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COMPREHENSIVE INVESTIGATION OF NEOLITHIC CERAMIC SAMPLES: FIRING TECHNOLOGY AND AGE INSIGHTS[†]

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Thermogravimetric (TG/DTG), thermoluminescence (TL), and X-ray powder diffraction (XRD) techniques were applied to characterize samples collected from the archaeological site of Polutepe in Azerbaijan, dating to the Neolithic period, and gave new information on the firing technology. The thermogravimetric analysis of ceramic shards from Polutepe revealed that the firing temperature of the samples was in the range of 700°C, based on the presence of calcite in the sample. XRD analysis confirmed the presence of quartz, feldspar, and clay minerals in the ceramic samples. According to XTD analysis the mineral composition of the ceramic sample from Polutepe site was as follows: Quartz-33.8 mass%, Feldspar (albite)-21.7 mass%, Muscovite- 33.6 mass%, and Calcite- 10.9 mass%. TL glow-curve intensity at 325°C was measured to estimate the historical dose of the sample, which was found to be 22.19±1.36 Gy. The concentration of U, Th, and K were 2.24±0.20 ppm, 8.31±0.80 ppm, 2.39±0.23% respectively. Dose rate and age calculation were conducted using the DRAC, version 1.2 and output results are as follows: Environmental dose rate: 3.46±0.19 mGy/a; Age of the sample: 4.400±530 BC years which are in line with the stratigraphically estimated age of this area and with the radiocarbon age (4270±160 BC) reported in our previous work. The results obtained from this multidisciplinary approach provide insights into the firing technology and age of the ceramic samples.
Keywords: *Thermogravimetry; X-ray powder diffraction; Ancient ceramic; Firing temperature; Clay; Quartz; Feldspar*
PACS: 78.60.Kn

INTRODUCTION

Archaeology in modern times is adopting an interdisciplinary methodology that employs a range of instrumental techniques to examine ancient artifacts. The defining characteristic of the Neolithic period is pottery, and a detailed account of ancient pottery typically involves an explanation of its mineralogical, chemical, and thermal attributes. The outcomes of the analyses conducted through these methods can help make significant findings in studies of dating and the evolution of ancient technologies. Thermal analysis has been extensively employed to scrutinize ancient ceramics using a variety of approaches such as powder X-ray diffraction, thermogravimetry, simultaneous thermal analysis, and thermoluminescence.

To check the quality of ceramics, thermal analysis methods are widely used, allowing you to control the processes during firing [1][2]. The traditional approach is that if gas is released from the sample during heat treatment, then the thermal transformation of minerals in the clay composition is considered irreversible [3]–[7]. When reheating, i.e., when a ceramic product is analyzed, exothermic reactions with gas release occur only at temperatures above the first heating.

Thermogravimetric studies of ancient ceramics and pottery are based on these considerations. Based on these studies, the production conditions are reconstructed, and attempts are made to identify sources of raw clay, which enables archaeologists to guess the technological level of the ancient potters and restore ancient trade links between regions by comparing ceramics from different localities.

Ceramics usually consists of clay minerals and various additives like quartz, feldspars, calcite, etc. These minerals contain unique information about the firing conditions of raw materials. Because quartz and feldspars are thermally very stable, only clay and calcite constituent minerals undergo significant changes during firing. Clay minerals (smectites and kaolinite) transform into an amorphous phase, while calcite decomposes to form CO_2. The powder X-ray diffraction (PXRD) [1] method provides adequate information on the mineral composition of ceramics, thereby allowing estimation of the firing temperatures of ancient ceramics. And the presence of certain minerals helps to establish the origin of ceramics. The possibility of measuring the TL luminescence properties of quartz in order to determine the firing temperature of archeological ceramic artifacts was also investigated in [8].

MATERIALS AND METHODS

The Institute of Archeology, Ethnography, and Anthropology of ANAS provided samples of single fragments of ceramics found at the archeological site Polutepe. It is located on the eastern outskirts of Uchtepe village of Jalilabad region, Azerbaijan Republic, on the right (southern) bank of the Injachai river (39°19' 37. 67" N, 48° 27' 05.71" E) at 38 m above sea level. A ceramic sample for analysis was taken at the base of the furnace, at a depth of 6.3 m from the standard reference point, 5.3 m into the Neolithic layer, and 0.7 m above the base of the settlement. 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.

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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≤2Θ ≤75° at a scanning speed of 1.2°/min. 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 range from ambient to 950°C, heating rate 5°C, balance sensitivity- 0.1µg, and nitrogen gas flow-20 ml/min.

The Harshaw TLD 3500 Manual Reader is used to measure the characteristics of TL samples. TL measurements were performed using a linear heating rate 20ºC/s from 50ºC to 400ºC. Three aliquots of 5 mg each of the samples were used for each measurement. TL data points represent the average of three different aliquots of the sample. A thin and uniform layer of feldspar grains was laid on the planchet surface in order to get full contact that ensures uniform TL signal from the sample.

In order to estimate the natural dose rate soil samples were collected from the site and U, Th, and K content analysis by gamma spectrometry Canberra GR4520 which has a low-level gamma spectrometry system with 15 cm lead shielding and high-resolution GeHP hyper pure germanium detector, having 43.5% resolution efficiency for 661.6 keV.

RESULTS AND DISCUSSIONS

Thermogravimetric analysis

The results of the TG and DTG analysis of the ceramic shred from Polutepe are presented in Fig. 1.

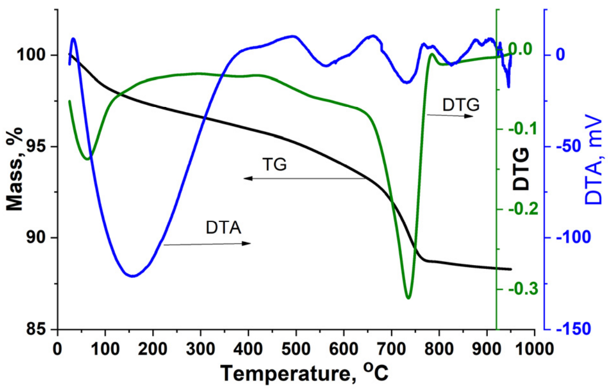

Figure 1. TG, DTG and DTA curves of ceramic shred from Polutepe

The DTG curve has a small peak at about 100°C and a deep peak at 650-750°C. A large peak in the temperature ranges from 100 to 400°C on the DTA curve indicates endothermic processes due to dehydration/dihydroxylation. Mass loss figures are summarized in Table 1. The total mass loss (m3) is 11.8%. Mass loss in the region ≤350C occurs due to dehydration (m1) and is 4.05%, and mass loss due to dehydroxylation (m2) occurs in the region of 350C÷600C and is 2.71%. Mass loss above a temperature of 600°C can be attributed to the decomposition of calcite (m3=5.12%) according to the reaction:

$$CaCO_3=CaO+CO_2$$

There are different approaches in the literature for determining the firing temperature of ancient pottery [9]. The basic idea of the thermogravimetric method is that only reversible thermal transformations will be detected if the sample is heated a second time. Upon reheating, transformations not observed in the previous heating will be detected only at temperatures above the upper-temperature limit of the first heating. The irreversibility of thermal transformations in clay occurs due to chemical transformations with the release of gaseous products, the formation of new minerals, or irreversible phase transformations.

Calcite is the most common "fingerprint" for determining the provenance of ceramics and, to some extent, for determining the firing temperature since it can be added to ceramic paste or found in the original clays as a natural impurity. The presence of calcite in ancient pottery is considered today the sign of low-temperature firing at about 700°C [4]. The concentration of calcite in the investigated sample determined by XRD method is 5.12% ; therefore, according to the traditional interpretation, the firing temperature of the samples was in the range of 700°C. The presence of calcite in ceramic samples from Polutepe was studied by exposing the ceramic powder to hydrochloric acid. The ceramic powder was kept in a 10% HCl solution for a week and periodically mixed. After that, the ceramic powder was thoroughly washed and dried at a temperature of 50°C for 48 hours. The results of the TG/DTG analysis of a ceramic sample treated in an HCl solution are shown in Figs. 2. The total mass loss (m3) is 8.28%. Mass loss in the region ≤350C occurs due to dehydration (m1) and is 5.42%, and mass loss due to dehydroxylation (m2) occurs in the region of 350C÷600°C and is 2.01%. Mass loss above a temperature of 600°C was 0.81 %, indicating the decomposition of the significant part of calcite.

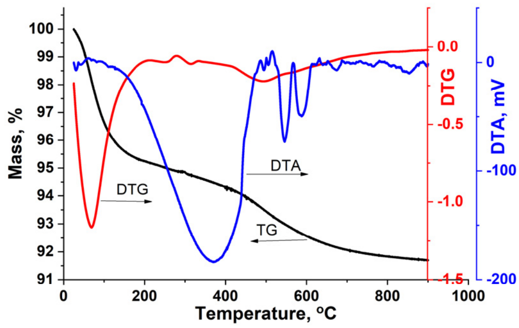

Figure 2. TG/DTG/DTA analysis of a ceramic sample treated in HCl solution X-ray phase analysis also reveals the calcite in the sample from Polutepe (Fig. 3).

Table 1. Mass-loss of ancient ceramic sample from Polutepe

Sample	Mass loss ≤350C, %	Mass loss ≤600C %	Mass loss ≤850C, %	m1 %	m2 %	m3 %	Total mass loss, %	m2/m1
Polutepe, natural	95.95	93.24	88.12	4.05	2.71	5.12	11.8	0.67
Polutepe, with HCl	94.58	92.57	91.76	5.42	2.01	0.81	8.28	0.37

Chemical and XRD analysis

XRD analysis of ceramic shreds reveals that all investigated samples contain similar minerals: quartz, feldspar, and clay (Fig.3).

Feldspars (in our case, albite) can be introduced into the ceramic mass as a hardening or be present in the composition of the original clay as a natural admixture since the clays themselves are weathering products of feldspar. Quartz is a significant component of tempering materials and also exists in raw clay as a natural mixture. Quartz undergoes a phase transition around 573°C when heated, but this process is reversible, and no signs of previous heating could be detected after cooling.

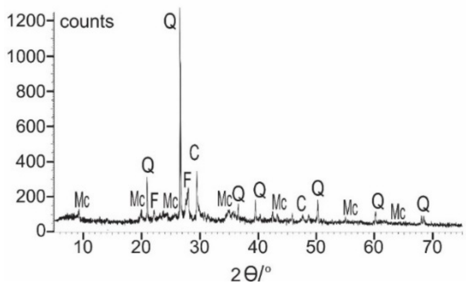

Figure 3. XRD patterns of ceramic shred from Polutepe. Mc-muscovite; Q-quartz; F-feldspar (albite); C-calcite.

According to XTD analysis the mineral composition of the ceramic sample from Polutepe site was as follows: Quartz-33.8 mass%, Feldspar (albite)-21.7 mass%, Muscovite- 33.6 mass%, and Calcite- 10.9 mass%.

TL analysis

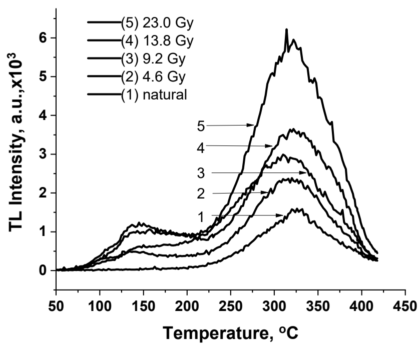

Figure 4. TL glow-curve of quartz samples extracted from ancient ceramic at different additional laboratory doses. (1) The TL glow curve of unirradiated quartz extracted from pottery sample. The four aliquots of quartz were irradiated with additional laboratory doses 4.6 (2); 9.2 (3); 13.8 (4); and 23 Gy (5) respectively. Dose rate- 0.194 Gy/s.

Fig. 4 illustrates the dose dependence of the TL glow curve from 0 to 24 Gy. Samples were irradiated with ^{60}Co gamma source then TL glow-curves measured after two days. Plotting the TL glow-curve intensity at 325°C against the dose adsorbed and backward extrapolation enables the estimation of historical dose equal to 22.19±1.36 Gy.

Soil sample collected from the close proximity of the pottery sample was air dried and kept in a closed environment for one month. The concentration of U, Th, and K were 2.24±0.20 ppm, 8.31±0.80 ppm, 2.39±0.23 % respectively. Dose rate and age calculation were conducted using the DRAC version 1.2 and output results are as follows: Environmental dose rate: 3.46±0.19 mGy/a and; Age of the sample: 4.400±530 BC years which are in line with the stratigraphically estimated age of this area and with the radiocarbon age (4270±160 BC) reported in our previous work [10].

CONCLUSIONS

TG and DTG analysis of the ceramic shred from Polutepe showed a total mass loss of 11.8%, with mass loss above 600°C attributed to the decomposition of calcite. The presence of calcite in the ceramic samples suggested a firing temperature of around 700°C. The studied ceramic shred from Polutepe consisted, as it was deduced from XRPD studies, mainly of quartz, calcite, feldspar (albite), and micas (muscovite).

The thermal properties of the studied ceramic sample from Polutepe obtained from the TG/DTG analysis were consistent with their mineralogical data.

The TL glow curve and dose rate calculations indicated an estimated historical dose of 22.19±1.36 Gy and an age of the sample of 4.400±530 BC years, respectively, which are in line with the stratigraphically estimated age of the area and previous radiocarbon dating results.

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КОМПЛЕКСНЕ ДОСЛІДЖЕННЯ ЗРАЗКІВ КЕРАМІКИ НЕОЛІТУ: ТЕХНОЛОГІЯ ВІДПАЛУ ТА ВІК

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Методи термогравіметрії (TG/DTG), термолюмінесценції (TL) і рентгенівської порошкової дифракції (XRD) були застосовані для характеристики зразків, зібраних з археологічної стоянки Полутепе в Азербайджані, що датуються періодом неоліту, і дали нову інформацію про технології відпалу. Термогравіметричний аналіз черепків кераміки з Полутепе показав, що температура відпалу зразків була в межах 700°C, виходячи з наявності кальциту в зразку. XRD аналіз підтвердив наявність кварцу, польового шпату та глинистих мінералів у зразках кераміки. За даними ХТD-аналізу, мінеральний склад зразка кераміки з стоянки Полутепе був таким: кварц – 33,8 мас.%, польовий шпат (альбіт) – 21,7 мас.%, мусковіт – 33,6 мас.%, кальцит – 10,9 мас.%. Інтенсивність кривої світіння TL при 325°C була виміряна для оцінки історичної дози зразка, яка виявилася 22,19±1,36 Гр. Концентрації U, Th і K становили 2,24±0,20 ppm, 8,31±0,80 ppm, 2,39±0,23% відповідно. Розрахунок потужності дози та віку було проведено за допомогою DRAC, версія 1.2, і отримані результати такі: потужність дози в навколишньому середовищі: 3,46±0,19 мГр/рік; вік зразка: 4,400±530 років до н.е., що відповідає стратиграфічно оціненому віку цієї території та радіовуглецевому віку (4270±160 до н.е.), про які ми повідомляли в попередній роботі. Результати, отримані в результаті цього мультидисциплінарного підходу, дають змогу зрозуміти технологію випалу та вік зразків кераміки.

Ключові слова: *термогравіметрія; рентгенівська порошкова дифракція; старовинна кераміка; температура відпалу; глина; кварц; польовий шпат*