

THERMOLUMINESCENCE ARCHAEOLOGICAL DATING OF POTTERY IN THE EGYPTIAN PYRAMIDS ZONE

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The paper deals with the thermoluminescence (TL) dating of ancient Egyptian pottery taken from a site in the Giza pyramids zone. To ensure accurate dating, the annual dose rate and archaeological dose of the basic equation were obtained using γ -spectrometer with a hyper-pure germanium detector. The annual dose rate was 3.519 ± 0.131 mGy/year. The age of the pottery shreds was calculated by an additive dose method giving a mean value of age 4388 ± 166 years. This age is consistent with that estimated by archaeological tombs attributed to the fourth dynasty in the Old Kingdom. The uncertainty of the TL dating is much lower than the age range predicted by archaeological investigation.

INTRODUCTION

Impurities or lattice defects in solids trap unpaired electrons and holes produced in minerals by natural radiation. The effect of radiation is cumulative and hence the actual amount of the defects can be used in age determination. The defects are metastable and can be released (relaxed), for example by laboratory heating, when the pairs electron/hole are recombined (at characteristic temperatures), that is accompanied by light emission; that is why the process is called thermoluminescence (TL) [1-7]. The emission intensity is proportional to the concentration of trapped electrons/holes pairs and therefore to the radiation dose that the material has received since the last annealing of the defects, e.g. since the last thermal treatment. In the case of pottery its firing was the zero-setting event: during firing the electron/hole pairs of the pottery raw material was recombined, and from that point the new accumulation of the defects has started.

Methods for TL dating of a number of inorganic materials have been developed considerably in the last decades. Reliable and systematic studies of TL dating have been directed to fired ceramics of archaeological objects [1-5] and geologic materials [6,7] like losses and other solids containing quartz, feldspars, zircon, and other minerals [1,5]. The principle, procedures and radiation dosimetry required for the age determination from total dose (TD) or equivalent dose (ED) in ESR

dating are essentially identical to those in TL dating. The time range covered by TL or ESR dating depends on the stability of the trapped electrons, i.e., on the depth of the trap in the energy band scheme, or on the temperature at which TL occurs.

A fundamental procedure in TL dating is the determination of the radiation dose, D_E , that sample has received in its geological past [8]. Any random or systematic errors in the assessment of D_E are directly reflected in the corresponding TL estimate of the age. In many TL dating studies, the D_E values are derived from plateau in the dose vs. temperature plot. This study presents simulations of TL glow curves containing in ideal case the first- and second-order kinetics TL peaks. The TL intensities and corresponding doses were approximated by a single saturating exponential function. The results imply that there is a wide range of possibilities to estimate incorrect D_E values from plateau in the dose vs. temperature plot even when only the first-order TL peaks are involved. However, it can in principle produce correct D_E estimates for the first- and second-order kinetics TL peaks.

Trautman et al. [9] indicated that so widespread natural minerals like quartz and feldspars, have appropriate physical properties to be used as radiation dosimeters. In the last few decades, the recombination of the radiation defects accompanied by luminescence has enabled age determination of various materials important for quaternary geochronometry and archaeometry.

For the first time, the developed techniques were based on the light-emitting transitions of electrons from the conduction band to an optically sensitive electron trap. Several advantages can be derived from such direct measurements of metastable electron density in this particular trap, which produces the age-dependent signal. The method is able to date the last light exposure of feldspar grains in a range of a few hundred to more than two hundred thousand years. The results of a basic study of feldspar radioluminescence also shed light on effects not sufficiently understood in conventional dating by luminescence techniques, especially in infrared optically stimulated luminescence dating of feldspar.

Manufacture of ancient Egyptian pottery

The ancient Egyptian pottery has been divided into two types according to the raw materials. The first one, most abundant, was the alluvial Nile silt clay throughout Egypt on the banks of the Nile and in the cultivated areas bordering the river. This raw was rich in silica and iron oxides and when it was fired in an oxidizing atmosphere, it turned to a reddish brown colour. It is quite porous and often has grey cores due to an incomplete oxidation. The second kind of the raw was marl clay, stone-like before the treatment. It contained a high percentage of calcium carbonate from nearby occurring limestone, found on the desert edge and under the cultivation near the desert. It is geologically older than the Nile silt clay. After firing in an oxidizing atmosphere, this type of clay can develop a wide scale of colours from pale yellow to greenish white.

The clay was subjected to various processes to be converted to a raw suitable for the pottery. After having been dug, the clay was soaked with water in a pit, both to break it down and make it workable, that was particularly necessary in the case of marls, to separate the coarser particles, and/or to add a tempering material such as sand, crushed limestone, straw and grog from crushed pottery. Following this was either kneaded or trodden to produce an even texture and remove excess air. The clay was then formed into conical lumps and delivered to the potter.

Throughout the history of pottery manufacturing in Pharaonic Egypt, several different manufacture techniques were employed. It is possible to document a development in these techniques, from vessels entirely handmade to those thrown on a kick-wheel. However, because several methods were employed simultaneously and some were retained for certain types or sizes of vessel, before they were replaced by more advanced techniques, the dating of the ceramics cannot hence be made just by evaluating the technological level of the artefacts. The principal methods of manufacture used by the Egyptian potters were hand forming and finishing in a stand and forming wheel [10].

EXPERIMENTAL

Sample extraction

The pottery shreds were collected from a uniform soil, which was relatively free from rocks and building materials. The pottery was obtained from the depth ranging from 1.5 to 2.0 m taking into account that the nearest boundary (edge of pit, wall or rock surface) must be at least 0.3 m.

The thickness of pottery shreds varied from 7 to 20 mm. The ceramic samples were immediately after extracting put into double plastic bags to preserve the original content of water in the shreds. It was necessary to avoid exposure of the samples to any kind of irradiation from ultraviolet to infrared light including strong sources of heating. A sufficient amount of soil surrounding the buried pottery was also taken to estimate the dose rate from the radioactive elements to which ceramics was exposed.

Sample treatment

The Fleming technique [4] was used based on the extraction of quartz inclusions from samples. The pottery fabric was broken by gentle crushing in an agate mortar. Too large crystal grains ($> 200 \mu\text{m}$) were removed manually, because such quartz grains are able to self-absorb α - and β -radiation. TL measurements were performed with the size fraction of 100-200 μm obtained by sieving.

The crystals of the sample were usually coloured due to diffusion of elements from the clay matrix into the outer regions of the crystals during the firing process. This outer layer was removed by etching with hydrofluoric acid to increase the transparency of the sample that is necessary for registering TL emission. Furthermore, in order to separate quartz grains in the form as pure as possible the following procedures were employed: 1) strongly magnetic grains were separated by using a hand magnet, 2) an isodynamic separator was used consisting of an inclined vibration plain with adjustable forward slope and side tilt, and 3) because the non-magnetic fraction consisted not only of quartz and feldspar, but also other minerals like calcite; hydrofluoric acid treatment was used to purify quartz.

X-ray diffraction analysis

The samples were analyzed by X-ray diffractometer Philips (Germany), with Cu-K $_{\alpha}$ radiation and Ni-filter at room temperature in the Central Research Laboratories of Tanta University.

Thermoluminescence technique

For the thermoluminescence measurements, TL-readout system Harshow 5400 (Harshow Chemical Company in Ohio, USA) was used. The quartz grain was placed on a heated tray (plainchant). The plainchant temperature was controlled by a contact thermocouple. The light emitted by TL-material passed through an optical system consisting of a collecting lens and IR-filter, which focused the light on the photocathode of a photomultiplier by the photon counting technique. The photo multiplier pulse (due to a single TL photon interaction with the photo cathode) is amplified once and fed through a fast discriminator (to eliminate dynode noise pulse) before the detection by a multi-channel analyzer in a multi-scale mode.

γ -ray spectrometry and activity measurement

γ -ray spectrometer (figure 1) was used to determine the radioactive elements present in the soil surrounding the pottery. The spectrometer consists of hyper-pure germanium detector, electronic and recording devices. The Ge-detector operated at near the temperature of liquid nitrogen to decrease the leakage current and hence the noise of the system.

Samples were put in a closed plastic container for one month to fulfil the radioactive equilibrium condition. The radioactivity of the elements in the samples was determined by γ -spectrometer using the hyper-pure

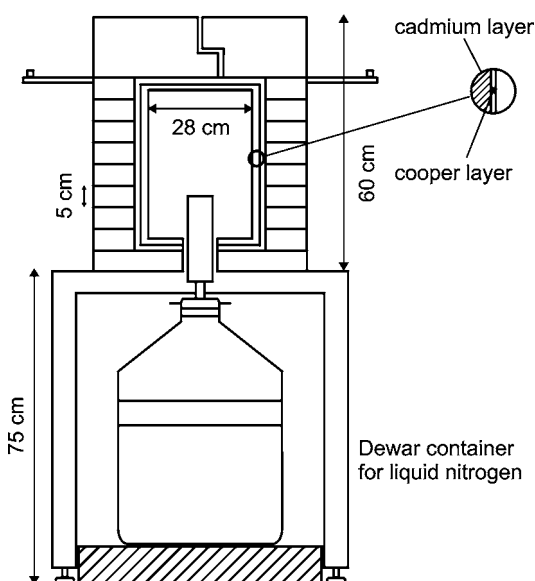


Figure 1. γ -ray spectrometer having hyper pure germanium detector.

Ge detector. The sample in the container was placed to detector inside a cylindrical cavity of copper and cadmium layers shielded by lead wall to protect it from the environmental γ -ray background. The detector was biased to 12300 V (DC). The accumulated intensity (number of counts) versus radiation energy (from 37 to 2417 keV) was obtained for samples and background (doubly distilled water). After background subtraction the activities were estimated according to equation (1)

$$A = [\text{Net } (C/S)/(I\epsilon)] \quad (1)$$

where A is the activity of the γ spectral line, Net (C/S) is the net detected counts per second, ϵ is the absolute efficiency of the used detector at the corresponding energy of the γ -spectral line, and I is the photo-disintegration.

Irradiation facilities

^{137}Cs source at National Institute for Standards (NIS) supplied by Canadian Atomic Energy (Canada) was used as a γ -ray source. Farmer dosimeter (type 570 A) provided with a special ionization chamber of high sensitivity was used to calibrate dose rate (0.266 Gy/min at the distance of 30 cm).

Annealing procedure

The quartz grains were heated for two hours at 500°C to remove the effect of accumulated exposure of sample both the original samples and samples after intentional irradiation. The annealing was carried out in an electric furnace model VULCAN 3.550-NEY (USA).

RESULTS AND DISCUSSION

X-ray diffraction

Results of X-ray diffraction (see figure 2 and table 1) show that the concentration of quartz in the corresponding fraction from pottery was 99.3 %.

Determination of radiation doses of pottery

The basic formula used in TL age determination is

$$\text{Age (years)} = \frac{\text{Archaeological dose (Gy)}}{\text{Annual dose rate (Gy/year)}} \quad (2)$$

Table 1. The crystalline phases developed in the studied glasses.

Peak No.	2 θ (°)	Crystalline phase	Relative intensity (%)
1	20.9	α-quartz	71
2	23.8	albite	2
3	26.5	α-quartz	100
4	36.7	α-quartz	34
5	39.4	α-quartz	10
6	39.8	α-quartz	20
7	42.5	α-quartz	27
8	45.8	α-quartz	13
9	50.2	α-quartz	49

Table 2. The activities of Th-series, U-series and K-40 found in soil.

Element	Activity (Bq/kg)	Concentration (ppm)
²³⁸ U	32.977 ± 0.5	2.672 ± 0.04
²³² Th	19.282 ± 1.7	4.772 ± 0.42
⁴⁰ K	296.501 ± 1.04	9.728 ± 0.03

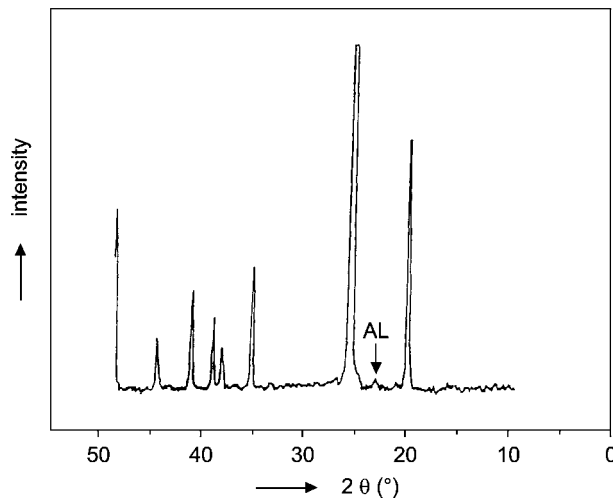


Figure 2. X-ray diffraction pattern of extracted quartz at room temperature. AL denotes the diffraction of albite.

In equation (2), the most important term is annual dose rate that was determined by γ -spectroscopy.

Quartz grains in the pottery were naturally exposed to α , β -, and γ -radiation mainly from traces of radioactive elements of thorium series, uranium series, potassium-40 and rubidium present in soil, and from cosmic rays:

$$\text{Annual dose} = D_{\alpha} + D_{\beta} + D_{\gamma} + D_e \quad (3)$$

where U and Th contribute to D_{α} ; and U, Th, and K to both D_{β} and D_{γ} . In quartz grains, α -particles penetrates ~6 μm , β -particles 2 mm, and γ -rays 30 cm [11]. γ -Spectroscopy can be used to determine the activity of the radioactive trace elements; therefore the effect of γ -and β -rays, and α -particles emitted from the radioactive trace elements in the soil could be determined.

Because uranium and thorium ores should be in series equilibrium with their daughter products, the most suitable characteristic γ -ray energies are 1.764 MeV due to ²¹⁴Bi, 2.615 MeV due to ²⁰⁸Tl and 1.462 MeV due to ⁴⁰K, that was used to detect the presence of equivalent uranium, equivalent thorium and equivalent potassium-40, respectively, measure their concentration. The results of the activities and the concentration of radioactive elements is shown in table 2.

The dose rates according to the data presented by Liritzis and Kokkoris [12] and revised by Ogah et al. [13] with zero radon loss is shown in table 3, with their effective values which were estimated using the Aitken effective ratio [14].

The dose by cosmic rays at ambient conditions was assumed according to ref. [15] as $150 \pm 11 \mu\text{Gy/year}$ at a depth of around 1 m for typical soil, and the following attenuation factors with depth are used for common soil: 0.84 at 2 m, 0.71 at 3 m and 0.22 at 10 m. The estimation of the cosmic ray dose rate affecting the pottery was $(126 \pm 9) \mu\text{Gy/year}$.

Effect of water content

The regions of buried pottery carried a significant amount of water that has an effect on "diluting" the radioactivity in the sense that the energy absorbed per gram is decreased [11].

Table 3. The concentration of the natural radioactive series in the soil and the corresponding effective annual dose rates (mGy/year) [14].

Concentration of radioactive (R.A.) series in soil	D_{α}	D_{β}	D_{γ}	Total dose	Effective value
²³⁸ U series 2.672 ± 0.04 ppm	7.192 ± 0.108	0.381 ± 0.006	0.273 ± 0.004	7.846 ± 0.118	1.934 ± 0.029
²³² Th series 4.772 ± 0.42 ppm	3.517 ± 0.309	0.132 ± 0.012	0.243 ± 0.021	3.892 ± 0.342	0.854 ± 0.075
⁴⁰ K-concentration (0.83 ± 0.03) %		0.564 ± 0.021	0.168 ± 0.006	0.732 ± 0.027	0.732 ± 0.027
Total effective annual dose rate					3.519 ± 0.131

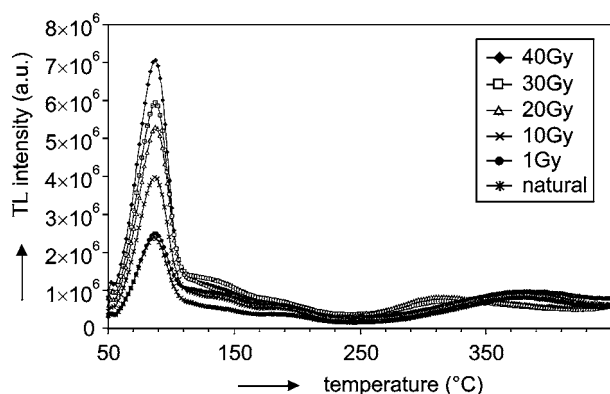


Figure 3. TL-glow curves of natural and irradiated quartz samples.

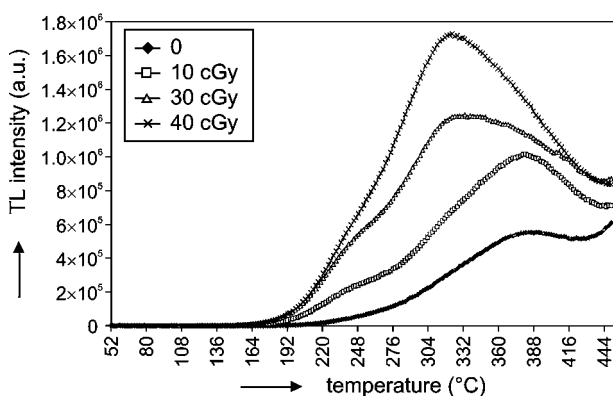


Figure 4a. TL-glow curves of quartz samples irradiated by different doses with γ source.

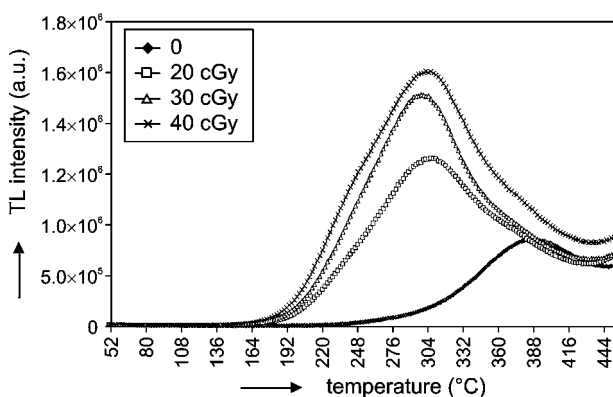


Figure 4b. TL-glow curves of quartz samples irradiated by different doses with γ source after annealing at 500°C for two hours.

Consequently, to evaluate the actual dose rate that affected the pottery, the water content must be measured in the soil or pottery shreds after extraction from excavations and removing the water content by heating at 100°C for 3 days. The water content in pottery was $(3.1 \pm 0.2) \%$, and hence the annual dose must be decreased by 3.1 % which will be equal to $3.532 \pm \pm 0.34$ mGy/year.

The annual dose combining all kinds of irradiation become $3.519 \pm 0.131 + 0.126 \pm 0.009 = 3.645 \pm \pm 0.139$ mGy/year.

Thermoluminescence data

For measurement, the sample is heated, thereby emptying the traps with defects, and faint emission of light resulting from acceptance of some of the released electrons into luminescence centres is detected. The lifetime of an electron in a trap is not infinite but depends on the type of trap, that is associated with the characteristic temperature at which the trap is emptied and TL is emitted. "Shallower" traps with shorter lifetimes are emptied earlier (at lower temperatures) than "deeper" traps, which stay immune to the lattice vibrations until a higher temperature is reached. In quartz the TL peak close to 100°C is associated with traps having a lifetime of a few hours at room temperature, whereas the lifetime of traps responsible for the TL peaks at about 350°C is up to million years.

Figure 3 shows the TL glow-curve for a samples of six extracted quartz samples, one natural and five irradiated with γ doses 1, 10, 20, 30, and 40 Gy. The characteristic glow curves were recorded using the optimum-heating rate of 5°C/s from 52°C to 452°C. The figure displays three peaks at 92°C, 312°C and 395°C. The more suitable steady plateau level is above 300°C. This plateau indicates that the TL in that temperature region is associated with trap lifetimes that are much longer than the period over which natural radiation defects have been accumulated, i.e. there has been negligible leakage from the traps concerned. A level plateau has also other significance, one of these is that heating in antiquity was sufficient to empty all traps, and another that TL observed is true radiation-induced TL rather than spurious TL arising from parasitic surface effects. For dating analysis with suitable intensity, the peak at $305 \pm 5^\circ\text{C}$ (figure 4a) is separated by heating the samples to 200°C and repeating to 450°C, for natural samples and irradiated with 20, 30, and 40 Gy doses of γ -irradiation. The same conditioning is repeated with annealed natural sample and samples irradiated with 10, 30, and 40 Gy as shown in figure 4b.

To obtain the past radiation dose (archaeological dose) a comparison between the natural TL-signal with

that induced in the same sample by a subsequent irradiation have been achieved. The "additive method" is used to overcome the problem of the change in the sensitivity of the sample above 500°C. An empirical way of correcting for supra-linearity is to already glow portions to determine the second-glow growth characteristic and to assume that in spite of a change in the sensitivity on heating, there is no change in the intercept correction (B). Thus the archaeological absorbed dose AD is a sum of natural absorbed dose ED and intercept B

$$AD = ED + B \quad (4)$$

In the present investigation, we applied the additive dose procedure ($AD = 13 + 2.5 = 15.5$ Gy) using eight samples shown in figure 5 getting

$$Age = \frac{15\ 500}{3.532 \pm 0.134} = (4\ 388 \pm 166) \text{ years}$$

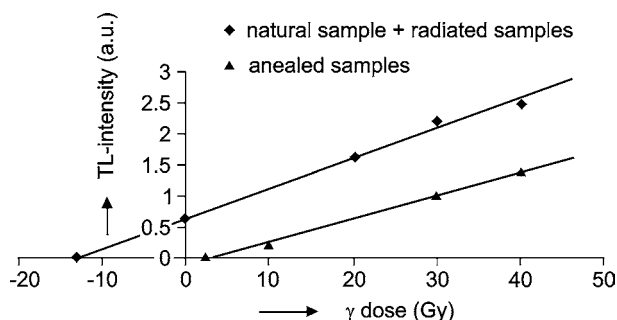


Figure 5. The growth curves representing the variation of TL-intensity as a function of the dose for extracted quartz grain samples.

CONCLUSION

Thermoluminescence was used for dating ancient Egyptian pottery. The site examined in the present study was in the Pyramid zone by 150 m far from El-Giza Pyramid Zone. For accurate dating, two terms, namely the annual dose rate and archaeological dose of the basic equation (2), must have been obtained.

The errors generated in the TL dating method depend mainly on the errors of the dose-rate measurements. For this reason, a study of the background γ -radiation spectrum was performed. The absolute dose for the γ lines belonging to elements of the nature radioactive series ^{238}U and ^{232}Th as well as the ^{40}K was calculated and an estimation of the total absorbed dose rate in air was taken for the γ -lines detected. The annual dose rate so obtained was 3.519 ± 0.131 mGy/year.

The age of the pottery shreds was then calculated using additive method that gave a mean value equal to 4388 ± 166 year. The latter is consistent with that estimated by archaeological tombs attributed to the fourth dynasty in the Old Kingdom. The obtained age show that the uncertainties in TL dating taking the used technique are much lower than the age range of the archaeologists.

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TERMOLUMINESČNÍ DATOVÁNÍ KERAMIKY Z OBLASTI PYRAMID V EGYPTĚ

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Práce pojednává o termoluminescenčním (TL) datování staré egyptské keramiky získané z lokality v oblasti pyramid v Gíze. K zajištění správnosti datování pomocí základní rovnice byly metodou γ -spektrometrie s detektorem z velmi čistého Ge získány roční dávkové rychlosti a archeologické dávky. Průměrná roční dávková rychlost byla 3.519 ± 0.131 mGy/rok. Stáří keramických střepek bylo vypočteno přídavkovou metodou s výsledkem 4388 ± 166 let. Toto stáří je ve shodě s odhadem stáří náhrobků ze čtvrté dynastie staré říše. Nejistota TL datování je mnohem menší než časové rozmezí určené archeology.