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Insights into ancient ceramic technology: a comprehensive analysis of mineralogy, chemistry and firing conditions

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ABSTRACT

The intensive integration of Azerbaijan into the global economy, mainly through international gas and oil pipeline construction, has led to significant archaeological research in the past two decades. The construction of the Baku-Tbilisi-Ceyhan oil pipeline (BTC) and the Southern Caucasus Pipeline gas pipeline (SCP) prompted a four-year archaeological fieldwork program, followed by a six-year post-excavation program. The current work applied an interdisciplinary approach using various instrumental methods for studying ancient artifacts found during those projects. The thermogravimetric method and differential thermal analysis were employed to obtain insights into the production technology of the ancient pottery and information about the mineralogy of the ceramic sherds. The complex processes involved in firing the ceramic paste have been studied extensively, and patterns in mass loss ratios during different temperature ranges have been established. In total, 15 samples were investigated, and the thermogravimetric analysis of ceramic shards revealed that the firing temperature of the samples was in the range of 700 °C. XRD analysis confirmed the presence of quartz, feldspar, and clay minerals in the ceramic samples. The presence of calcite and other specific minerals is subject to the origin of the ceramic materials. The results obtained from this multidisciplinary approach provide insights into the firing technology and the origin of the ceramic samples.

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INTRODUCTION

Modern archeology increasingly turns to an interdisciplinary approach using various instrumental methods for studying ancient artifacts (Meyvel *et al*., 2012). Pottery is the most critical attribute for defining the Neolithic era, and a comprehensive description of ancient pottery most often includes a description of its mineralogical, chemical, and thermal properties. The analytical results obtained using these methods can lead to essential conclusions in dating studies and the development of ancient technologies. Thermal analysis has been widely applied to investigate ancient ceramics in various combinations: thermogravimetry (Molodin *et al*., 2019; Mammadov *et al*., 2023), simultaneous thermal analysis, thermoluminescence (Polymeris *et al*., 2007), etc. One of the aims of the investigations was the estimation of firing temperature, as it is considered a characteristic of the technological level of ancient society (Papadopoulou *et al*., 2006; Meyvel *et al*., 2012). Under normal conditions, the initial firing temperature in the kiln is higher than the temperature on the bonfire or in the cooking oven (Chatfield, 2010). When firing pottery on an open fire, ceramics are heated up to 800 °C. The temperature in the kiln can reach a maximum temperature of up to 1250 °C (Legodi & de Waal, 2007). Ideally, thermal analysis could help distinguish between ceramics made by different technologies and thus act as an indirect tool to determine the origin of ceramics. This method can be used to track the development of furnace technology. Although the accuracy of the reported dates has been questioned (Drebushchak *et al*., 2018), the applicability of these methods remains one of the valuable tools for estimating the firing temperature of ceramics, alongside other newly developed methods (Rasmussen *et al*., 2012). This study aimed to analyze 12 ancient ceramic sherds including five samples (samples N5, N6, N9, N10 and N11) from the Baku Tbilisi Ceyhan oil pipeline (BTC) funded archaeological program area and a local raw ceramic paste sample using TG/DTG-DTA and PXRD techniques. The primary objectives of this work were to characterize the ancient ceramics in terms of their mineralogical and chemical content, investigate their thermal behavior to determine their firing temperature, and classify them with similar properties. When discussing the experimental findings, we will refer to these samples as indicated in Tables 1 and 2.

Table 1: Mass-loss of ancient ceramic samples and raw ceramic pastes in the temperature intervals

Sample code	Sample location	Mass loss, %			m1, % ≤350 °C	m2, % 300- 650 °C	m3, % 650- 850 °C	Total mass loss, %
		≤350 °C	≤600 °C	≤850 °C				
N1	Leletepe	98.70	97.90	96.32	1.30	0.80	1.58	3.68
N2	Leletepe	96.47	94.4	91.72	3.53	2.07	2.68	8.28
N3	Leletepe	97.33	95.59	94.64	2.67	1.74	0.95	5.36
N4	Leletepe	97.98	96.56	94.75	2.02	1.42	1.81	5.25
N5	Shomutepe	96.93	95.31	92.10	3.07	1.61	3.21	7.90
N6	Menteshtepe	98.48	97.52	97.11	1.52	0.96	0.41	2.89
N7	Polutepe	96.30	93.98	88.51	3.70	2.32	5.47	11.49
N8	Ismailtepe	95.57	92.82	88.33	4.43	2.75	4.49	11.67
N9	Hesensu	97.29	96.26	95.82	2.71	1.03	0.44	4.23
N10	HajiElimkhanli	96.76	96.52	95.26	3.24	0.24	1.26	4.74
N11	Goytepe	98.16	96.68	95.44	1.84	1.48	1.24	4.56
N12	Lenkeran	97.99	96.87	96.26	2.01	0.62	0.61	3.74
CP1	Modern ceramic paste	91.94	88.78	87.68	8.06	3.16	1.1	12.32
CP2	Modern ceramic paste	85	79.55	78.61	15	5.45	0.94	21.39

Table 2: Mineral compositions of ancient ceramic sherds and modern ceramic pastes

Sample Code	Sample location	Quartz, mass %	Feldspar, mass %	Calcite, mass %	Clay minerals, mass %	Other minerals, mass%
N1	Leletepe	26.7	Albite -31.3 Microline-22.6	0	Muscovite -8.9	Diopside -10.4
N2	Leletepe	54.8	Anorthite -29.3	3.7	Muscovite -10.3	Maghemite1.9
N3	Leletepe	40.0	Anorthite-29.8	1.9	Muscovite -27.1	Maghemite1.2
N4	Leletepe	29.1	Albite-39.0	8.6	Muscovite -7.3	Diopside -16.0
N5	Shomutepe	42.4	Albite -28.9	16.2	Muscovite -12.5	
N6	Menteshtepe	42.9	Anorthite -22.1		Muscovite -35.0	
N7	Polutepe	33.8	Albite -21.7	10.9	Muscovite -33.6	
N8	Ismailtepe	35.2	Albite -21.3	17.7	Muscovite -23.0	Brushite-2.8
N9	Hesensu	37.4	Albite -43.7	6.1	Muscovite -12.8	
N10	Haji Elmkhanli	27.4	Albite -42.4	5.6	Muscovite -24.6	
N11	Goytepe	56.3	Albite -41.8	1.9		
N12	Ballabur Castle	30.0	Albite -55.4		Muscovite -7.4	Zeolite-7.2
N13	Yardimli	44.1	Albite -31.8	13.8	Muscovite -10.3	
CP1	Modern ceramic paste	42.6	Albite -9.5	0	Muscovite -40.5 Montmorillonite-7.3	
CP2	Modern ceramic paste	42.0	Albite -14.7	0	Muscovite-36.2 Montmorillonite-7.3	

MATERIALS AND METHODS

The Institute of Archeology, Ethnography, and Anthropology of Azerbaijan National Academy of Sciences provided the samples of single fragments of ceramics found during the Baku Tbilisi Ceyhan oil pipeline (BTC) funded archaeological fieldwork program was conducted from 2001 to 2011 and "Karabakh Neolithic-Eneolithic Expedition" in the territory of the Republic of Azerbaijan. Most of these specimens are believed to be from the Neolithic period and may have been used for cooking or preserving food. The samples were air-dried overnight at 50 °C before analysis and finely powdered in an agate mortar. Two raw ceramic paste samples were also analyzed as reference material (Samples CP1 and CP2).

PXRD was performed using a D2Phaser (Bruker) diffractometer with Ni-filtered CuKα radiation on randomly oriented samples. The samples were scanned at the region of $5 \leq 2\Theta \leq 75°$ at a 1.2 °/min scanning speed. Semi-quantitative estimates of the abundance of the mineral phases were derived from the PXRD data, using the intensity of specific reflections, the density, and the mass absorption coefficients of the elements for CuKα radiation.

Thermogravimetric and differential thermal analysis of ceramic powders were carried out in a Perkin Elmer STA6000 Simultaneous Thermal Analyzer with the following parameters: heating ranges from ambient to 950 °C, heating rate 5 °C, balance sensitivity- 0.1 µg, and nitrogen gas flow-20 mL/min.

Background, Location, and Accession of Archaeological Materials

Azerbaijan's integration into the world economy, especially the construction of international gas and oil pipelines, has triggered an intensification of research in the field of archeology over the past two decades. The Baku Tbilisi Ceyhan oil pipeline (BTC) construction took three years. It was in 2005 and was preceded by an archaeological program that began in 2001 and ended in 2009 with a series of reports (Lyonnet *et al.*, 2008, 2012, 2016; Lyonnet & Guliyev, 2010; Herrscher *et al.*, 2018; Palumbi *et al.*, 2018; Maynard *et al.*, 2022) analyzing excavation data and subsequent studies. A detailed map of the research area is provided elsewhere (Nishiaki *et al.*, 2019a). The BTC was built first, from the Caspian Coast to the Georgian border in 2003 and 2004, while the Southern Caucasus Pipeline gas pipeline (SCP) was built in 2005, running from the Georgian border towards the Caspian and parallel to the BTC. A four-year archaeological fieldwork program was conducted from 2001 to 2005, followed by a six-year post-excavation program ending in early 2011 (Taylor & Maynard, 2011). The project "Ancient Kura" was established in 2010 as a joint research group between colleagues from Azerbaijani and Georgian research institutions, funded by ANR (Agence Nationale de la Recherche) in France and DFG (Deutsche Forschungs gemeinschaft) in Germany. The group aimed to investigate the interaction and interdependency between humans and the landscape from early sedentism to the beginning of the Bronze Age, from the 6th to the 3rd millennium BCE. The group sought to understand the significant transformations in the settlement history of the Southern Caucasus, such as the Neolithisation, the development of short-term settlements, the appearance of ostentatious burial sites, and the role of environmental factors in these developments. The project challenged assumptions that favorable conditions in the early Holocene invited human communities to settle and develop a subsistence economy in the 6th millennium BCE and that the shift to archaeologically less visible lifeways afterward was solely due to environmental constraints.

Göytepe and Hacı Elamxanlı Tepe have been excavated in the Middle Kura Valley of West Azerbaijan within the "Ancient Kura" project (Nishiaki *et al.*, 2013, 2015; Nishiaki & Guliyev, 2021). Both sites are located approximately 40 km east of Shomutepe and are considered some of the largest mounds known in the region. Along with Shomutepe, these sites are among the oldest agricultural villages found thus far in the area.

The lithic industry at these sites also shows similarities and differences to Göytepe. The radiocarbon dates for the Neolithic layers of Göytepe (Nishiaki *et al.*, 2015; Nishiaki & Guliyev, 2021) and Haci Elmchanli Tepe (Nishiaki *et al.*, 2013) vary from 6300 (BP) to 7000 (BP) (Cal B.C.E. from 5400 to 6000). These excavations have contributed significantly to our understanding of the earliest agricultural villages in the Middle Kura Valley and the relationship between these settlements and those in other regions.

The excavations at Göytepe and Hacı Elamxanlı Tepe in West Azerbaijan provide a glimpse into developing agricultural settlements in the Middle Kura Valley. These sites offer valuable insight into the Neolithic period and the relationship between the earliest pottery Neolithic settlements in the region and those in other areas, such as Upper Mesopotamia.

The 2012 excavations at Hacı Elamxanlı Tepe (Nishiaki *et al.*, 2013) were aimed at determining the site's chronology and its relationship to the Shomutepe-Shulaveri phase. The excavations revealed radiocarbon dates from the latest levels of the site dating back to the very early centuries of the 6th millennium BCE, earlier than generally known for the Shomutepe-Shulaveri sites. These new circumstances make Hacı Elamxanlı Tepe the oldest Pottery Neolithic settlement known in the Middle Kura Valley and one of the oldest Neolithic sites in the southern Caucasus. The study shows that Neolithization was almost simultaneously underway on both sides of the Lesser Caucasus Mountains.

Most pottery found at these sites is plain mineral-tempered, similar to the wares found in the lowest levels of Göytepe. However, two pieces of finely painted ware were also found that are reminiscent of the Upper Mesopotamian traditions of Samarra and Early Halaf. These pieces' paste and decoration patterns strongly suggest that they originated in other remote regions. This painted pottery has never been found in the larger pottery assemblages from Göytepe or other sites in the Middle Kura. Still, parallels are known from the Araxes Valley. The discovery of this pottery at Hacı Elamxanlı Tepe represents the first example of this type from the north, suggesting that contact with contemporary societies in Upper Mesopotamia extended to the northern side of the Lesser Caucasus.

The 2016-2019 excavations at Damjili Cave (Nishiaki *et al.*, 2019a, 2022) showed that the Neolithic economy in the region emerged abruptly around 6000 BC and revealed continuity in the use and manufacture of tools from the Mesolithic to the Neolithic period. Although the research on the earliest Neolithic in the South Caucasus is still in its early stages, the radiocarbon dates obtained from Göytepe (Nishiaki *et al.*, 2015, 2019b) and Hacı Elamxanlı Tepe suggest that several settlements representing the earliest pottery Neolithic emerged almost simultaneously at the beginning of the sixth millennium BC in the northern and southern foothills of the Lesser Caucasus Mountains. The radiocarbon dates from Damjili Cave overlap the occupation period of Goytepe (~7640-7450 cal BP) and include two dates pointing to the late 8th-millennium cal BP (Nishiaki *et al.*, 2019a).

Since then, new calibrated dates and further research have established with certainty that the Shomutepe-Shulaveri Culture (SSC) belongs to the Late Neolithic and developed during the 6th millennium. Mentesh tepe is among the earliest known settlements of the SSC (Lyonnet *et al.*, 2016). Radiocarbon conventional ages for the Mentesh Tepe are between 6600 to 6900 BP. Therefore, contrary to the previous proposals, Mentesh Tepe is among the earliest known settlements of the SSC and Hacı Elamxanlı Tepe.

The study of the Neolithic-Eneolithic monuments in Mughan began in the 1960s and continued until 1979. A new stage in the study of the Mughan of the Neolithic-Eneolithic period was begun in 2004. The Mughan Neolithic-Eneolithic expedition is conducting archaeological research on Polutepe and Alkhantepe. Despite being close to each other, these sites represent completely different ethnocultural traditions and stages of the studied epoch. Simultaneous study of genetically and chronologically different monuments located in the same territory has allowed for the revealing and tracing of more ethnocultural aspects and other processes. Based on stratigraphic estimations, the age of the Neolithic-Eneolithic layer of the settlement of Polutepe is approximately from the end of the fifth to the beginning of the fourth millennium BC (Akhundov *et al.*, 2018).

Modern physical and chemical analysis methods were applied within the project's framework. In particular, more than 40 radiocarbon determinations were carried out, the first large series of such dates in Azerbaijan. Florida-based Beta Analytic provided all dates, and reports are available from the ADS archive (Beta Analytic 2005; 2006a; 2006b; 2006c). The mineralogical analysis of the clay samples and pottery fragments (three fragments originating from Kamiltepe) revealed important information about the raw materials used and the firing process of the pottery (Lyonnet *et al.*, 2012). The X-ray diffraction analysis of the samples revealed that calcite is present until a firing temperature of 700 °C, indicating the reaction of calcite with clay minerals to form aluminosilicates between 700 °C and 800 °C (Lyonnet *et al.*, 2012). The presence of wollastonite in some pottery fragments suggests the occurrence of this reaction during the firing process. Investigating the mineralogical composition using an electron microprobe analysis system (EMPA) equipped with an EDX unit provided further insight into the different feldspar minerals in the samples.

RESULTS AND DISCUSSIONS

The ceramic paste used in row pottery comprises clay (smectites and kaolinites) and tempering materials such as sand, calcite, and organic fillers. The only component that changes during a mild firing (around 700 °C) is the clay because the tempering materials are more thermally stable than the clay. These changes include dehydration (≤350 °C), decomposition of hydroxyls (350-600 °C), and decomposition of carbonates, mainly calcite (600-850 °C) (Papadopoulou *et al.*, 2006; Drebushchak *et al.*, 2007; Stratis *et al.*, 2011), if present in the source material. Higher firing temperatures above 1000 °C cause the ceramic paste to transform into a glassy substance containing particles of added temper materials, resulting in a product vastly different from the original paste.

It is significant to note that compared to kaolinite, which starts to lose mass due to dehydroxylation at temperatures of about 400 °C and higher, these changes are more pronounced in montmorillonite clay because it contains bound water and hydroxyl groups. However, both clay minerals are transformed into an anhydrous amorphous phase during firing. The TG/DTG/DTA curves in Figure 1 show the weight loss and weight loss rate of sample N1, which is representative of the 14 samples described above. The DTG curve is a derivative of mass loss and indicates the steps of mass loss. There are three distinct peaks on the DTG curve in Figure 1; two of them, located in the low-temperature region, can be attributed to the processes of dehydration and dehydroxylation. Therefore, both processes also occur when ancient pottery is heated. And the third peak is more likely associated with the decomposition of calcite. The DTA curve shows four different regions of endothermic processes: three of them instead indicate the same conclusions based on the DTG analysis. The fourth endothermic peak around 900 °C is common to many different ceramic samples described elsewhere (Papadopoulou *et al.*, 2006) and may be attributed to the polymorphic transformation of muscovite or illite.

Figure 2 shows the results of TG/DTG experiments carried out on a raw ceramic paste sample: mass loss values for the ceramic paste sample were 8.06% upon dehydration and 3.16% upon decomposition of hydroxyls. Dehydration and dehydroxylation occur at temperatures between 50 and 350, and 600 degrees Celsius, respectively, showing that the material under investigation experiences two mass loss steps and lacks calcite.

The mass loss patterns of 14 ceramic samples are summarized in Table 1 according to the temperature intervals of t≤350 °C (m_1 - dehydration), 350-600 °C (m_2 - dehydroxylation), and 600-850 °C (m_3 - decomposition of carbonates, micas, etc.). These TG results vary among the ceramic samples and differ from those of the ceramic paste samples. Various techniques exist in the literature to determine the firing temperature of ancient pottery (Meyvel *et al.*, 2012). The thermogravimetric method detects only reversible thermal transformations during the second heating of the sample. New transformations will only be observed at temperatures above the upper limit of the first

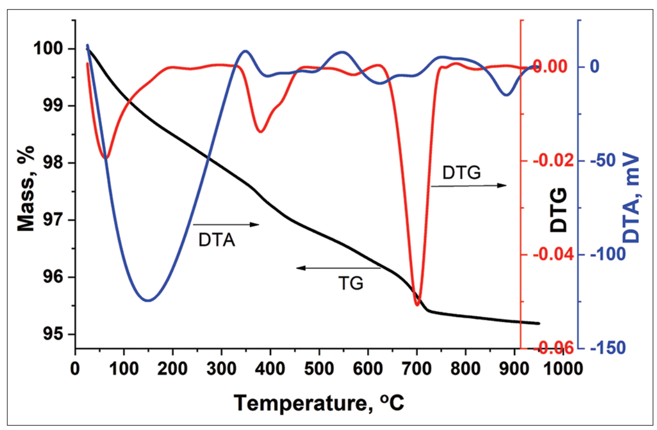

Figure 1: Representative TG, DTG and DTA profile of ceramic shred from Hesensu archeological site (Sample N9)

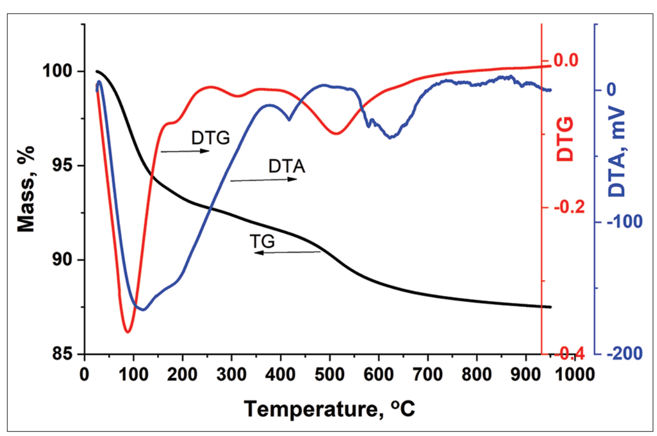

Figure 2: TG/TDG/DTA profile of the raw ceramic paste (Sample CP1)

heating. Thermal transformations in clay become irreversible due to chemical reactions that release gaseous products, form new minerals or undergo irreversible phase transformations. The endothermic peaks in differential thermal analysis can identify the upper limit of temperature intervals for the loss of chemically combined hydroxyl groups by clay minerals such as smectites and kaolin. It has been suggested that if such peaks are present, the pottery has not previously been heated above this temperature. If they are absent, it has been fired above this temperature (Meyvel *et al.*, 2012). However, this statement applies only to freshly prepared ceramic products (Drebushchak *et al.*, 2005). Experimental data show that most ancient ceramics lose water, i.e., hydroxyl groups when heated to 550 °C (Drebushchak *et al.*, 2018). Therefore, it must be assumed that the firing temperature of ancient ceramics was below 550 °C or that the decomposition of hydroxyls is reversible.

Nonetheless, studies suggest that the dehydration and dehydroxylation of clay fired up to 700 °C (mild firing) is a partially reversible process (Fajnor & Jesenák, 1996; Shoval *et al.*, 2011; Gallet & Le Goff, 2015). Barrett (2015) demonstrated that the dehydroxylation of clay heated up to 700-800 °C is reversible and can also be used to date ancient ceramics after re-hydroxylation at ambient conditions. Therefore, dehydroxylation upon reheating ancient pottery indicates a low or short-term firing temperature.

The data from Table 1 suggest that raw ceramic paste generally experiences a larger mass loss percentage during hydroxylation and dehydration than ancient ceramic shards. Additionally, the total mass loss percentage during hydroxylation and dehydration is typically higher for raw ceramic paste. Finally, the results indicate that as ceramics age, they tend to experience a larger mass loss percentage during hydroxylation. While this is not a precise measure, it may provide a helpful clue to distinguish between recently-fired ceramics and older ones.

In total, 15 samples were analyzed by the XRD method. Figure 3 is a representative XRD pattern of the ceramic sherd from the Hasansu archeological site. Findings from the XRD analysis are summarized in Table 2. X-ray diffraction analysis of ceramic fragments shows that all studied samples contain comparable minerals, including quartz, feldspar, clay (Figure 3 & Table 2), and some associated minerals.

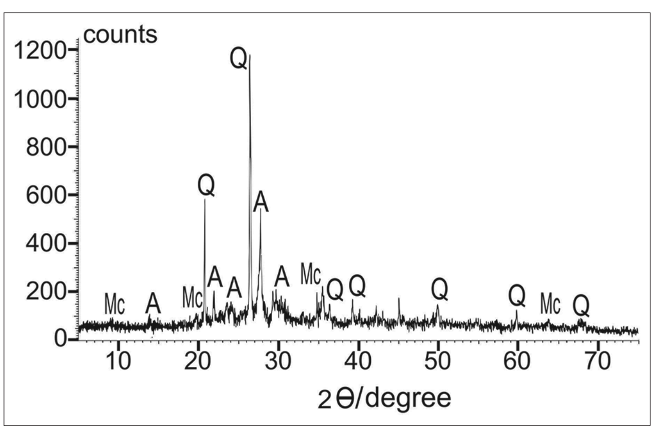

Figure 3: Representative XRD patterns of the ceramic sherd from Hasansu archeological site (Sample N9); Mc-muscovite, A- Albite, Q-quartz

The raw ceramic pastes, CP1 and CP2, were produced by a local potter using local raw materials, serving as modern examples. Table 2 shows that calcite is absent in the raw ceramic paste samples. XRD patterns of raw ceramic paste show the existence of clay minerals, quartz, and feldspars used as tempering materials. Similarly, samples N1 and N6 do not contain calcite. Calcite serves as a frequently employed indicator for identifying the origin of ceramics, particularly when Ca-rich raw clay deposits are detectable in proximity to the archaeological site. Additionally, it can provide some insight into the firing temperature to a certain extent. It can be added to ceramic paste or found in the original clay as a natural impurity. The presence of calcite in ancient pottery has been associated with low-temperature firing at approximately 700 °C (Kloužková *et al.*, 2014). However, it is not always clear-cut since silicates generated from clay minerals can selectively absorb carbon dioxide from the atmosphere (Kalinkin *et al.*, 2008, 2009). On the other hand, it's important to note that the lack of calcite or its minimal presence does not necessarily signify that the ceramic material was fired at temperatures exceeding 700 °C due to the possibility that the original ceramic mixture might not have contained any calcite in the first place.

The XRD analysis indicates that diopside is present in samples N1 and N4, and maghemite is in samples N2 and N3. These minerals were not found in the analysis of the raw ceramic mass, indicating potential differences between ancient and modern ceramic origins. At the same time, muscovite is present in all the studied samples listed in Table 2. The findings align with a prior study in which X-ray powder diffraction patterns of ceramic samples show that diopsides are present at temperatures higher than 900 °C, while calcite and muscovite disappear at 800 °C (Rasmussen *et al.*, 2012). Therefore, it is reasonable to infer that the samples labeled N1 and N4 were subjected to firing temperatures lower than 800 °C. The same likely holds for all other ceramic fragments listed in Table 1, given that muscovite is present in all of them.

Feldspars, such as albite, microcline, and anorthite, can be added to the ceramic mass as a tempering agent or present in the original clay as a natural impurity since clay is believed to be a weathering product of feldspar. Feldspars remain stable at temperatures up to 950 °C (Stubna *et al.*, 2013). Alkaline feldspars remain in a glassy state for a long time when melted, while anorthite crystallizes quickly. Therefore, the presence of feldspars cannot accurately indicate the firing temperature of ceramics. Table 2 illustrates that most of the ceramic samples contain albite. In the case of samples N2 and N3, feldspar is presented by anorthite (30 mass%), and sample N1 contains around 23 mass% of microcline along with 31 mass% of albite.

Quartz is a significant component of tempering materials and can also exist in raw clay as a natural impurity. Quartz is a constant constituent component in all examined samples, ranging from 26 to 56 mass%, as shown in Table 2. When heated, quartz undergoes a phase transition at approximately 573 °C, and it appears as a small endothermic peak in DTA curves. However, this process is reversible, and no evidence of prior heating can be detected after cooling.

The presence of muscovite or illite in the samples suggests that the temperature at which they were fired was less than 950 °C. In contrast, the existence of calcite suggests that the firing temperature was approximately 700 °C (Papadopoulou *et al.*, 2006).

CONCLUSIONS

The firing temperature of ancient pottery can be determined using the changes in the ceramic paste during firing. The thermogravimetric analysis suggests that raw ceramic paste generally experiences a larger mass loss percentage during hydroxylation and dehydration than ancient ceramic shards. As ceramics age, they tend to experience a larger mass loss percentage during hydroxylation. These findings can be used to distinguish between recently-fired ceramics and ancient ones.

X-ray diffraction analysis can provide information about the mineralogy of the pottery, which might be essential to establishing the origin of ancient ceramics.

Overall, the mineralogical analysis of the clay and pottery samples has shed light on the raw materials used and the firing process of the pottery. These results will help reveal the potential of applied methods as a tool for analyzing earthenware pottery shards and their production methods in Azerbaijan. This information can be used to comprehend ancient civilizations' production techniques and use of natural resources.

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