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THERMAL ANALYSIS IN THE INVESTIGATION OF ANCIENT CERAMICS FROM THE POLUTEPE ARCHEOLOGICAL SITE

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Abstract: 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. TG/DTG analysis exhibits a characteristic profile of dehydration and dehydroxylation processes and calcite decomposition, which are traditionally interpreted as mild firing. The ceramic sample was characterized by X-ray powder diffraction for the mineralogical composition, and it consisted mainly of quartz, calcite, feldspars, and muscovite. For investigated ceramic sample, the thermal behavior investigation is consistent with their mineralogical findings and resulted in the firing temperature at 700 ◦C due to the existence of calcite.

Keywords: Thermogravimetry; X-ray powder diffraction; ancient ceramic; clay; quartz; feldspar

1. Introduction

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 to determine the firing temperature of archeological ceramic artifacts was also investigated in [8].

2. 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.

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 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 950ºC, heating rate 5ºC, 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 of 20ºC/s from 50ºC to 400ºC. Three aliquots of 5 mg of 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 to get full contact that ensures a uniform TL signal from the sample.

3. Results and discussions

Thermogravimetric analysis

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

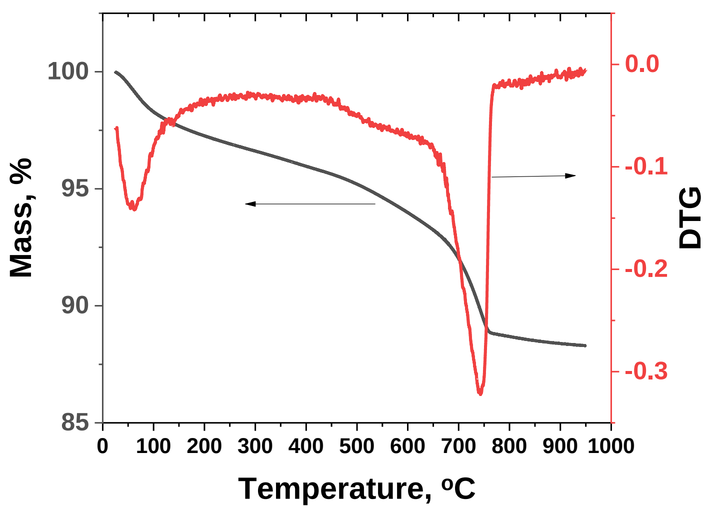

Fig. 1. TG and DTG curves of ceramic shred from Polutepe

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 600C 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 a sample is 5.12% (Table 2); 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 50C for 48 hours. The results of the TG/DTG analysis of a ceramic sample treated in an HCl solution are shown in Fig. 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÷600C and is 2.01%. Mass loss above a temperature of 600C was 0.81 %, indicating the decomposition of the significant part of calcite.

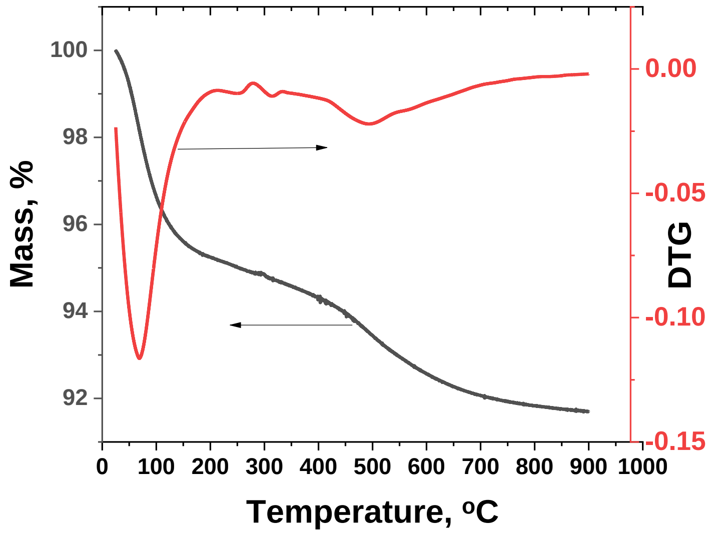

Fig. 2. TG/DTG analysis of a ceramic sample treated in HCl solution

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 and Table 2).

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.

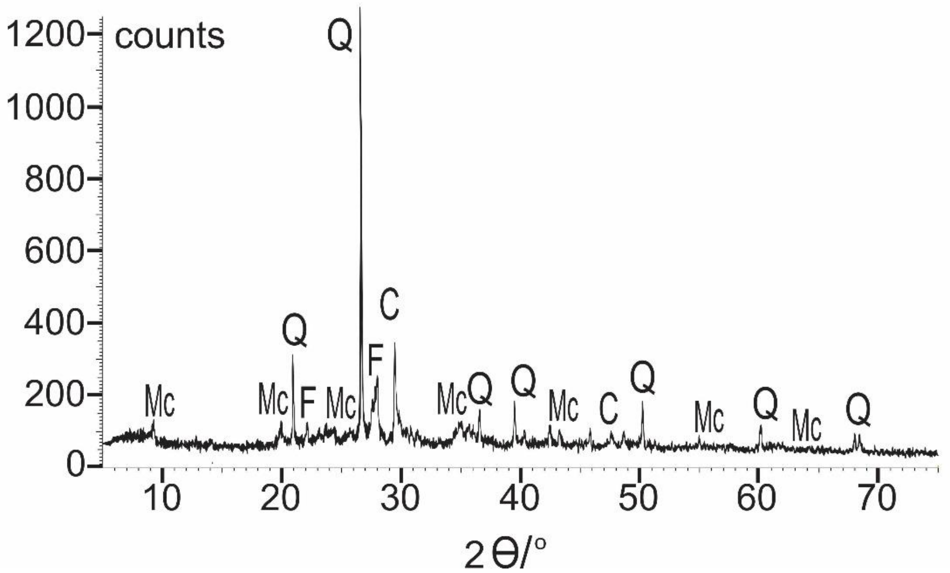

Fig. 3. XRD patterns of ceramic shred from Polutepe. Mc-muscovite; Q-quartz; F-feldspar (albite); C-calcite.

Table 2

Mineral composition of the ceramic sample from Polutepe

Sample	Quartz, mass %	Feldspar Albite, mass %	Muscovite, mass %	Calcite, mass %
PL1	33.8	21.7	33.6	10.9

TL analysis

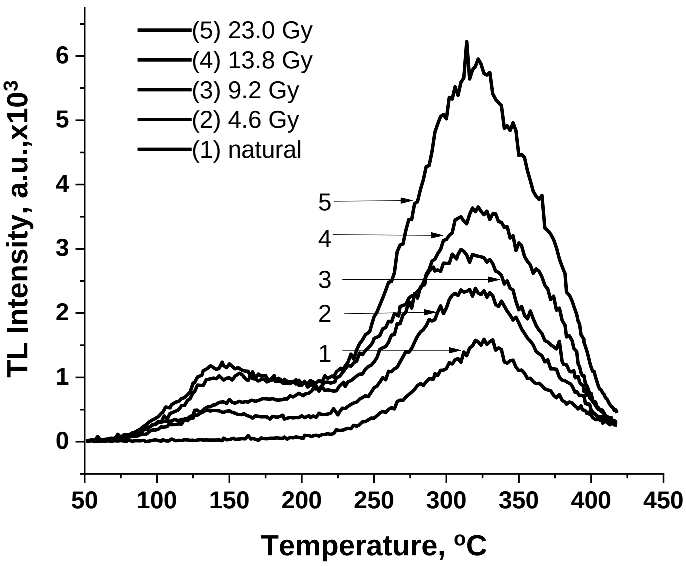

Fig. 4. TL glow-curve of quartz samples extracted from ancient ceramic at different additional laboratory doses. (1) The TL glow curve of unirradiated quartz extracted from pottery sample. The four aliquots of quartz were irradiated with additional laboratory doses of 4.6 (2); 9.2 (3); 13.8 (4); and 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 were measured after two days. Plotting the TL glow-curve intensity at 325°C against the dose adsorbed and backward extrapolation enables the estimation of a historical dose equal to 22.19±1.36 Gy.

Soil sample collected from the proximity of the pottery sample was air-dried and kept in a closed environment for one month. The concentration of U, Th, and K was 2.24±0.20 ppm, 8.31±0.80 ppm, and 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].

4. Conclusions

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. They resulted in a firing temperature of 700°C due to the presence of calcite.

The estimated age of the sample from the Polutepe archeological site is 4.400±530 BC years.

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ТЕРМИЧЕСКИЙ АНАЛИЗА ПРИ ИССЛЕДОВАНИИ ДРЕВНЕЙ КЕРАМИКИ, ИЗ АРХЕОЛОГИЧЕСКОГО ПАМЯТНИКА «ПОЛУТЕПЕ»

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Резюме: Методы ТГ/ДТГ и Рентген Структурный Анализ были применены для характеристики образцов, собранных на археологических раскопках Полутепе в Азербайджане, относящихся к периоду неолита, и предоставили новую информацию о технологии обжига. Анализ ТГ/ДТГ демонстрирует характерный профиль процессов дегидратации и дегидроксилирование, а также разложения кальцита, которые традиционно интерпретируются как мягкое обжигание. Керамический образец был охарактеризован методом рентгенофазового анализа на минералогический состав. Он состоял в основном из кварца, кальцита, полевых шпатов и мусковита. Для исследованного керамического образца исследование термического поведения согласуется с их минералогическими данными и привело к температуре обжига 700°C из-за наличия кальцита.

Ключевые слова: термогравиметрия; рентгеновская порошковая дифракция; старинная керамика; глина; кварц; полевой шпат

POLUTƏPƏ ARXEOLOJİ ƏRAZİSİNDƏN TAPILMIŞ QƏDİM KERAMİKA NÜMUNƏSİNİN TERMOQRAVİMETRİK ANALİZİ

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Xülasə: Neolit dövrünə aid olan Polutəpə Arxeoloji Ərazisindən Tapılmış Keramika Nümunəsinin xasssələrini tədqiq etmək üçün termoqravimetrik və rentgen struktur analizi aparılmışdır. Tədqiqatın nəticələrinə əsasən qədim keramikanın bişirilmə temperaturu təyin edilmişdir. TQ/DTQ analizinin nəticələri göstərir ki, keramikanı qızdırdıqda o, dehidratlaşma və dehidroksilləşmə mərhələsindən keçir və daha yüksək temperturda karbonatların parçalanması ilə tamamlanır. Bu isə öz növbəsində keramikanın ilkin olaraq çox da yüksək olmayan "mülayim" temperatur şəraitində bişirildiyinin göstəricisidir. Rentgen struktur analizin nəticələri gösərdi ki, tədqiq olan nümunə kvars, çol şpatı, kalsit və muskovit minerallarından və gilin qızdırılma məhsulu olan amorf fazadan ibarətdir. Tədqiq olunmuş nümunədə TG/DTQ analizinin nəticələri rentgen struktur analizinin nəticələri ilə uzlaşır və keramikanın tərkibində kalsitin olması qədim keramikanın təxminən 700°C də bişirildiyini deməyə əsas verir.

Açar sözlər: termoqravimetriya; rentgen struktur analiz; qədim keramika; gil; kvars; çöl şpatı