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THERMOLUMINESCENCE DATING THE AGE OF BALLABUR CASTLE

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The presented work was the first attempt to increase the accuracy of dating natural archeological monuments, namely, the Ballabur castle in Lenkaran of Azerbaijan Republic, by employing the Thermoluminescence (TL) dating method. Luminescence measurements were performed to find out the equivalent dose (ED). Registration of TL signal was carried out using the HarshowTLD 3500 Manual Reader. The irradiation was performed at an ambient temperature from a ^{60}Co source at different dose levels, and a dose rate of the ^{60}Co source was determined by EPR spectrometric method using an individually wrapped Alanine Dosimeter. Soil samples were collected close to the pottery sample to determine the natural dose rate. Uranium, Thorium, and Potassium concentrations in soil. The annual dose rate was obtained using a γ-spectrometer with a hyper-pure germanium detector, which was 2.98±0.19 mGy/year. the cosmic dose rate, which pertains to radiation from cosmic sources, was also calculated and found to be 0.10±0.01 Gy/ka. Online dose rate and age calculator calculated the sample's age as 920±50 years which is in line with the age of this area estimated by historians.
Keywords: *Ballabur castle; Thermoluminescence dating; Annual dose rate; Quartz*
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INTRODUCTION

Determining the age of various archaeological objects is one of the most critical problems of geological science and practice. The thermoluminescence (TL) method is a well-established method for determining the age of archaeological ceramics [1–3]. This method is based on the effect of the accumulation of nonequilibrium charge carriers on defects in dielectrics, which is generated by ionizing radiation from natural radionuclides contained in dating objects or their environment. In the case of ceramics, the determined age corresponds to the time interval from the moment of the firing of the ceramics to the moment of its removal from the burial [4, 5].

Presently, the only ways to determine the age of the brickwork in many standing buildings from Azerbaijan's late medieval and early modern periods (11th to 19th centuries AD) are through historical records or by comparing their design and style. However, this typological dating method can only determine the age if there were any writing records. This research study seeks to establish a standard procedure for dating the bricks from medieval structures in Azerbaijan. We have collected two brick samples from an early medieval castle in Ballabur, Lankaran, Azerbaijan, where architectural experts have already assigned the dates as ~1000 years old.

MATERIAL AND METHODS

Quartz is a common mineral that is permanently present in raw ceramic paste. During its heat treatment (600-700^{0}C), the quartz contained in it loses all the previously accumulated charge carriers, the accumulation of which has occurred since the formation of quartz as a mineral. Thus, when dating by the thermoluminescence method, a zero-moment is realized by heating during ceramics or pottery manufacturing.

However, in solids, including quartz crystals, traps for electrons and holes are located at different levels. To determine the age of ceramics, the lifetime of trapped electrons (holes) at ambient temperature should be at least 10–20 times greater than the age of the objects under study. In practice, it can be considered that in quartz and feldspars, the TL peaks with a luminescence maximum of 230-375◦C are suitable for dating. The methodology to use TL to determine the absolute (in years) age of various artifacts is based on the fact that, up to a specific limit, the accumulation of TL in traps occurs approximately in proportion to the radiation dose, which in turn depends on the irradiation intensity and exposure time [6].

It is possible to calculate the age of the material under study by experimentally determining the increase in TL per unit of absorbed radiation dose and the rate of natural radioactivity [7, 8].

1. Preparation of ceramic samples for research.

Luminescence measurements were performed to find out the equivalent dose (ED). The brick samples' outer surface was discarded, the rest was crushed into powder, and the remaining material was crushed and sieved into three-size fractions. The 90÷150 mm fraction was then etched in HF and washed in HCl [7]. The measurement sample comprised quartz inclusions with a size greater than 90 mm and a density between 2.63 and 2.67 g/cm3, separated using sodium poly tungstate [9, 10]. The grains were preheated before ED measurements to eliminate the influence of unstable traps on luminescence counts. The measurements showed that 200°C and 12 min were suitable for the sample. The measurements' uncertainties were calculated while considering the anomalous fading losses. As a result of the development of the methodology, it was found that the best measurement results are obtained when using powder samples, thus achieving more uniform heating; the weight of the sample is about 5 mg, and the particle size is 0.1-0.25 mm.

2. Measurement of TL of non-irradiated samples.

Registration of natural TL was carried out using the HarshowTLD 3500 Manual Reader. Five measurements were made for each of the non-irradiated samples. For TL analysis, an essential condition is the heating linearity. The linear heating rate of the sample was 5ºC/s in the temperature range of up to 400°C, which meets the requirements for instruments for TL analysis.

3. Measurement of artificial TL of irradiated samples.

The irradiation was performed at an ambient temperature from a ^{60}Co source at different dose levels ranging from 5 to 25 Gy. Magnettech Miniscope MS400 EPR Spectrometer using individually wrapped, barcode-labeled BioMax Alanine Dosimeter Films (developed by Eastman Kodak Company) has determined a dose rate of the ^{60}Co source. The irradiated samples were weighed to 5±0.5 mg and read out after one day in an N_2 atmosphere in a Harshaw 3500 manual reader using the linear heating rate of 5ºC/s.

Soil samples were collected close to the pottery sample to determine the natural dose rate. Uranium, Thorium, and Potassium concentrations in soil were measured by gamma spectrometry Canberra GR4520 that 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 DISCUSSION

Quartz, a mineral commonly found in raw ceramic paste, undergoes a significant transformation when exposed to heat treatment (600-700°C). This transformation eradicates all previously accumulated charge carriers within the quartz, which have been accumulating since the mineral's formation. As a result, when utilizing the thermoluminescence method for dating, the heating process during ceramics, bricks, or pottery manufacturing effectively resets the quartz to a pristine state.

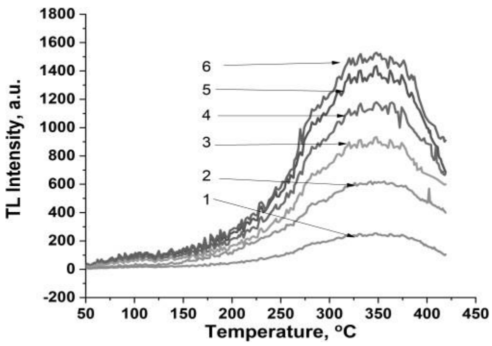

Fig. 1. Dose-dependent TL intensity of irradiated quartz at various doses: (1) Natural quartz extracted from the brick; Quartz irradiated at (2) 5 Gy, (3) 10 Gy, (4) 15 Gy, (5) 20 Gy, and (6) 25 Gy.

However, in solid materials like quartz crystals, there exist traps at various energy levels for both electrons and holes. In order to determine the age of ceramics, it is necessary for the trapped electrons (or holes) to have a lifetime at room temperature that is at least 10-20 times longer than the age of the studied objects. In practical terms, the TL peaks in quartz and feldspars, exhibiting a luminescence maximum of 230-375°C, are highly suitable for the purpose of dating.

Irradiated quartz grains exhibit several TL peaks when heated from room temperature to 500°C [11]. Two peaks above 300°C were observed for quartz inclusions extracted from pottery. The peak observed at 375°C is considered preferable to the peak on the lower shoulder of this peak, around 325°C. Another peak that emerges under laboratory irradiation is around 110°C that became the basis of the "pre-dose dating" method. It has demonstrated that the peak height could be used to monitor dose-dependent sensitivity changes observed after heating to 500°C. Figure 1 illustrates the dose dependence of the TL glow curve. Samples were irradiated with a ^{60}Co gamma source then TL glow-curves were measured after two days.

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 are illustrated in Table 1.

Accurate determination of the environmental radiation dose rate is of utmost importance when employing trapped charge dating methods such as luminescence and electron spin resonance dating

Table 1.

The concentration of U, Th, and K in the brick sample from the Balabur castle

Uranium, ppm	Thorium, ppm	Potassium, %
2.21±0.20	9.71±1.10	1.90±0.10

Although the calculation of the environmental radiation dose rate itself may not be excessively complex, incorporating multiple variables and accounting for uncertainties can pose challenges. To address this issue, the Dose Rate and Age Calculator (DRAC) has been developed as a user-friendly web-based tool [12]. DRAC enables users to swiftly calculate environmental dose rates for various trapped charge dating applications by selecting a range of recently published attenuation and conversion factors. This ensures robust and reproducible calculations of the environmental radiation dose rate, thereby enhancing the accuracy of age estimations [12]. In this study, the DRAC version 1.2 software was utilized to perform dose rate and age calculations. Plotting the TL glow-curve intensity at 350°C against the dose adsorbed and backward extrapolation enables the estimated historical dose to equal 2.93±0.36 Gy (Figure 2).

The output results of the calculations indicate that the environmental dose rate was determined to be 2.98±0.19 Gy/ka (gray per kilo annum), which signifies the rate of radiation absorbed from the surrounding environment. The moisture content of a sample plays a significant role in trapped charge dating due to its impact on water dose absorption. When archaeological samples contain water, the water, hindering the radiation energy from reaching the quartz grains, absorbs a portion of the radiation. As a result, the dose rate of a dry sample can be higher than that of a moist sample. This disparity can potentially lead to an underestimation of the sample's age. Therefore, it is crucial to determine the percentage of water through laboratory analysis of the samples and consider it when calculating the dose rate.

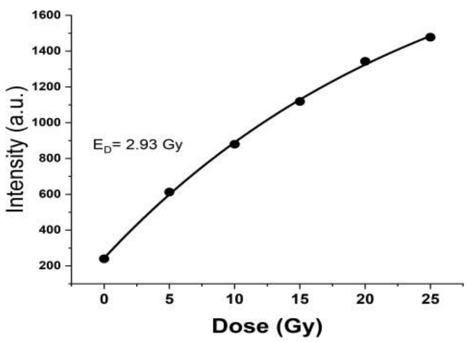

Fig . 2. Dependence of the intensity of the TL signal (in arbitrary units) in quartz extracted from bricks taken from the castle of Ballabur on the adsorbed dose

Furthermore, the cosmic dose rate, which pertains to radiation from cosmic sources, was also calculated and found to be 0.10±0.01 Gy/ka. Based on these dose rate calculations, the age of the sample was estimated to be 920±50 years.

These findings emphasize the significance of accurately assessing the environmental radiation dose rate in trapped charge dating. The utilization of tools like DRAC and careful consideration of factors such as moisture content contribute to more precise age estimations in archaeological research, enabling a deeper understanding of the timelines of ancient artifacts and structures.

CONCLUSION

Despite being in its initial phase and utilizing a limited number of samples, this study has effectively demonstrated the potential of using the thermoluminescence (TL) technique on quartz inclusions to determine the luminescence ages of late medieval bricks. The application of TL dating has yielded valuable insights into the age determination of archaeological ceramics, specifically in the context of the Ballabur castle in Lenkaran, Azerbaijan Republic. Through the analysis of TL peaks and measurements conducted on both irradiated and non-irradiated samples, significant progress has been made in establishing a standardized procedure for dating medieval brick structures.

The evaluation of environmental dose rate and cosmic dose rate, facilitated by software such as DRAC, has provided crucial information for age calculations. Taking into account factors like the concentration of Uranium, Thorium, and Potassium in the soil, as well as the historical dose estimation from TL glow-curve intensity, the age of the sample from the Ballabur castle was estimated to be approximately 920±50 years.

These findings underscore the importance of TL dating methods in archaeological research, particularly concerning historical ceramics. The methodology and measurements presented in this study contribute to a broader understanding and more precise dating of medieval structures in Azerbaijan. Ongoing advancements in TL dating techniques will further enrich our knowledge of ancient civilizations and assist in unraveling past mysteries.

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TERMOLÜMİNESANS METODU İLƏ BALLABUR QALASININ YAŞININ TƏYİN OLUNMASI

A.Z. Abışov, S.Q. Məmmədov

Azərbaycan Respublikasının Lənkəran şəhərindəki Bələbür qalası kimi tanınan təbii arxeoloji abidələrin tarixinin dəqiqliyini artırmaq üçün Termolüminesans tarixləndirməarixi (TL) metodundan istifadə edilmişdir. Ekvivalent dozanı (ED) tapmaq üçün lüminesans ölçmələri aparılmlş və TL siqnalının qeydə alınması HarshowTLD 3500 Reader istifadə edərək həyata keçirilmişdir. Nümunələrin süalanması ^{60}Co mənbəyindən istifadə etməklə aparılmışdırş. ^{60}Co mənbəyinin doza gücü fərdi şəkildə sarılmış Alanin Dozimetrindən istifadə edərək EPR spektrometrik metodu ilə təyin edilmişdir. Təbii doza gücünü müəyyən etmək üçün nümunəyə yaxın olan yerdən torpaq nümunələri götürülmüşdür. Torpaqda uran, torium və kaliumun konsentrasiyaları müəyyən edilmişdir. İllik doza dərəcəsi hipertəmiz germanium detektoru ilə γ-spektrometrdən istifadə etməklə təyin edilmiş və 2,98±0,19 mGy/il olduğu müəyyən edilmişdir. Bundan əlavə kosmik doza gücü hesablanmış və 0,10±0,01 Gy/il olduğu müəyyən edilmişdir.

Abidənin yaşı onlayn doza gücü və yaş kalkulyatorundan istifadə edərək 920±50 il hesablanmışdır ki, bu da tarixçilərin bu abidə üçün müəyyən etdiyi təxmini yaşa uyğundur.

Açar sözlər: *Ballabur qalası, Termolüminesens yaş təyini, İllik doza gücü, Kvars*

ТЕРМОЛЮМИНЕСЦЕНТНАЯ ДАТИРОВКА ЭПОХИ ЗАМКА БАЛЛАБУР

А.З. Абышов, С.Г. Маммадов

Представленная работа была первой попыткой повысить точность датирования природных археологических памятников, а именно замка Баллабур в Ленкорани Азербайджанской Республики, с применением метода термолюминесцентного датирования (ТЛ). Измерения люминесценции проводились для определения эквивалентной дозы (ЭД). Регистрацию сигнала TL проводили с помощью считывателя HarshowTLD 3500 Manual Reader. Облучение проводили при температуре окружающей среды от источника 60Co при различных уровнях дозы, а мощность дозы источника 60Co определяли спектрометрическим методом ЭПР с использованием дозиметра с аланином в индивидуальной упаковке. Образцы почвы были отобраны рядом с образцом глиняной посуды для определения естественной мощности дозы. Содержание урана, тория и калия в почве. Годовая мощность дозы получена с помощью γ-спектрометра с детектором из сверхчистого германия и составила 2,98±0,19 мГр/год. мощность космической дозы, относящаяся к излучению космических источников, также была рассчитана и составила 0,10±0,01 Гр/тыс. лет.

Возраст образца был рассчитан онлайн-калькулятором мощности дозы и возраста как 920 ± 50 лет, что соответствует возрасту этой области, оцененному историками.

Ключевые слова: *замок Баллабур, термолюминесцентное датирование, годовая мощность дозы, Кварц*