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ADVANCEMENTS IN THERMOLUMINESCENCE DATING: A CASE STUDY OF MEDIEVAL BRICK STRUCTURES IN AZERBAIJAN[†]

Sahib Mammadov*, Aqshin Abishov
Institute of Radiation Problems, ANAS, Azerbaijan
**Corresponding Author e-mail: mammadov.irp@gmail.com*
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The study aimed to improve the precision of dating historical landmarks, specifically the Ballabur castle in Lenkaran, Azerbaijan Republic, using the thermoluminescence dating (TL) method. The annual dose rate, calculated with γ-spectrometer equipped with a hyper-pure germanium detector, was found to be 2.98±0.19 mGy/year. By employing an online dose rate and age calculator, the sample's age was determined to be 920±50 years, consistent with the historical estimates of this region.
Keywords: *Ballabur castle; Thermoluminescence dating; Annual dose rate; Quartz*
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INTRODUCTION

Determining the age of archaeological artifacts poses a significant challenge in geological science and practice. This method exploits the accumulation of nonequilibrium charge carriers on defects in dielectric materials caused by ionizing radiation from natural radionuclides present in the objects being dated or their surroundings. The thermoluminescence (TL) method has proven to be a reliable technique for dating archaeological ceramics [1]–[3]. In the case of fired bricks, the determined age corresponds to the time elapsed between the firing of the product and their removal from the burial site [4], [5].

The age of brickwork in many standing buildings from Azerbaijan's late medieval and early modern periods (11^{th} to 19th centuries AD) can only be determined through historical records or by analyzing their design and style. However, this typological dating method relies on the availability of written records. This research aims to establish a standardized procedure for dating medieval brick structures in Azerbaijan. We collected two brick samples from the Ballabur castle in Lankaran, Azerbaijan, which architectural experts have already estimated to be approximately 1000 years old.

MATERIALS AND METHODS

Quartz, a commonly occurring mineral in raw ceramic paste, undergoes a significant change during the heat treatment (600-700°C). This change eliminates all previously accumulated charge carriers within the quartz, which have been building up since the mineral's formation. Consequently, when employing the thermoluminescence method for dating, a reset to a zero state occurs through the heating process during ceramics, bricks, or pottery manufacturing.

However, in solid materials like quartz crystals, there are traps at various energy levels for both electrons and holes. To determine the age of ceramics, the trapped electrons' (or holes') lifetime at room temperature should be at least 10-20 times longer than the age of the studied objects. In practical terms, the TL peaks with a luminescence maximum of 230-375°C in quartz and feldspars are well-suited for dating purposes.

The methodology for using thermoluminescence (TL) to determine the absolute age of artifacts is based on the observation that, up to a specific limit, the accumulation of TL in traps is roughly proportional to the radiation dose. This dose, in turn, depends on the intensity of irradiation and the duration of exposure [6]. The age of the studied material was calculated by experimentally determining the increase in TL per unit of absorbed radiation dose and the rate of natural radioactivity according to the protocol described in [2], [7].

The experiment utilized quartz samples extracted from two bricks sourced from Bellabur Castle through conventional chemical separation techniques [8]. The brick samples exhibit a light red color attributed to hematite (Fe_2O_3), known for its strong coloring properties in pottery. Even a minimal concentration of 1% hematite was sufficient to produce a reddish hue during the firing process under oxidizing conditions [4]. The brick sample underwent a series of steps, including crushing and sieving, to obtain grain size fractions of 80 to 120 µm. The targeted grain fraction was then treated with HCl, subjected to heavy liquid separation, and etched in 40% HF [9], [10]. Precipitated fluorides were subsequently dissolved using HCl. To ensure the purity of the quartz concentration, XRF analysis was performed, and the amount of SiO2 in the extracted samples was 98.5%.

As a result of methodological advancements, it was discovered that the most favorable measurement outcomes were achieved using powder samples weighing approximately 5 mg, with particle sizes ranging from 0.1 to 0.25 mm.

Before conducting the ED measurements, the grains underwent a preheating process to eliminate any influence from unstable traps on luminescence counts. Experimenting determined that preheating the grains at 200°C for 12 minutes

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yielded relevant results. The uncertainties in the measurements were calculated, taking into account the losses caused by anomalous fading.

The samples' natural TL (thermoluminescence) was recorded using the HarshowTLD 3500 Manual Reader. Each non-irradiated sample underwent five measurements. For accurate TL analysis, it is crucial to maintain linearity during the heating process. In this study, the sample was heated linearly up to 400°C at a rate of 5°C/s, which met the needs of the TL analysis instruments. A 3 mm heat-absorbing filter (Schott KG-1) was positioned in front of the tube.

To safeguard the photomultiplier tube against blackbody radiation. The irradiation process was conducted at room temperature using a ^{60}Co source at various dose levels ranging from 5 to 25 Gy. The dose rate of the ^{60}Co source was determined using the Magnettech Miniscope MS400 EPR Spectrometer. The dose was measured using individually wrapped BioMax Alanine Dosimeter Films with barcode labels developed by Eastman Kodak Company [11]. The irradiated samples, weighing approximately 5±0.5 mg, were then read after two days in an N2 atmosphere using a Harshaw 3500 manual reader, employing a linear heating rate of 5°C/s.

One of the fundamental steps in luminescence dating is calculating the annual dose rate, which represents the radiation dose received by the sample per year. In our study, this dose rate comprises three components: i) the beta dose contribution originating from the brick samples themselves, ii) the gamma dose contribution arising from the surrounding soil, and iii) a specific contribution from cosmic radiation. Soil samples were collected close to the pottery sample to determine the natural dose rate. The concentrations of Uranium, Thorium, and Potassium in the soil were measured using the Canberra GR4520 gamma spectrometry system. This system is equipped with a high-resolution GeHP (hyper-pure germanium) detector and 15 cm lead shielding, providing a resolution efficiency of 43.5% for 661.6 keV.

RESULTS AND DISCUSSIONS

When irradiated quartz grains are heated from room temperature to 500°C, multiple TL (thermoluminescence) peaks can be observed [12]. In the case of quartz inclusions extracted from pottery, two peaks were identified above 300°C. The peak observed at the temperature of 375°C is considered more favorable compared to the lower shoulder peak of around 325°C. Another peak that emerges under laboratory irradiation is observed around 110°C, the basis for the "pre-dose dating" method. This method utilizes the peak height to monitor dose-dependent sensitivity changes after heating to 500°C. Fig. 1 depicts the dose-response of the TL glow curve, where samples were irradiated using a ^{60}Co gamma source, and TL glow curves were measured two days after irradiation.

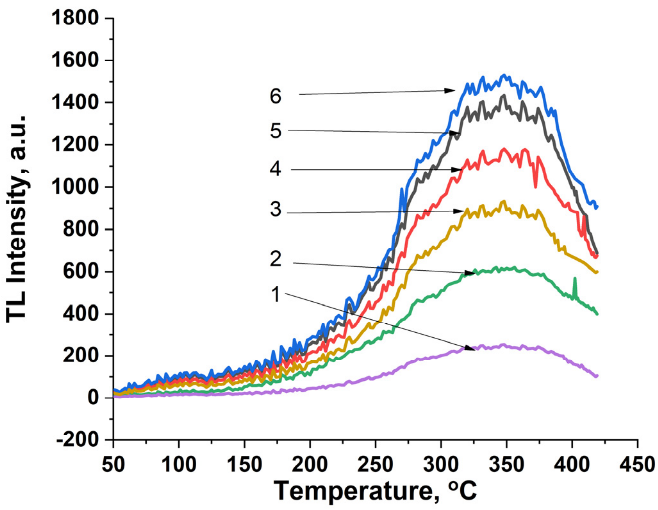

Figure 1. Dose-dependent TL intensity of irradiated quartz at various doses: (1) Natural quartz extracted from the brick; Quartz irradiated at (2) 5 Gy, (3) 10 Gy, (4) 15 Gy, (5) 20 Gy, and (6) 25 Gy

To assess the environmental dose rate, a soil sample collected near the pottery sample was air-dried and kept in a closed environment for one month. The determined concentrations of Uranium (U), Thorium (Th), and Potassium (K) were found to be 2.21±0.20 ppm, 9.71±1.10 ppm, and 1.90±0.10%, respectively.

To identify a stable temperature range for the glow curve of the samples, the plateau test, as described by [12], was conducted. This procedure involved comparing the natural TL glow curve with the glow curve obtained after laboratory irradiation. The region exhibiting a plateau indicated thermal stability, as the ratio between the natural TL signal and the signal from the laboratory-irradiated sample remained constant. The archaeological dose was determined by integrating the plateau region of the respective glow curves and subtracting the background signals recorded after each measurement.

By plotting the intensity of the TL glow-curve at 350°C against the absorbed dose and extrapolating backward, the estimated historical dose was determined to be 2.93±0.30 Gy (Fig. 2).

Precise determination of the environmental radiation dose rate is crucial for trapped charge datings methods like luminescence and electron spin resonance dating. While the calculation of the environmental radiation dose rate itself may not be mathematically intricate, incorporating multiple variables and accounting for uncertainties can present challenges. The Dose Rate and Age Calculator (DRAC) has been developed as an accessible web-based tool [13] to address this issue. DRAC allows users to swiftly calculate environmental dose rates for various trapped charge dating applications by selecting a range of recently published attenuation and conversion factors that ensures robust and reproducible environmental radiation dose rate calculations, enhancing the accuracy of age estimations [13]. Using the DRAC version 1.2 software, dose rate and age calculations were performed. The output results are as follows: The environmental dose rate was determined to be 2.98±0.19 Gy/ka (gray per kilo annum), indicating the rate of radiation absorbed from the surroundings. The moisture content of a sample plays a significant role due to its impact on water dose absorption. When archaeological samples contain water, it absorbs a portion of the radiation, impeding the radiation energy from reaching the quartz grains. As a result, a dry sample's dose rate can be higher than a moist sample. This disparity can potentially lead to an underestimation of the sample's age. Hence, it is crucial to determine the percentage of water in the laboratory analysis of the samples and to consider when the dose rate is calculated.

Additionally, the cosmic dose rate, which refers to radiation from cosmic sources, was calculated to be 0.10±0.01 Gy/ka. Based on these calculations, the sample's age was estimated to be 920±50 years.

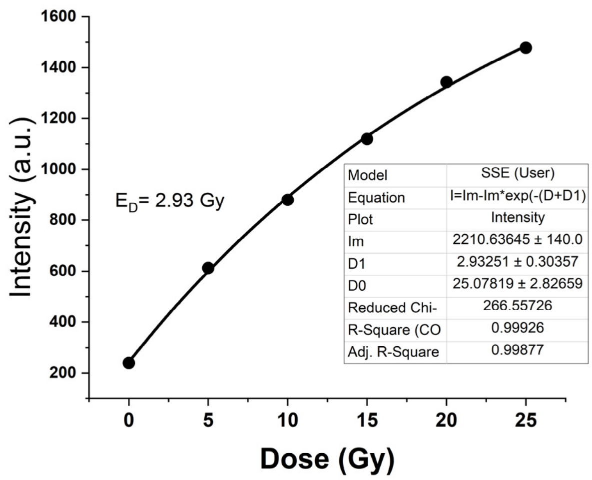

Figure 2. Relationship between TL signal intensity (in arbitrary units) and adsorbed dose in quartz extracted from bricks at Ballabur Castle

CONCLUSION

Despite being in its preliminary stage and involving a limited range of samples, this study has successfully showcased the potential of utilizing the TL technique on quartz inclusions for obtaining luminescence ages of late medieval bricks. Applying the thermoluminescence (TL) dating method has provided valuable insights into the age determination of archaeological ceramics, specifically in the case of the Ballabur castle in Lenkaran, Azerbaijan Republic. By analyzing the TL peaks and conducting measurements on both irradiated and non-irradiated samples, significant progress has been made in establishing a standardized procedure for dating medieval brick structures.

The assessment of the environmental dose rate and cosmic dose rate, conducted with the help of software like DRAC, has provided vital information for age calculations. Considering factors such as the concentration of Uranium, Thorium, and Potassium in the soil, along with the historical dose estimation from TL glow-curve intensity, the age of the sample from the Ballabur castle was approximately 920±50 years.

These findings highlight the significance of TL dating methods in archaeological research, particularly for historical ceramics. The established methodology and measurements presented in this study contribute to the broader understanding and precise dating of medieval structures in Azerbaijan. Continued advancements in TL dating techniques will enhance our knowledge of ancient civilizations and aid in uncovering past mysteries.

ORCID
Sahib Mammadov, https://orcid.org/0000-0002-4547-4491; **Aqshin Abishov,** https://orcid.org/0000-0003-2467-4344

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УСПІХИ В ТЕРМОЛЮМІНЕСЦЕНТНОМУ ДАТУВАННІ: ПРИКЛАД СЕРЕДНЬОВІЧНИХ ЦЕГЛЯНИХ КОНСТРУКЦІЙ В АЗЕРБАЙДЖАНІ

Сахіб Мамедов, Акшин Абішов
Інститут радіаційних проблем НАНА, Азербайджан

Дослідження мало на меті покращити точність датування історичних пам'яток, зокрема замку Баллабур у Ленкорані, Азербайджанська Республіка, за допомогою методу термолюмінесцентного датування (TL). Річна потужність дози, розрахована за допомогою γ-спектрометра, оснащеного детектором надчистого германію, виявилася 2,98±0,19 мГр/рік. За допомогою онлайн-калькулятора потужності дози та віку було визначено, що вік зразка становить 920±50 років, що відповідає історичним оцінкам цього регіону.

Ключові слова: *замок Баллабур; термолюмінесцентне датування; річна потужність дози; кварц*