and/ or different manufacturing techniques, such as different sieving procedures, in these two periods.

XRD investigations on selected representative samples of the three periods, revealed high abundances of quartz, feldspar, and pyroxene group minerals in all samples, while presence of hematite and mica minerals were also observed both in Chalcolithic and Iron Age samples, but underlying the use of micaceous raw materials mostly in Iron Age. This evidence may again support the use of different sources for the raw materials in these two periods as already mentioned above. In the XRD traces of the investigated sherds of Chalcolithic and Iron Ages, the absence of clay fractions both in the bulk and oriented samples, supports a minimum firing temperature of around 800- 850 °C, while the presence of mullite phases both in XRD and SEM – EDX results, a product of chemical reactions occurring around 1050°C, showed the possible use of high firing temperatures, in the range of 950–1050° C, starting from Chalcolithic Age. This type of application usually results in good mechanical properties, low permeability and high chemical resistivity of the pottery. Supporting these evidences, vitreous- glassy morphology and secondary pores (results of high firing temperature applications) containing needle- like mullite crystal structures at the inner faces, were also observed in the SEM- EDX investigations of both Chalcolithic and Iron Age samples.

All these observations indicate a rather developed ceramic production technology used in Değirmentepe Settlement starting from Chalcolithic Age (5^{th} millennium BC).

Chemical compositions of major oxides obtained ICP – OES analyses exhibit similar compositions both for Chalcolithic and Iron Age samples. Few exceptions observed may indicate possible use of different raw material and/or different manufacturing technique.

REFERENCES

Birgül, O., 1981, İkiztepe ve Değirmentepe Seramik Örneklerinin Element Analizi ile İlgili Ön Çalışmaları, *Arkeometri Ünitesi Bilimsel Toplantı Bildirileri 2*

Chakraborty, A. K. and D. K. Ghosh, 1978, Reexamination of the Kaolinite-to-Mullite Reaction Series, *Journal of the American Ceramic Society* 61(3-4): 170-173.

Chen, Chuin-Shan; Chou, Chia-Ching; Chang, Shu-Wei; Fischer, Reinhard X.; Schneider, H., 2010, First-principles study on variation of lattice parameters of mullite Al4+2xSi2-2xO10-x (x = 0.125, 0.250, 0.375), *American Mineralogist*, 95: 1617-1623

Erarslan, A., 2008, Ubaid Period in the Urbanisation Process: The Birth of Urbanism in the Near East (5500-3800 BC), *Belleten*, Sayı 264, Ağustos 2008, 395-412

Esin, U., 1984, Değirmentepe (Malatya) Kazısı 1983 Yılı Raporu, *VI. Kazı Sonuçları Toplantısı*, 1984 Ankara

Esin, U., 1981, 1980 Yılı Değirmentepe (Malatya) Kazısı Sonuçları, *III. Kazı Sonuçları Toplantısı*, 2-19 Şubat 1981, Ankara, Kültür Bakanlığı Eski eserler ve Müzeler Genel Müdürlüğü

Esin, U., 1982, Değirmentepe (Malatya) Kazısı 1981 Yılı Sonuçları, *IV. Kazı Sonuçları Toplantısı,* 1982 Ankara

Esin, U., 1983, Arkeometrik Açından Değirmentepe (Malatya) Kazıları, *Tübitak Arütob III*

Esin, U., 1986, Değirmentepe (Malatya) Kazıları Arkeometrik Araştırmalarına Toplu Bakış, *Arkeometri Ünitesi Bilimsel Toplantı Bildirileri* VI, 131-53, Tübitak Yayınları 622

Esin, U., Arsebük G., 1983, 1982 Yılı Değirmentepe (Malatya) Kurtarma Kazısı, *V. Kazı Sonuçları Toplantısı*, 1983

Esin, U., Arsebük, G., Özdoğan, M., 1987, Değirmentepe Excavations 1978, *Lower Euphrates Project 1978-1979 Activities 1/3*, METU, Lower Euphrates Project Publications, Ankara

Esin, U., Birgül, O., Yaffe, L., 1985, Değirmentepe Keramiklerinin Eser Element Analizi, *Arkeometri Ünitesi Bilimsel Toplantı Bildirileri* 5, 1985

Esin, U., Birgül, O., Yaffe, L., Marshall, H., 1989, Değirmentepe (Malatya) Çanak Çömleği İz Element Analizlerine Ait Bazı Sonuçlar, *TÜBİTAK AKSAY Ünitesi bilimsel Toplantı Bildirileri* 1, 1988

Esin, U., Harmankaya, S., 1985, 1984 Değirmentepe (Malatya) Kurtarma Kazısı, , *VII. Kazı Sonuçları Toplantısı*, 1985, Ankara

Esin, U., Harmankaya, S., 1986, 1985 Değirmentepe (Malatya – İmamlı Köyü) Kurtarma Kazısı, , *VIII. Kazı Sonuçları Toplantısı*, 1986, Ankara

Esin, U., Harmankaya, S.,1987, Değirmentepe (Malatya) Kurtarma Kazısı, 1986, *Kazı, Araştırma ve Arkeometri Sunuçları Toplantısı I*, 1987, Ankara

Grim, R. E., 1968, *Clay mineralogy 2nd ed*., McGraw-Hill (New York), USA

Gürdil, 2006, Exploring Social Organizational Aspects of the Ubaid Communities: A Case Study of Degirmentepe in Eastern Turkey., in *Beyond the Ubaid: Transformation and integration in the late prehistoric societies of the Middle East*, eds A. Carter and Graham Philip, Studies in Ancient Oriental Civilization 63 Chicago: The Oriental Institute of the University of Chicago, 2010, p 361 - 376.

Harmankaya, Tanındı, Özbaşaran, 1998, Türkiye Arkeolojik Yerleşmeleri *TAY 3, Kalkolitik, Ege Yayınları*, İstanbul

Henderson, 2000, *The science and archaeology of materials: an investigation of inorganic materials*, Routledge

Jackson, M.L. 1956. *Soil chemical analysis - advanced course*. Published by the author, Dep. of Soil Science,Univ. of Wisconsin, Madison, WI.

Lee, W. E., Souza, G. P., McConville, C. J., Tarvornpanich, T., Iqbal, Y., 2008, Mullite formation in clays and clay-derived vitreous ceramics, *Journal of the European Ceramic Society*, vol. 28 (2), 465-471

Nesse, 2004, *Introduction to optical mineralogy 3rd edt*., Oxford University Press

Özbal, 1986, Değirmentepe Metal-Curuf ve Filiz Analizleri, *Arkeometri Ünitesi Bilimsel Toplantı Bildirileri* 6, 1986, Ankara

Özdoğan, 1977, Lower Euphrates Basin 1977 Survey, *Metu Lower Euphrates Project Publications*, Series 1, No 2, Ankara

Pichler and Schmitt – Riegraf, 1997, *Rock-Forming Minerals in Thin Section*, Chapman & Hall, UK

Pollock, 1999, *Ancient Mesopotamia: the Eden that never was*, Cambridge University Press, UK

Rice, 1987, *Pottery analysis: A Source Book*, University of Chicago Press, Chicago

Serdaroğlu, 1975, 1975 *Surveys in the Lower Euphrates Basin*, ODTÜ Aşağı Fırat Projesi Yayınları Seri 1, No 1, Ankara

Tite M. S. and Maniatis Y., 1975, *Examination of ancient pottery using the scanning electron microscope*, Nature 257, 122 - 123

Tite, 2008, Ceramic Production, Provenance and Use - a Review, *Archaeometry*, vol. 50 (2), 216-231

Türkmenoğlu A.G., Göktürk E. H., 1994, An Investigation on The Manufacturing Technology of The Değirmentepe (Malatya) Pottery, *The Proceedings of The 29th International Symposium on Archaeometry*

Türkmenoğlu A.G., Bakırer Ö., Caner E., 1985, Değirmentepe Seramiklerinin Mineralojisi ve Petrografisi, Bölüm 1: İnce Kesit Çalışması, *Arkeometri Ünitesi Bilimsel Toplantı Bildirileri 5*,

Türkmenoğlu, 1989, Değirmentepe (Malatya) Keramiklerinin Kil Mineralojisi: X Işınları Toz Diffraksiyon Analizi, *TÜBİTAK AKSAY Ünitesi Bilimsel Toplantı Bildirileri 1*,

Velde B., Druc, I. C., 1998, *Archaeological Ceramic Materials*. Origin and Utilisation. Springer-Verlag Berlin/Heidelberg

William E. Lee, W.Mark Rainforth, 1994, *Ceramic Microstructures: Property Control by Processing*, Chapman and Hall, United Kingdom

APPENDIX A

GLOSSARY

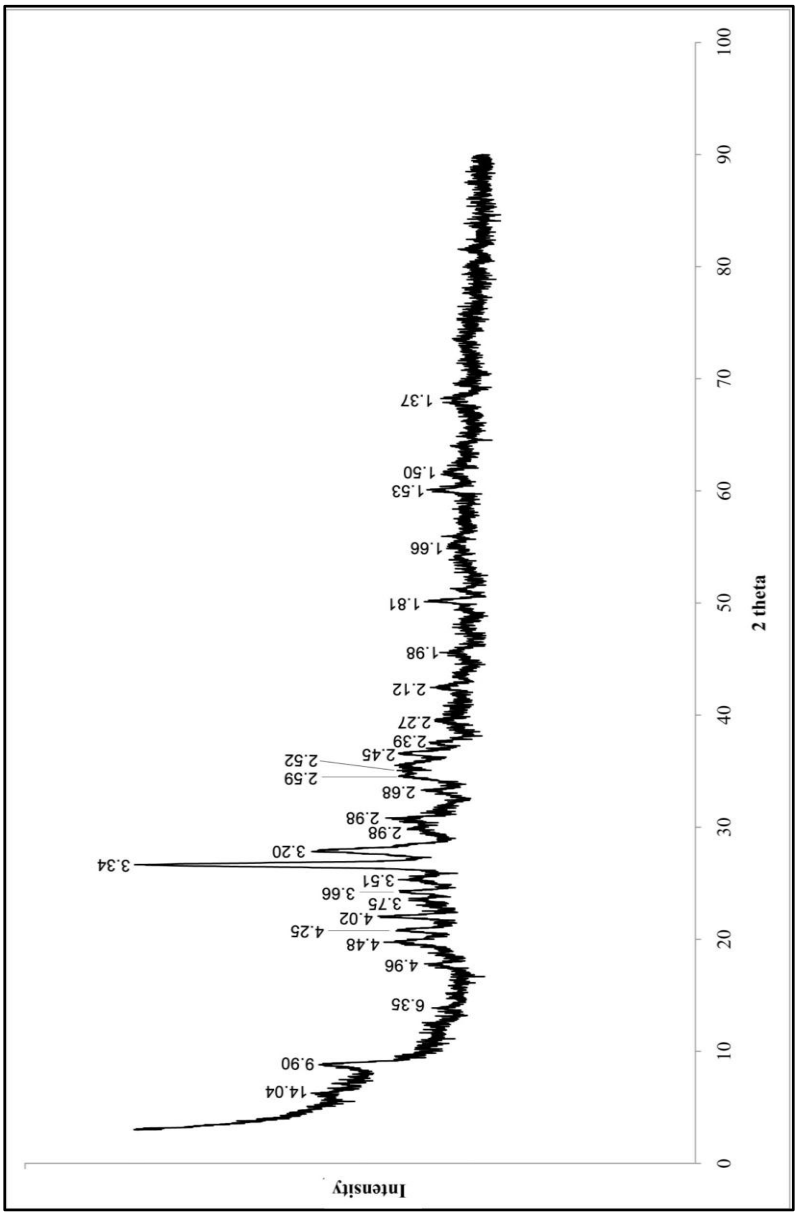
Agglutinated layout is an attached settlement plan which is characteristic in Ubaid Period

Bullea is an unbaked clay lump pressed on the rope which binds the jars and vessels prior to the posting of the goods.

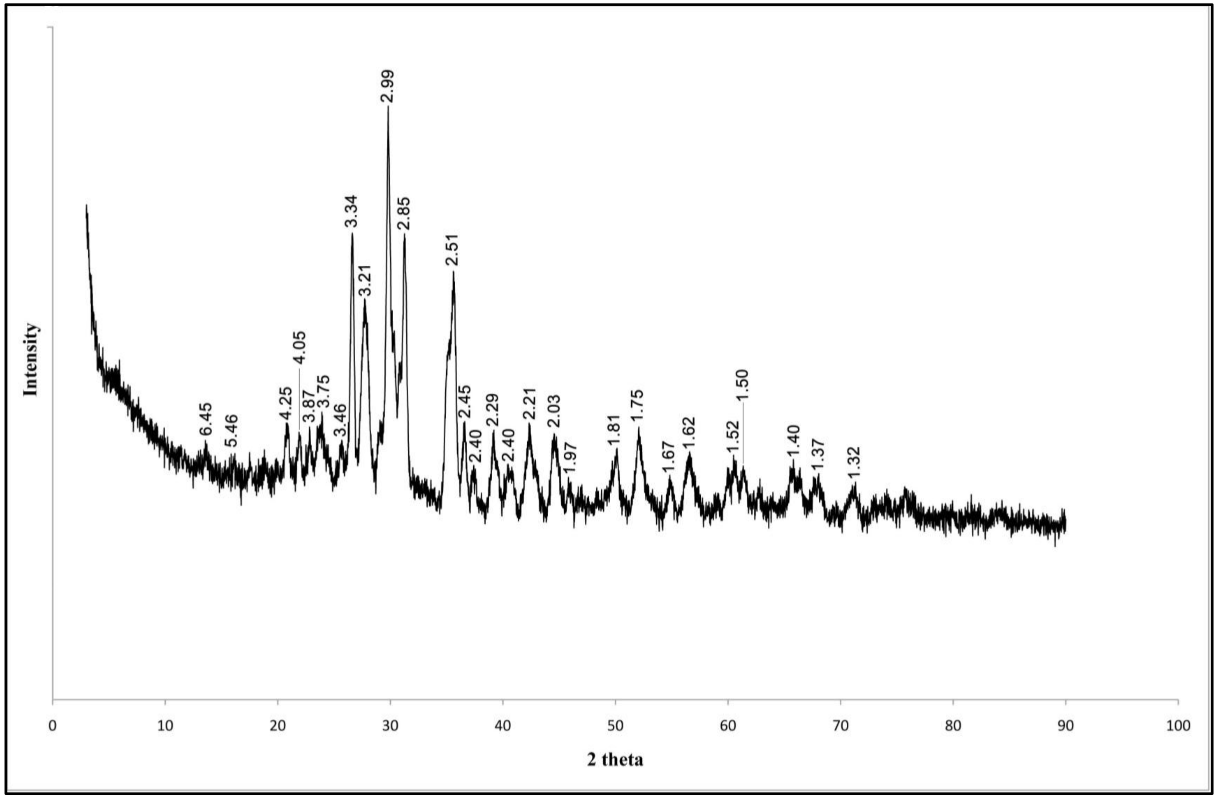
Seal is a stone object used to stamp the clay to create figures on it

APPENDIX B

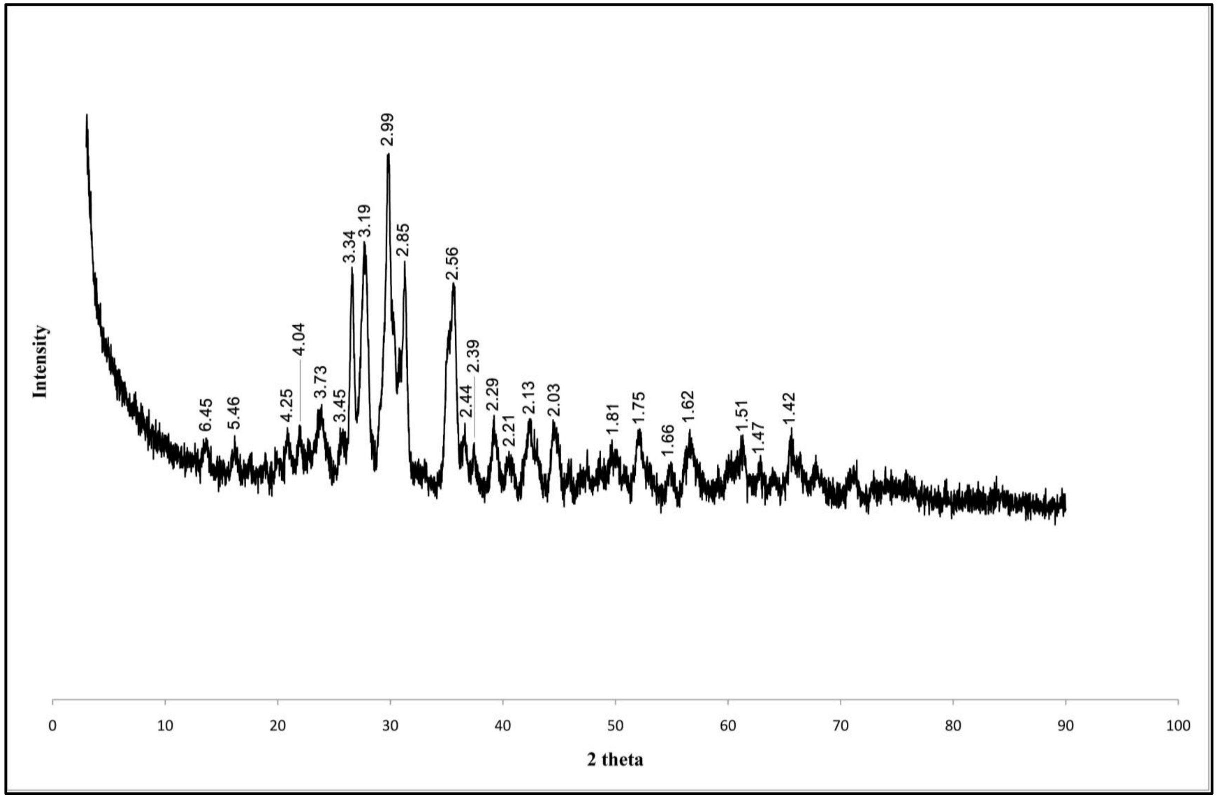
XRD SPECTRA



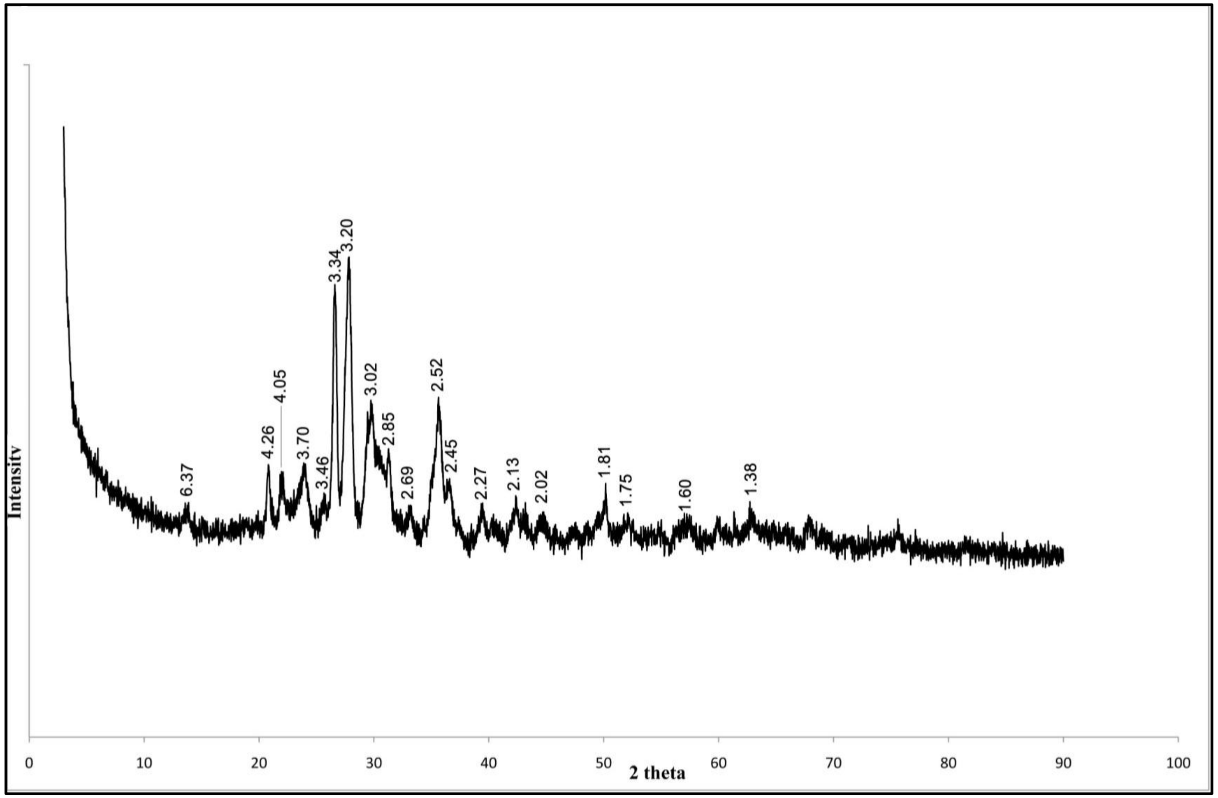
XRD spectrum of sample 151



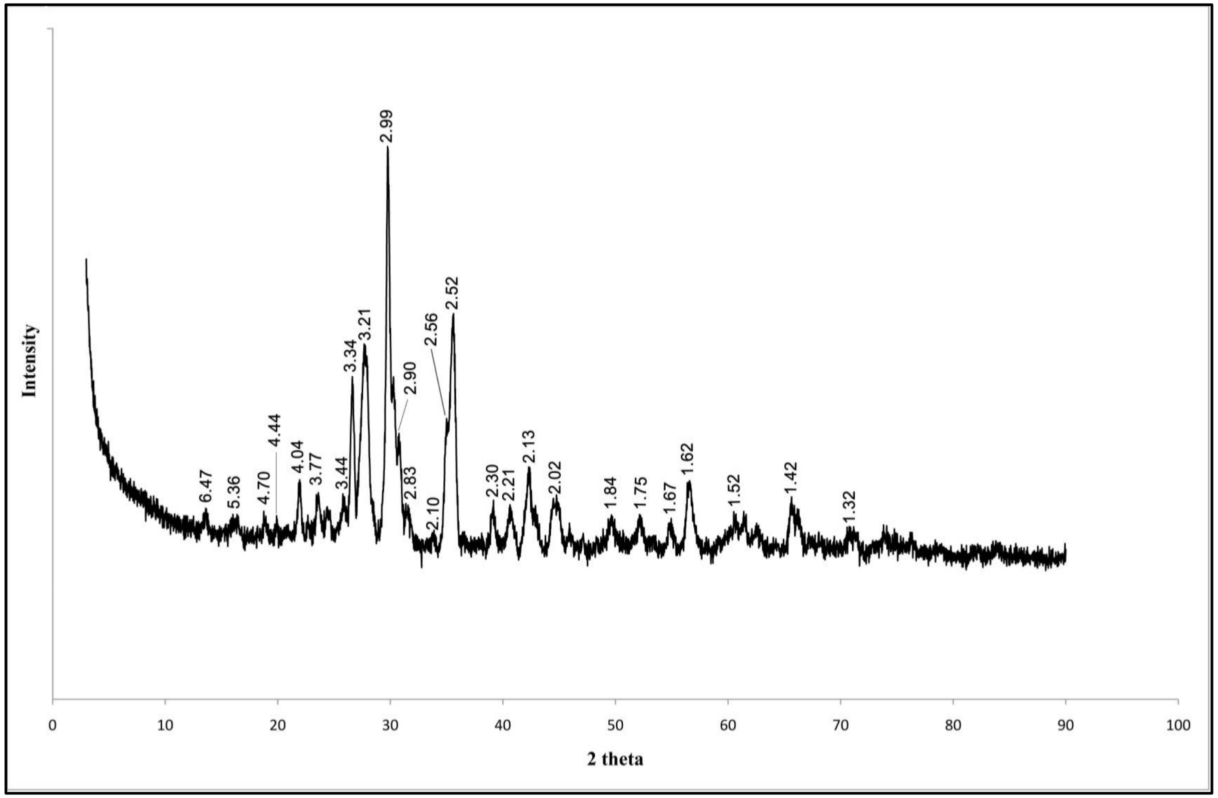
XRD spectrum of sample 210



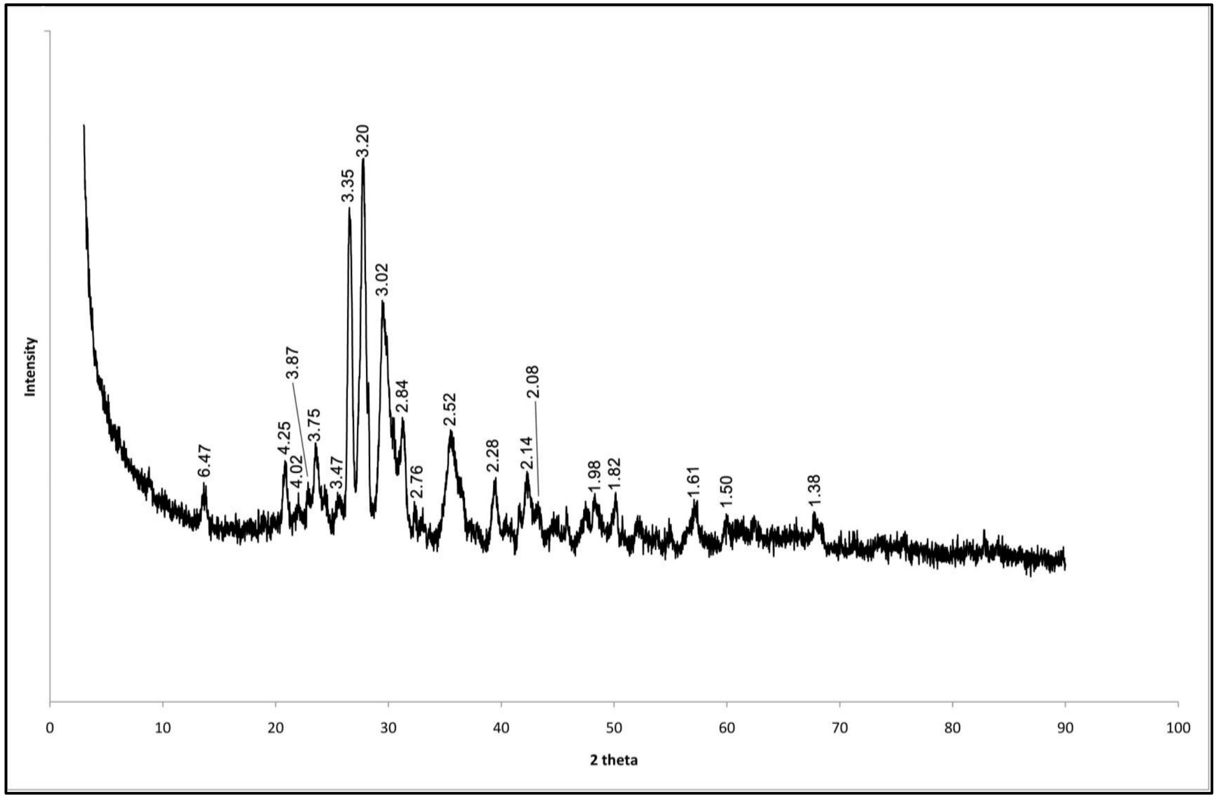
XRD spectrum of sample 230



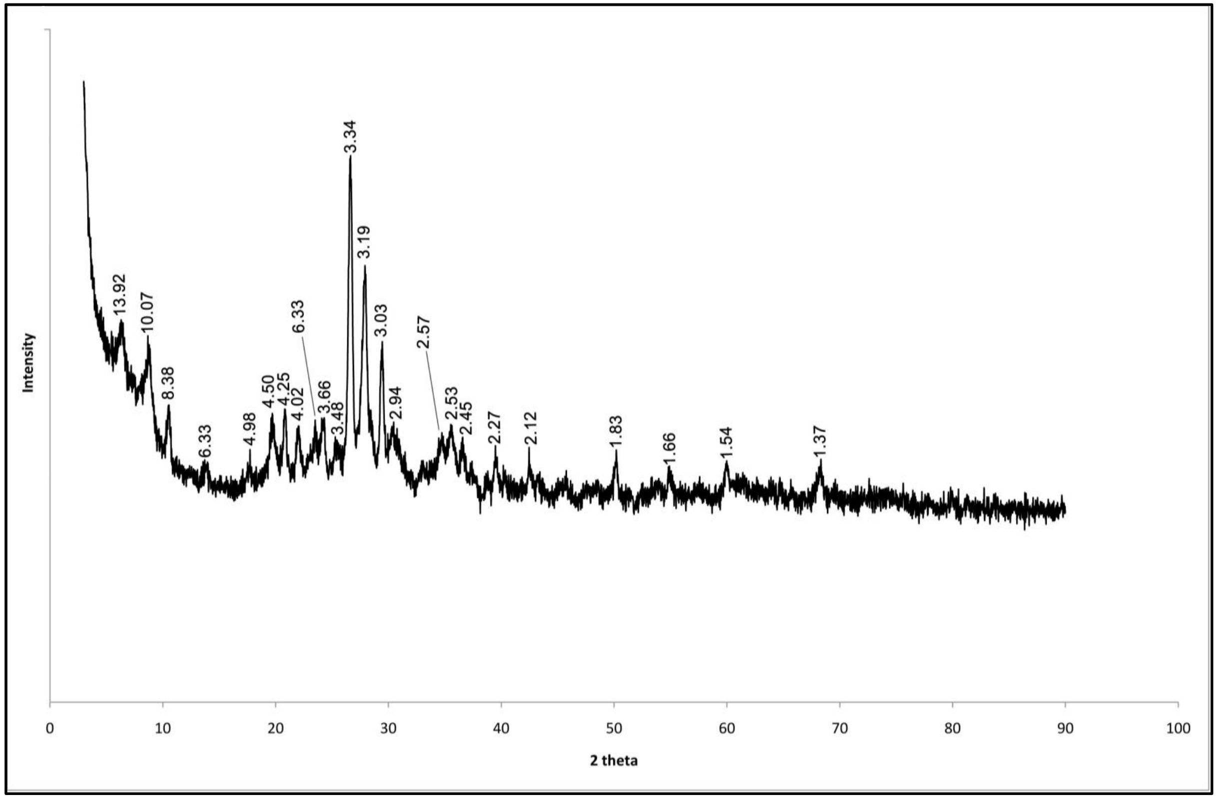
XRD spectrum of sample 246



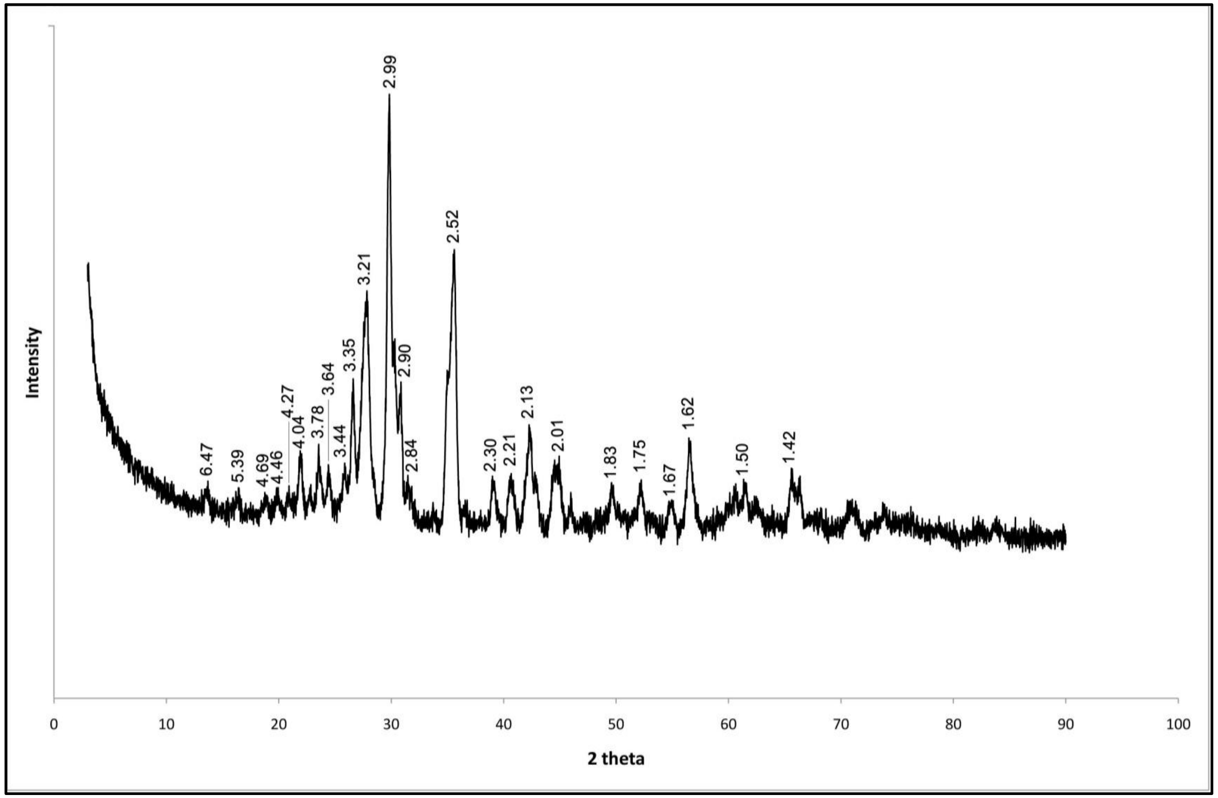
XRD spectrum of sample 248



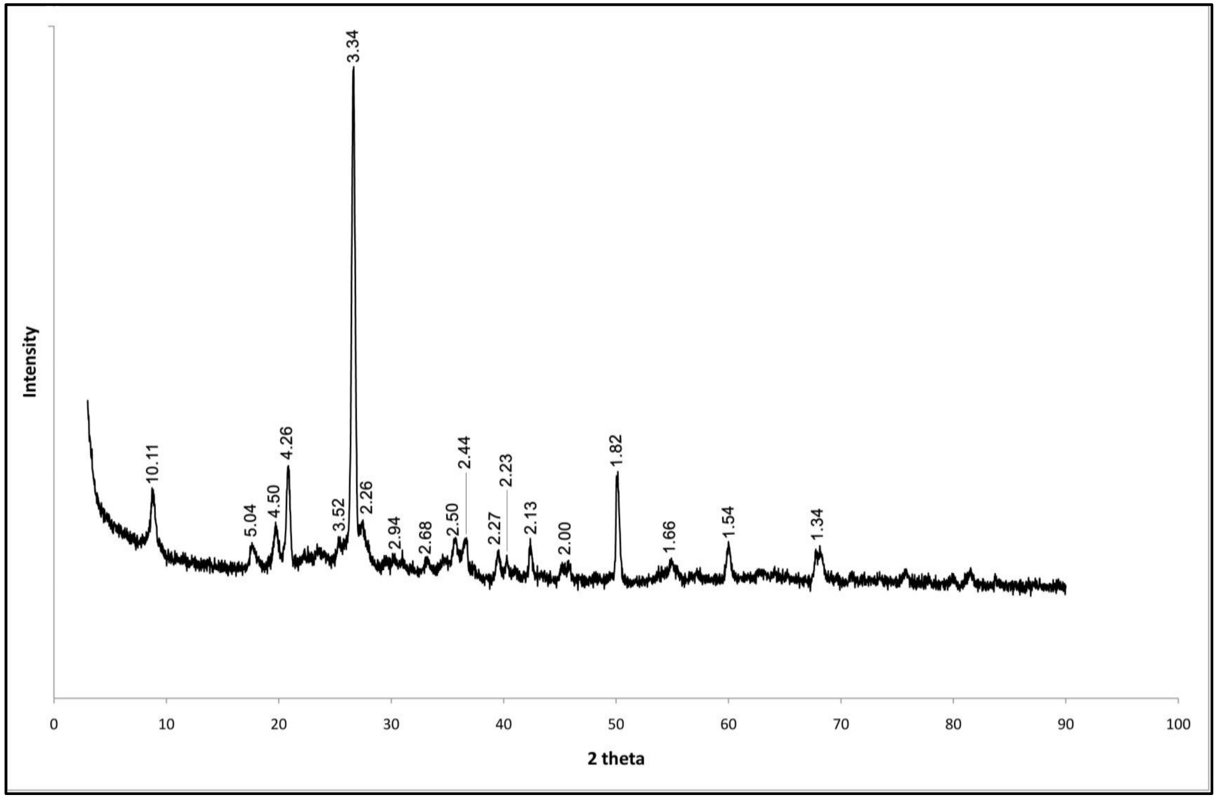
XRD spectrum of sample E1



XRD spectrum of sample N3



XRD spectrum of sample S1



XRD spectrum of sample S4