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Research Article

Provenance of Kinet Höyük Ceramics Uncovered in Excavations: Petrography, XRF and Raman Analysis

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ABSTRACT: The archaeological finds unearthed at Kinet Höyük are a sensitive indicator of the forces that shaped the economic relationship in the Eastern Mediterranean during these centuries. Among the archaeological finds, pottery is especially important evidence for the determination of cultural and economic relations at important chronological moments.

Petrographic, XRF (X-rays fluorescence) and Raman analysis techniques were used to determine the mineralogical-petrographic and chemical contents of the pottery selected from stratified levels dating to the Bronze Age, Iron Age and Hellenistic Period unearthed during the excavations at Kinet Höyük and clay samples taken from the environment. It was determined that some of the studied samples were compatible with the samples taken from the regional geological formations and clay beds, and it was determined that they were local production.

KEYWORDS: Kinet Höyük, Ceramics, Provenance, Petrographic, XRF, Raman

1. INTRODUCTION

Kinet Höyük is an important port settlement (Figure 1). located near the town of Dörtyol in Hatay province. Excavations on the mound and surrounding fields recovered an occupational sequence from Early Bronze II through the Hellenistic Period, accounting for thirty-two phases with multiple subdivisions and no notable gaps. The Early Bronze, Middle Bronze, and Late Bronze to Iron Age exposures were carried out in three separate areas, but firm stratigraphic overlaps connect them to form an unbroken sequence applicable throughout the site. Twenty years of archaeological research at Kinet Höyük were carried out as a Bilkent University project directed by M.-H. Gates (1992-2012).

Samples excavated at Kinet from five chronological time frames of the Bronze, Iron and Hellenistic occupations were selected from Phases VI (Early Bronze), V (Middle Bronze), IV (Late Bronze), III. (Early Iron) and II (Hellenistic). Mineralogical, petrographic and chemical analyses were conducted on them. This study was supported within the scope of Kastamonu University Scientific Research Projects with Project number KÜ-BAP01/2020-80.

Petrographic, XRF (X-rays fluorescence) and Raman analysis were made to answer different research questions determined according to the specific periods of excavation and their archaeological components.

In addition, the pottery produced and imported in Kinet Höyük during five chronological time frames of the Bronze, Iron and Hellenistic was defined and regional pottery activity was understood. The results obtained will contribute to the understanding of the commercial, economic and cultural relations of Kinet Höyük with the Aegean, Mediterranean, Syria and Anatolia in these periods and the geographical dimension of this relationship, and will form a database for future similar studies.

[1] In the coding, **KHK** (=Kinet Höyük Excavation), **B1** code refers to the ceramic sample no 1. Clay/torak samples taken from the environment were coded as **KHK-D.**

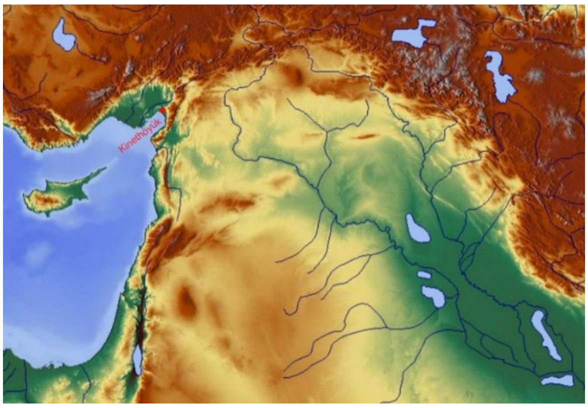

Figure 1. Kinet Höyük (Ceyhan, Erzin and Arsuz Plains) and their location in Near East, physical map (https://maps-for-free.com/)

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2. MATERIALS AND METHODS

A total of 240 pottery sherds were sampled from the layers dated to the Early, Middle, Late Bronze Age and Iron Age, together with the Halaf and Ubaid (Late Neolithic-Early Chalcolithic) periods, in order to determine the early period of the Early Bronze Age samples and their relationship with their first production. Care was taken to ensure that the samples selected from different strata were sufficient to represent the group from which they were taken in terms of their functional and cultural characteristics. Before proceeding to the analysis phase, information such as the location, period, pottery shape and paste texture of each sample was recorded, and a documentation was made by taking photographs of each sample.

20 clay samples taken from Kinet Höyük and the surrounding area were marked on the location map (Figure 2)[1].

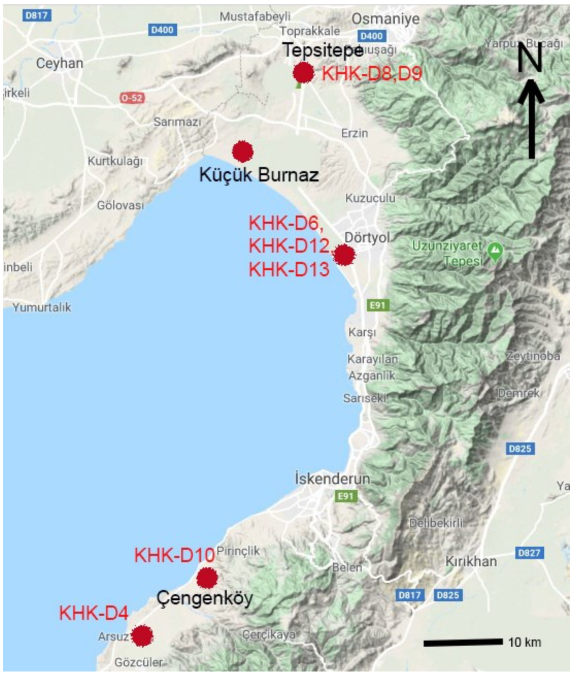


Figure 2. Location of clay samples taken from Kinet Höyük

In this study, SPECTRO X-Lab 2000 brand spectrometer works in the Polarized Energy Dispersive X-Ray (PEDX) system. For analysis, 4 g powder samples were taken from the pottery samples. After the powder samples were pressed into pellets with a diameter of 35 mm, they were analyzed by wavelength dispersion XRF. With the XRF method, the concentrations of many elements with atomic numbers between Be and U elements can be obtained.

The concentrations of major (> 1% wt) and minor (between 1% - 0.01%wt) elements found in the pottery samples were calculated as percent oxide, and the concentrations of trace elements (<0.01%wt) were calculated as ppm. In theory, major and minor oxide concentrations provide a general data on the raw material used in the production of pottery, while similarities and differences in trace element concentrations are a more sensitive indicator. The concentrations of major, minor and trace elements in the samples were evaluated together and the geochemical fingerprints of the analyzed pottery were revealed.

Raman spectroscopy relies on measuring the scattered beam from a specific angle by irradiating a sample with a powerful laser source consisting of a visible or near-IR monochromatic beam. In Raman experiments, a monochromatic light beam is sent into the sample. When molecules interact with an intense monochromatic beam, most of the light is scattered as it passes through the molecule. During light scattering, the energy of most of the scattered light is equal to the energy of the light interacting with the matter, and this type of elastic scattering is called Rayleigh scattering. Point analysis, line length analysis, mapping and intensity analysis can be performed with Confocal Raman Spectrometer. In general, point analysis is applied in mineralogical determinations (Deniz, 2010; Güllü and Deniz, 2022).

Confocal Raman Spectrometer (CRS) measurements were made on Thermo Scientific brand DXR model devices.
Pyroxenes in ceramics and clay were measured in the form of point analysis using a 633 nm laser with a resolution of 2 cm-1 and a range of 100–1200 cm-1 (Deniz, 2021; Deniz and Kadıoğlu, 2021).

After the sampling and documentation phase, thin sections were prepared from the pottery samples and the thin sections were analyzed using an polarizing microscope. With thin section analysis, it is aimed to obtain technical data on the raw materials used in the production of pottery, raw material processing techniques, and production stages such as shaping and firing. Thin section analysis is a widely used method in the examination of archaeological finds. In addition to the pottery, other ceramic finds and samples taken from materials such as stone, mortar, plaster and mudbrick are also examined by thin section analysis.

A small piece cut from the pottery sample was glued to a glass microscope slide and the etching process was carried out until the thickness of this piece was reduced to 30 micrometers. When the thickness of the sample on the glass reaches 30 micrometers, the sample preparation process is completed by covering the sample with a second thin glass slide. The components (such as minerals and rock fragments) in the pottery sample become transparent to light at a thickness of 30 micrometers and can be identified and separated from each other according to their optical characteristics by examining them under a microscope. Sections of Kinet Höyük ceramic and clay samples were prepared and studied (Figure 3).

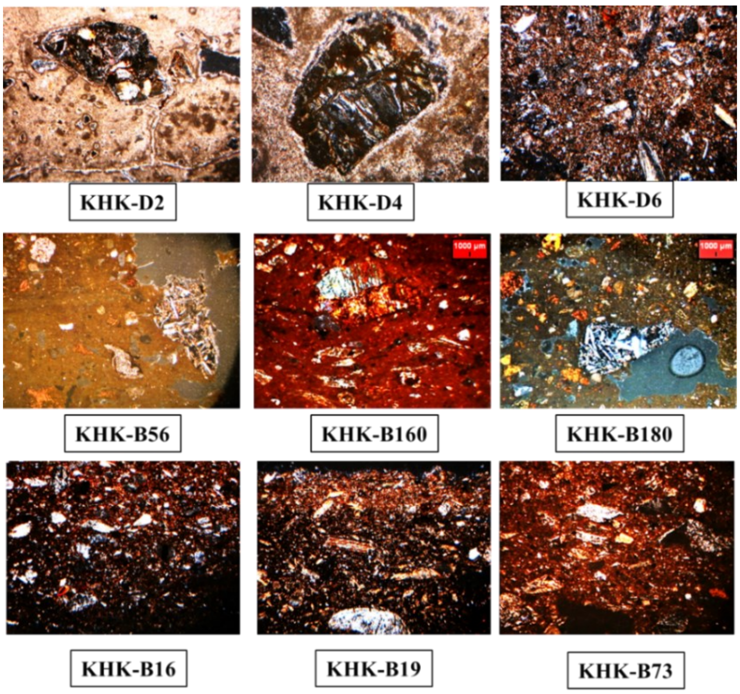


Figure 3. Kinet Höyük excavation ceramics and clay thin section samples

3. RESULTS and DISCUSSION

240 examples belonging to different periods were examined. Petrographic analysis was performed in all samples. XRF analysis was performed on selected eighty samples from the groups formed at the end of the petrographic analysis.

3.1 X-Ray Fluorescence (XRF) Analysis

XRF analysis was carried out to determine the chemical contents of selected samples from Kinet Höyük according to the results of petrographic analysis from different periods and clay/soil samples taken from the environment (Figure 4, Table 1).

According to the data obtained from the clay beds and the origin rocks of the ceramics, the geological formations around Kinet were determined first[2].

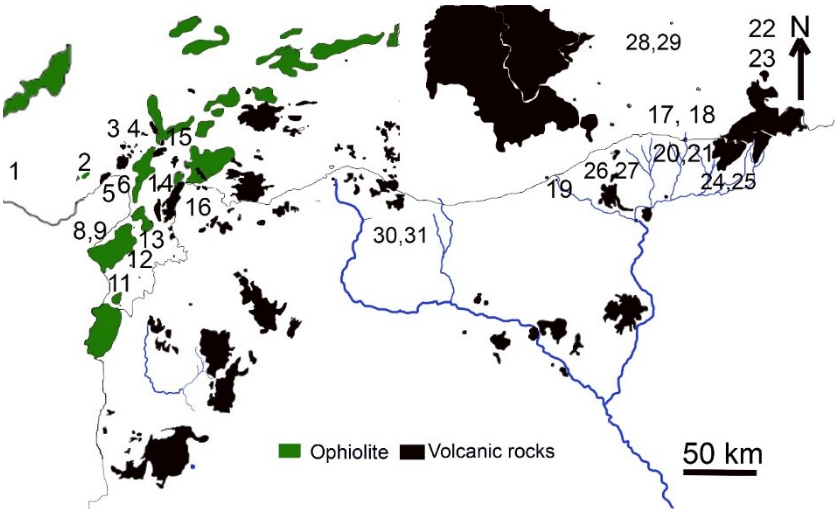


Figure 4. Clay samples from Ceyhan, Erzin, Arsuz, Amuk, Gedikli, Northern Syria Regions (Kibaroğlu, 2008, 2015) and geological formations (Sarıfakılıoğlu et al. 2017 and Türkecan, 2015, Lustrino, et al. 2006. publications)

After determining the regions where ophiolite and basalt formations are seen, the chemical contents of the clay/soil samples taken from these regions from previous studies and within the scope of this study were determined (Figure 4, Table 1).

Table1. Comparison of MgO, Al203, SiO2, Ca0, Fe2O3 and Cr2O3 values of clay samples from Ceyhan, Erzin, Arsuz, Amuk Plain, Gedikli, Northern Syria Regions (Kibaroğlu, 2008,2015 and Gutsuz 2017)

Element	Tarsus (D3)	Sirkeli	Sirkeli	Sirkeli aver.	Sirkeli Clay	Tepsitepe (D8)	Tepsitepe D9	Deliçay D12	Deliçay D13	Yeşilköy D6
Clay Sample Points	**1**	**2a**	**2b**	**2c**	**2d**	**3**	**4**	**5**	**6**	**7**
MgO	2,4	3	9,5	6,25	8,2	24,7	19,9	25,9	23,8	11,9
Al_2O_3	9,1	8,6	15,7	12,1	13,1	4,32	4,5	2,93	4,3	5,1
SiO_2	50,9	41,4	57,1	49,2	44,1	56,01	50,7	45,7	49,6	42,1
CaO	9,6	14	33	23,5	20,9	4,5	8,01	9,29	8,4	5,3
Fe_2O_3	6,1	4,6	9	6,8	9	7,4	7,2	5,8	5,7	5,9
Cr_2O_3	0,04				818	0,1	0,15	0,14	0,12	0,1

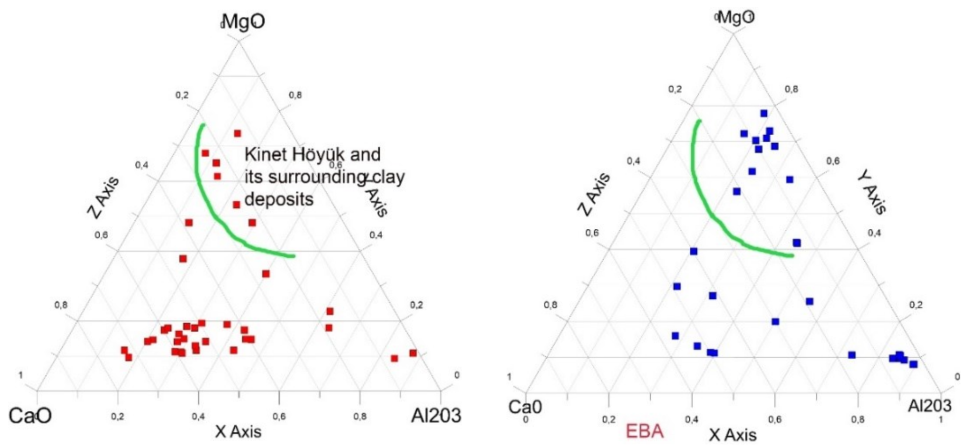
[1] **Ophiolite:** Serpantinit, amfibolit, spitilik bazalt, gabro, diyabaz, radiolaria, pelajik limestone, **Delihalil form. (Qd):**Alkaline Basalt, **Haydar form. (Th):** Serpentinite and limestone contain little quartz and chert pebbles, conglomerate and occasional marl. **Bulkurkaya (Tbul):** Recrystallized limestone and volcanic and ophiolite blocks are located in a debris flow complex mostly composed of serpentinites and volcanic rocks (gabro, basalt, spilite, andesite). In addition, sparse marble blocks contain secondary micaschists (Doyuran, 1982).

Element	Çengen D10	Arsuz D4	Arsuz Kil 1	Arsuz Kil 2	Asi Nehri	Asi Nehri	Karasu	Karasu	Kırıkhan	Kırıkhan	Tilmen	Tilmen
Clay Sample Points	**8**	**9**	**10a**	**10b**	**11a**	**11b**	**12a**	**12b**	**13a**	**13b**	**14a**	**14b**
MgO (%)	5,7	11,6	8,03	7,06	6,4	7,8	4,8	9,5	17,9	14,8	3,8	2,2
Al_2O_3	7,5	5,3	12,1	11,7	8,7	10,1	12,9	11,3	5,0	9,0	13,5	20,5
SiO_2	43,7	41,5	45,4	50,2	36,0	45,4	67,6	61,4	51,2	58,5	61,3	58,8
CaO	19,7	13,8	23,3	20,3	39,9	25,2	3,4	7,5	14,2	6,9	4,01	1,6
Fe_2O_3	5,0	4,6	6,9	6,2	6,1	8,5	6,3	6,5	8,1	7,3	11,2	9,5
Cr_2O_3 (ppm)	544	688	332	610	650	1420	610	960	2710	1180	1010	239

Element	Almanpınarı	Afrin	Afrin	Kamışlı	Kamışlı	Habur	ÇağÇağ 1	ÇağÇağ 2	İdil
Clay Sample Points	**15**	**16a**	**16b**	**17**	**18**	**19**	**20**	**21**	**22**
MgO	1,9	4,2	6,1	4,42	7,3	4,8	5,5	4,7	3,6
Al_2O_3	15,9	11,4	12,1	11,2	10,7	12,3	7,9	11,6	10,1
SiO_2	58,5	52,8	57,1	48,5	37,7	50,1	31,2	42	51
CaO	0,25	22,3	14,0	23,6	32,1	20,4	25,7	17,1	19,4
Fe_2O_3	8,0	6,5	7,8	5,71	5,1	6,2	4,1	6,1	4,8
Cr_2O_3	200	510	1050	342	206	277	187	254	533

Element	İdil	Jarah	Jarah	Tell Beydar	Tell Beydar	GDA 1	GDA 2	Syria 1	Syria 2
Clay Sample Points	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**
MgO	5,6	4,8	4,36	4,02	5,09				
Al_2O_3	13,7	15	13	7,4	10	16	10	16	7
SiO_2	51	54	49	28,9	42				
CaO	12,8	13	12	30,1	21	5	20	15	32
Fe_2O_3	7,3	8,1	7,38	3,8	5,8				
Cr_2O_3	314	273	235	169	311				

The chemical contents of the clay sources from the Kinet region and the ceramic samples were compared according to the $MgO+CaO+Al_2O_3$ main elements according to the periods (Figure 5).



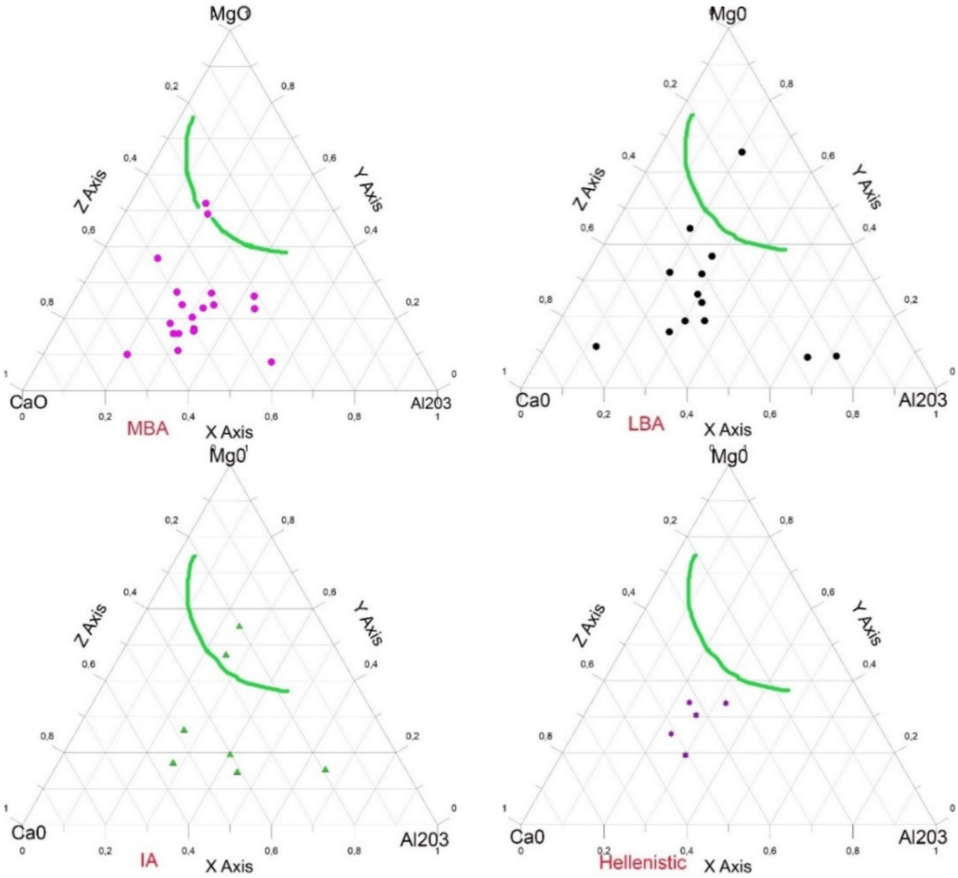


Figure 5. Grouping of clay, EBA, MBA, LBA, IA and Hellenistic period samples, respectively, according to $MgO+CaO+Al_2O_3$ main element contents based on PED-XRF analysis data (Triangle Plotting).

3.2 Confocal Raman Spectroscopy Analysis

Raman analysis was applied on the KHK-D6 sample taken from the closest point to Kinet Höyük, which has serpentinite as its parent rock, and on the pyroxene minerals in some ceramic samples whose origin rock is serpentinite (Figure 6).

As a result of the analysis, it was determined that pyroxene deteriorated into Antigorite from the serpentine group. It was determined that some of the analysed Kinet pottery samples matched up with the clay of KHK-D6.

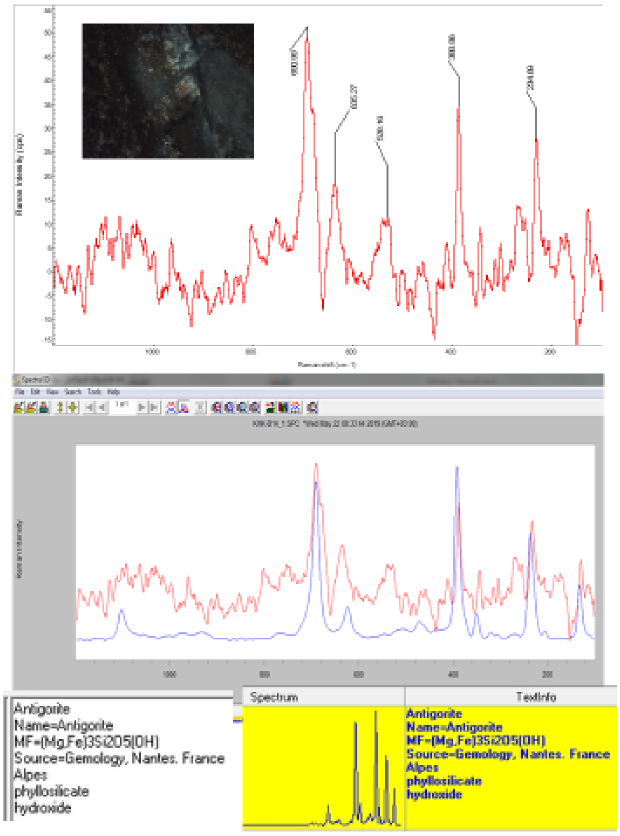


Figure 6. Comparative Raman spectra of ceramic and clay samples (KHK-B14).

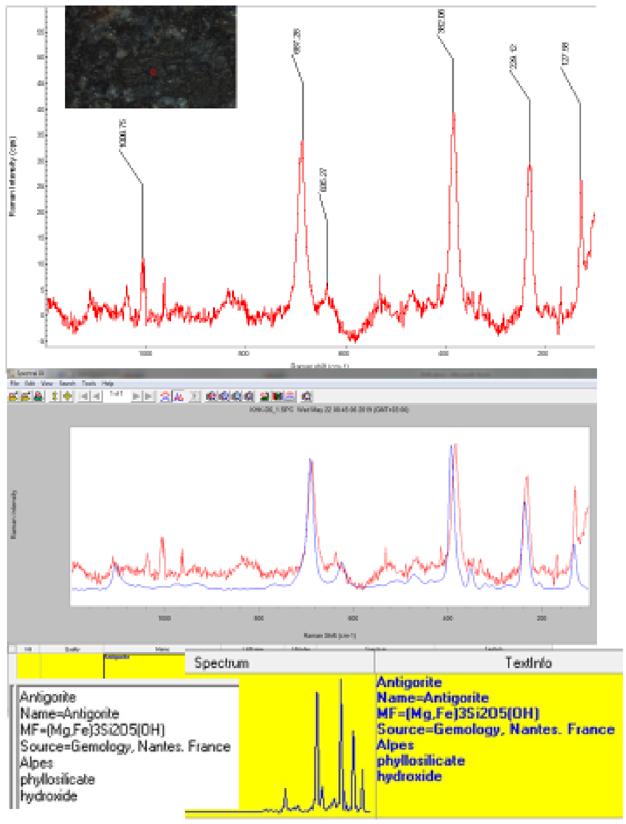


Figure 7. Comparative Raman spectra of ceramic and clay samples (KHK-D6)

3.3. Petrographic analysis

Petrographic analysis of 20 clay samples taken from Kinet Höyük and the surrounding area was carried out. Their locations were compared with the geological formations indicated on the map (Figure 4).

Alongside the Bronze Age samples, earlier Halaf and Ubaid ceramics were analysed to determine the relationships among them. Total sample numbers are as follows: Neolithic/Chalcolithic (20 samples); Early Bronze (78); Middle Bronze (73); Late Bronze (27); Iron Age (20) and Hellenistic (22) (Tables 1-3).

Table 2. The results of the petrographic analysis of the ceramics from different periods found in the Kinet Höyük Excavation, the ceramic clay parent rock, grouping according to their mineral content.

KHK-D5	Quartz, chert, clay, hematite, limonite, basalt rock fragments	KHK-D1	Aşağı Çengen
KHK-D6	Prx, Olv, Plj, L, Serpentinite rock fragments	KHK-D2	Arsuz
KHK-D14	Clay, Q, Ç	KHK-D3	Tarsus
KHK-D7	Phy, Q, serpantinit, listvenit, Ç,Q	KHK-D4	Arsuz
KHK-D8	Sericite, Q, Feldspar	KHK-D5	Çengen
KHK-D12, D13	Sericite, Q, Prx, Plj, Ç, hematite, limonite, ilmenite	KHK-D6	Yeşilköy
KHK-D9	Clay, Q, Ç, Sericite, Prx	KHK-D7	Almanpınarı
KHK-D3	Limonite, calcschist, Clayey limestone, Prx, Q, Ç	KHK-D8	Tepsitepe 1
KHK-D1, D2, D4	Clay, calcite, Q, Prx	KHK-D9	Tepsitepe 2
KHK-D10, D11	Clay, Q, Ç, Prx, Olv, hematite, limonite, ilmenite	KHK-D10	Çengenköy 1
		KHK-D11	Çengenköy 2
		KHK-D12	Deliçay 1
		KHK-D13	Deliçay 2
		KHK-D14	Çengen

Period	Alk. B.	Se	Amf.	Ofik.	And.	B.	G	S	Si	C. Si	Cs	C. L	F.L	Ş	F.
Chalc.		X	X			X		X	X					X	
EBA II	x	x				x		x	x		x	x		x	
EBA III (Early)	x		x			x		x	x						
EBA III (Late)	x		x			x	X	x	x						
MBA I												X			
MBA I/II					X	X				X					X
MBA II					X	X				X	X	X			
LBA I	X	X				X									
LBA II	X	X		X							X				
LBA III				X											
IA		X				X				X				X	X
Hellenistic	X					X		X			X		X	X	X

Chalc.: Chalcolite, **EBA:**Early Bronz Age**, MBA:**Middle Bronze Age, **LBA:** Late Bronze Age, **IA:** Iron Age **Alk. B.**: Alkaline Basalt, **B**:Basalt **Se**. Serpentine, **Amf**.: amphibolite, **Ofik.:** Ophicarbonate, **And.**: Andesite **G:** Granite **S.:** Sandstone **Si:** siltstone, **C. Si.** clayey silt stone, **Cs.** clay stone, **C. L.**:Clayey limestone, **F. L:** Fossil Limestone **Ş:** Schist, **Phy:** Phyllite , **Prx,** Pyroxene, **Olv:** Olivine , **Plj**: Plojaclase, **L:** Limestone, **Q**: Quartz

Among the formations in the region, there are ophiolitic, mainly gabbro, basalt, radiolarite and less silicified serpentinites (listevenite) formations. These compositions of ceramic content typically represent the ophiolitic rock group. The ophiolitic rock unit typically represents the oceanic crust and consists of a rock succession called pelagic limestone, basalt pillow lavas, diabase days, gabbro, harzburgite from the top to the bottom (Sarıfakılıoğlu et al., 2017)

Gabbro, basalt, and radiolarite rock fragments were found among the ceramic samples and are associated with ophiolites. Basalts in ophiolite, rocks that come into contact with sea water during their formation form spitic basalt and it is one of the distinguishing features in the determination of ophiolites.

There are metal mineralization (chromite, nickel) mineralization and mineral raw material resources (olivine, magnesite, manganese) associated with basic-ultrabasic rocks belonging to ophiolite formations.

Alkaline basalt is detected in Turkey, in Thrace, in Ezine-Taştepe and Tavşan Island volcanics in Northwest Anatolia, in Kula region from Western Anatolia Volcanites, Afyon volcanics, Niğde Ulukışla-Çamardı volcanics in South Anatolia Region, around Bucak district in Isparta Region volcanics. determined (Türkecan, A., 2015).
It contains alkali basalts within the Ceyhan-Osmaniye-Yumurtalık volcanics in the Amanos region. In addition, it has been determined that the volcanics of Karasu Valley (Hatay) in the Hatay region also contain alkaline basalt. This region is within the Oludeniz Rift Zone. Alkaline basalts were detected under the ophiolites (BaerBassit) in Syria **(Figure 4, 8)** (Türkecan, A., 2015).

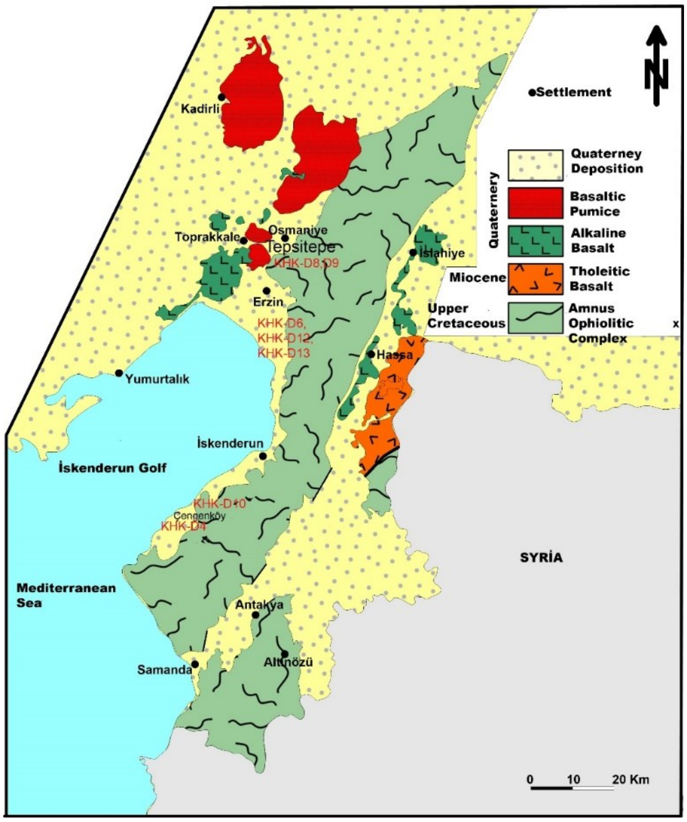


Figure 8. The locations of the clay samples analyzed in the study and the sample points analyzed before and the main geological formations (Kadıoğlu, 2018)

4. CONCLUSIONS

By petrographic analysis, the parent rocks of the ceramics and the rock fragments and minerals in the additives were divided into groups. According to these data, answers were sought for these questions, whether their possible sources were local or brought from outside. In this regard, firstly, the geological formations of the region and the formations related to the production places of the ceramics known to be produced in different regions were determined.

The question of whether the artifact found in archaeological studies was produced in that region, whether it was local or came from outside, is important. The answers to these questions provide the basis for explaining inter-regional relations and intercultural connections. This study also sought answers to these questions and formed a source for future studies.

Some of the Early Bronze Age samples are compatible with pre-Chalcolithic ceramics and suggest continuity. There are petrographic and chemical differences between the Early Bronze Period and the Middle Bronze Period samples of the later period. This must be related to the different communities that came to the region at the end of the Early Bronze Age, and it is important that this situation was also determined by archaeometric analysis.

With the study, the determination of the additives in the pastes of the ceramics, the surrounding clay sources and geological formations, and the ophiolite formation around Kinet Höyül and the contents of the alkaline basalt rocks are clues for the possible sources of the ceramics. It strengthens the idea that ceramics belonging to different periods were produced locally with clay material taken from the close environment according to their parent rocks. Of course, although ophiolite and alkaline basalt formations are known from different regions, it strengthens the possibility that they obtained and exploited the raw material source from the closest place.

Among the ceramics grouped according to their origin rocks, Serpentinite-amphibolite, Ophicarbonate, rocks associated with ophiolite, Alkaline basalt, andesite volcanic rocks are found in the region. The production places of this group of ceramics should be sought in these regions. While alkaline basalts are also known in the Gedikli region east of Amanoslar, the chemical contents of the clay and ceramic samples of this region differ.

According to the results of the chemical analysis, the high values of MgO and Cr_2O_3 (Chromium) in clay and samples due to the formation of ophiolite give an important clue, especially the samples taken from near Tepsitepe and Deliçay have this feature. The high MgO and Cr_2O_3 (Chromium) values in some ceramic samples give information about the production sites.

This study, which aims to determine both the differences in their own periods and the continuity relations in the later periods, in the ceramics recovered from Kinet Höyük in different periods will also form a database for future studies.

REFERENCES

Deniz K. Buzlukdağı (Kırşehir) alkali magmatik kayaçların jeolojisi, petrolojisi ve konfokal raman spektrometresi ile incelenmesi, yayınlanmış yüksek lisans tezi, Ankara üniversitesi fen bilimleri enstitüsü, Ankara. (2010).

Deniz K, Kadioglu, Y.K. "Geochemistry of salts and the effect of trace elements on human health: Turkey salt resources", International Journal of Environmental Analytical Chemistry, doi:10.1080/03067319.2021.1934830 (2021).

Doyuran, V. "Erzin ve Dörtyol ovalarının jeolojik ve hidrojeolojik özellikleri" Türkiye Jeoloji Kurumu Bülteni, *C.* 25, 151 - 160, Ağustos, (1982).

Gates, M.H. "Kinet Höyük (Hatay, Turkey) and MB Levantine chronology." Akkadica, 119-120, 77-101, (2000).

Gates, M.H. "Dating the hittite levels at kinet höyük: a revised chronology", In Structuring and Dating in Hittite Archaeology, edited by Dirk Paul Mielke, Ulf-Dietrich Schoop, and Jürgen Seeher, 293-309. BYZAS 4. Istanbul: Deutsches Archäologisches Institut, (2006).

Gutsuz P, Kibaroğlu, M G, Sunal, G, Hacıosmanoğlu, S. "Geochemical characterization of clay deposits in the Amuq valley (southern Turkey) and the implications for archaeometric study of ancient ceramics", Applied Clay Science,141, 316–333, (2017).

Kadıoglu Y.K, Deniz K. ve Koralay T. "Nature of quaternary basalts from amanus mountain: southern part of Turkey", 18th International Multidisciplinary Scientific GeoConference Sgem2018, 331-338, (2018).

Kibaroğlu M. "Petrographische und geochemische untersuchungen an archäologischer keramik aus Nordost-Syrien, SüdostAnatolien", Ost-Anatolien und Ost-Georgien vorgelegt von Mustafa Kibaroğlu aus Ardeşen/Türkei, (2008).

Kibaroğlu M. Archaeometric_investigations_of_kura-araxes ware, International Symposium on East Anatolia—South Caucasus Cultures: Proceedings I, Edited by Mehmet Işıklı and Birol Can, Cambridge Scholars Publishing, (2015).

Lustrino M, Sharkov E. "Neogene volcanic activity of western Syria and its relationship with arabian plate kinematics" Journal of Geodynamics 42,115–139, (2006).

Sarıfakılıoğlu, E, Sevin M, Dilek T. Türkiye ofiyolitleri. MTA, Özel Yayın Serisi:35, Ankara, (2017).

Türkecan, A.Türkiye'nin senozoyik volkanitleri. MTA Yayınları, Özel Yayın Serisi-33. (2015).