LUMINESCENCE AND CYCLOPEAN WALLS: Effects on Dating and Provenance

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ABSTRACT

A new method of dating ancient carved megalithic (cyclopean) buildings has been recently proposed (Liritzis[1,2,3], Theocaris et al[4]. It is based on the solar bleaching of thermoluminescence (TL) of carved surfaces of calcitic materials (limestones, marbles). The effects of the microcrystalline sreucture of limestones and their TL characteristics (e.g. TL peaks, bleaching rate, functional behaviour of solar bleaching of TL, radiation response etc.) upon dating and provenance, is discussed.

INTRODUCTION

The phenomenon of TL is extremely complicated and poorly understood as it offers a very large variety of behaviours, corresponding to the different physical systems under consideration.

Suffice it to say that to define such a physical system not only the crystal but also its impuruties and types of lattice defects should be considered.

Generally speaking, TL involves the thermal activation of charge carriers (that is, electrons and holes) and their radiative recombinations. All these transitions occur among levels within the energy gap of the dielectric crystal under consideration (Curie[5]).

The geological history of a rock e.g. limestone, quartz, provide distinct TL characteristics concerning its crystal sensitivity to artificial ionising radiation, presence of ions (traces of the impurities), production of local distortions of the crystal lattice, all of which provide different electron traps and luminescent centers.

TL is a well known technique for dating minerals e.g. quartz, feldspar, calcite, zircon, in geological or archaeological materials. It involves heating the minerals with a constant heating-rate from room temperature to 500 °C to obtain a glow-curve, whose shape and intensity refer to release of electrons from trap and recombination taken place in the crystal lattice (McKeever[6]).

The relationship between the natural TL and natural radioactivity led directly to the use of TL as a means of arriving at the geological age of the specimen. The principal assumption is that the TL is a measure of the absorbed radiation dose since the specimen was last heated, which in the case of a rock is its time of formation, while for sediments and carved stone sufaces is their bleach by solar radiation (Age=absorbed natural radiation dose/annual radiation dose).

Our present work refers to the *dating* and *provenance* of calcites. The former has prompted us to chose certain TL parameters and use them properly for clustering limestone (or marble) samples. Such groupings of calcitic samples are aided also by cathodoluminescence, a technique applied to the microcharacterization of material minerals (Remond et al.[7], Decrouez et.al[8]).

SAMPLING SITES-INSTRUMENTATION

The sampling for dating was made on two megalithic pyramidal buildings, the Hellenikon and Ligourio, one blockhouse, the Fichti of Mycenae, and from Mycenae in Argolid, Greece. Moreover, the idea of using TL to provenance calcites has been extended to a dozen of marbles from within the Delphi archaeological site.

The samples from Hellenikon are; Northern wall: E93/3, E93N, E93/1; Southern wall: E93S; Southern corridor: ETL5, ETL6; Eastern wall: E94E; Western wall: E93W. Those from Ligourio are: LIG or LIG94. Those from the blockhouse are: BLH1, BLH4, from top carved stones. The two samples from Mycenae come from the outer fortified wall. Those from Delphi derive from different monuments within the sanctuary, belonging to different city-states, each providing its own marbles to construct their treasure-houses or statues. Therefore, they are of different quarry origin, which is verified also by the present groupings. Their colours range from white, greyish to reddish.

The TL measurements were taken by two TL readers, i) a home-made computer-interfaced apparatus, using a green J520A and an IR-rejection MTO Ta2 filter, a rate of

4°C/sec (in CRIAA, Bordeaux), and ii) a home-made TL system computer interfaced (in Edinburgh, Galloway[9]); while radiation were performed by a beta source ($^{90}Sr/^{90}Y$; 4 Gbq).

The sample surface was cleaned with dilute HCl acid and powder was removed, sieved to a grain diameter less than 30 μm, diluted to 0.5% acetic acid, and deposited onto aluminium or copper discs for measurement.

THE NEW METHOD OF DATING: **Optical-Thermoluminescence (OTL)**

A new method of dating ancient carved megalithic (cyclopean) buildings has been recently proposed (Liritzis[1,2,3], Theocaris et al[4]. It is based on the solar bleaching of thermoluminescence (TL) of carved surfaces of calcitic materials (limestones, marbles).

Once the carved stone block is exposed to sunlight, electron evistion occurs from the optically sensitive electron traps in the upper around 0.5 mm of the surface. Upon the placement of the stone in to the appropriate position of the wall, the carved surface is no longer exposed to solar radiation. Thereafter, the environmental radiation fills the almost emptied electron traps continuously until present. The measurement of these traped electrons since the wall construction (when the carved surface, previously exposed to sunlight, is in darkness) provides the construction age.(Fig.1). The building OTL age equation is given by the formula: Age= Archaeological Equivalent Dose (AD)/ Dose-Rate (d). The dose-rate (d) for the carved or sculptured surface includes alpha, beta, gamma and cosmic radiation, as follows: $d = (d\alpha)_{cal} + (1/2d\beta)_{cal} + (1/2d\beta)_{pl} + (d\gamma)_{env} + (dc)$, where *cal* is for calcite, *pl* is for plaster or the mortar sometimes intervened between the contacts of two blocks, and, *env*, is for the environmental gamma radiation measured by a portable scintillometer or dosimeter. The coefficient (1/2) refers to 2π-geometry of betas from the sampled surface and the other (1/2) from the betas of the mortar. The attenuation of betas by the etched (during gentle 10% HCl cleaning) surface layer is compensated by the removed beta contribution of this layer (< 100 μm) (Fig.1).

In earlier work (Liritzis[1,2,4], the apparent TL level, after about 20-30 hours of daylight bleaching, was adopted as the representative "background TL signal", occurring in the antiquity, at the time of emplacement of the megalith to the masonry and overlaid by another block. The residual TL level subsequently, determined the equivalent accumulated archaeological dose AD. Further detailed experimental work indicates either the existence of an unbleachable TL residual or the continued exponential decay of the bleached TL, which after about 43 hours is very slow of the order of 20% per 100 h (in contrast to 10-60% per

10 h for the first 45 h of exposure (Fig.2).

One interesting aspect is the variation of residual TL shapes as a function of exposure time to sunlight. The different parts of the TL glow curve - TL intensity versus temperature- are bleached at different rates, being affected variably by solar radiation. Following this observation, the correct ancient TL residual level can be defined as that sun-exposure which yields a AD plateau of maximum length, in the construction of dose-plateau curves, that is, plots of AD versus temperature. This methodology defined a TL residual which together with appropriate TL dose and dose-rate measurements, produce a satisfactory age result for the Tample of Apollo (Delphi) (southern polygonic wall) of 420$\pm$300 years B.C, compared to the archaeological age of 550 B.C.

Also, this new OTL method has been applied to two pyramidal buildings in Argolid producing the ages of; 2730$\pm$630 for the Hellenikon and 2260$\pm$710 for the Ligourio pyramids. A Mycenean wall from the ancient Mycenae of archaeological age 1280 B.C. was dated to 1110$\pm$340 B.C.(Fig.3)

In the effort to develop this novel method of dating it was observed the wide variation in the measured TL parameters, between the rocks even of the same building.

This observation prompted us to use such TL characterestics to possibly provenance these rocks. Indeed, in several instances TL is very sensitive for detecting mineral source identification.

PROVENANCE

The TL can yield useful information on the properties of the various types of defect present within a mineral, since TL is sensitive to traces of impurities which give rise to the localised energy levels within the forbidden energy gap, but also, describe the defect state of a material. Thus, it can characterize different rock formed under different conditions.

The use of TL has progressed fast since 1960's (Aitken[10], McDougall[11], McKeever[6]).

Thus, TL has been used, i) as a means of 'fingerprinting' rocks of the same geological history, based mainly on their variation of their glow curves, ii) as geothermometry, iii) location and researches of geochemistry of uranium, iv) for intermittent geological heating and the possible origin of volcanoes, and v) determination of the age of rocks or artifacts due to initial heating or pressure effects.

In particular, for the limestones studied here, the TL capacity of a crystal of calcite is essentially related to the type and quantity of lattice defects present in the crystal resulting from the physico-chemical conditions which existed at the time of crystallization.

Some ions, especially Mn^{2+} can enter the lattice of calcite by substitution for Ca^{2+} and these ions can act as activators of TL. The entry of the activator elements into the crystal lattice does not only depend upon their concentration in the parent solution, but it is related in a very definite way to the conditions of temperature and pressure during the crystallization.

For example, it has been shown (Medlin[12]), that high temperature calcites exhibit a radiation sensitivity much higher than that of low temperature calcites, and preheating treatment - our first glow curve to 500°C- produced a decrease in the TL of irradiated samples only if they were crystallized at higher temperatures.

Several TL measurements were used as characterestic parameters per each sample (rock).

However, although there may be other TL parameters which may be used for the characterisation of limestone (e.g. regarding TL emission spectra, charge transport, kinetic parameters, Kirsh et al[13]), all of them should be interrelated, since their common mechanism lies on the energy level of traps-holes.

The samples were measured in different times by the two TL readers. The TL parameters measured in each phase of the project were determined according to the particular work carried out (Liritzis et al.[1,3,4].

In the first phase of the project, the following parameters were used: i) presence or absence of 280 and 350 °C TL peaks, ii) the slope for the two linear components of residual TL (R) after solar bleaching, versus the time of sun exposure (LogR, versus,Time), iii) the hours of sun exposure that reduced the geological TL to 50% of the initial signal, iv) the percentage of phototransferred TL at 180 °C to the 280 °C peak, and v) the time of sun exposure, that the two linear components of residual TL, against, time, are changing slope. These parameters produced the cluster of Fig.4a.

In the second phase of the project the following parameters were selected: i) the presence or absence of TL glow peaks 100, 150, 280, 350, 450 °C, ii) the TL sensitivity of the ~120 °C peak to beta radiation, iii) the slope of the first additive-dose build-up curve; while the concentration of U, Th and K was taken into account, too, in the discussion. These parameters produced the clusters of Fig.4b.

Both sets of parameters are essentially reduced to the basic TL phenomenon, and thus, the clustering of these parameters is of interest.

The aggregative hierarchical clusters analysis was performed on the both data sets. Mean Eucledean distance was calculated amongst all the samples. Clustering was performed on the distance matrix using the average linkage criterion. The obtained dendrograms are shown in Figs.4a,b.

a) Fig.4a: The obtained similar groups, as a function of their disimilarity distance from the initial vertical axis (raw of vertical numbers) are : 1) DEL3, DEL5, 2) E94N, 3) LIG94, E94S, 4) DEL1, 5) BLH1, 6) DEL2, 7) E93/1, BLH4, 8) DEL4, DEL8R, 9) DEL8W. (The DEL8R is the red component of the rock, and DEL8W the white vein crossing the red phase).

b) Fig.4b: The obtained similar groups are: 1) E93/3, E93W, ETL5, E93S, 2) MTL3, 3) E93E, following E93N, 4) MTL2, LIG, 5) ETL6. From (2) to (5) there exists a progressive dissimilarity.

DISCUSSION

The TL phenomenon applied to limestones (and similarly to marbles) has shown the potential development of a new method of dating anciend carved limestone blocks from cyclopean structures. The method has been improved regarding choice of sampling and measurement. Further dates should be produced to strengthen the applicability and reliability of the method.

Regarding the provenance, the obtained groupings for Delphi and Argolid samples, verify the long known property of marbles and limestones (Graig and Graig[14]); their variation within the same quarry or stone block. This feature has been observed in TL measurements of marble powder regarding several different TL characteristics.

The diversed nature of limestone samples, as evidenced here with the TL measurements, has been supported by cathodoluminescence (CL) and occasionally by XRD analyses. For example, preliminary CL imaging and spectrum analysis of CL by CCD camera (at CRIAA, Bordeaux) revealed variations in luminescence in the calcitic profiles, firstly, amongst the different samples and, secondly, within the depth of 1 mm from surface. The total luminescence from the CL ranged in colours; faint/intense orange luminescence, blue/dark orange luminescent veins, inhomogeneous distribution of inclusions etc. These differences comply with the obtained TL groupings of Figures 4a,b.

However, it is quite interesting to note the groupings between Delphi samples that derive from marble of different origin (e.g. Paros, Penteli, Naxos, local). From an in-situ inspection, the limestone blocks from Ligourio, Hellenikon and Fichti in Argolid, seem to have been cut from local limestone rock outcrop.

Noticeable is the similarity between the Mycenean sample MTL2, but not the MTL3, and the Ligourio (LIG), two different sites. Similarly, the E93/1 with BLH4, and DEL2 with BLH1, are similar though they come from quite distinct areas. Also, the two mineral phases of DEL8 (red and white marble) form different groupings, as expected. XRD analysis for DEL8white and DEL8red identified the marble and presence of impurities (quartz, illite, complex silicates) content, respectively, further verified from gamma-spectroscopy with the higher potassium content in the red phase.

CONCLUSION

A new physical mechanism of thermoluminescence (TL) has been proposed as a method of dating megalithic carved limestone buildings. This method (optical-thermoluminescence) has been tested, a) in the laboratory on simulation experiments, b) in the dating of two well dated archaeological monuments, in Delphi and Mycenae. Further it hs been applied on two pyramids from Argolid, providing an age of 2000-2500 B.C., much older than the archaeological one of 3rd to 4th century B.C.

The TL parameters used for dating have been properly employed for characterization studies of limestones. This idea has been made using clustering techniques corroborated by cathodoluminescence and microphotography of calcitic profiles. As the TL phenomenon characterises the lattice structure of the material, the proposed technique offers a new way to look for provenance marble and limestone blocks from ancient monuments regarding their quarry.

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REFERENCES

[1] Liritzis.I (1994) A new dating method by thermoluminescence of carved megalithic stone building. C.R. Acad. Sci. Paris, t.319, serie II, 603-610.

[2] Liritzis.I (1996) Archaeometry: Dating the past. ECISTICS (in press).

[3] Liritzis.I, Guibert.P, Foti.F, Schvoerer.M (1996) Solar bleaching of thermoluminescence of calcites. Nucl. Instr. Meth. B, 117, 260-268.

[4] Theocaris.P, Liritzis.I, Galloway.R.B (1996) Dating of two Hellenic pyramids by a novel application of thermoluminescence J. Archaeol. Sci (in press).

[5] Curie.D (1963) Luminescence in crystals. Methuen and Co Ltd. London. (translated in English by G.F.J.Garlick.)

[6] McKeever.S.W.S (1985) Thermoluminescence of solids. Cambridge University Press, Cambridge, pp.376.

[7] Remond.G, Cesbron.F, Chapoulie.R, Ohnenstetter.D, Roques-Carmes.C and Schvoerer.M (1992) Cathodoluminescence applied to the microcharacterization of mineral materials: a present status in experimentation and interpretation. Scanning Microscopy. 6, 1, 23-68.

[8] Decrouez.D, Barbin.V, Zambetakis-Lekkas.A, Lekkas.S and Ramseyer.K (1992) La cathodoluminescence des marbres blancs. Analysis Magazine. 20, 5.

[9] Galloway.R.B. (1990) Notes on a recently constructed TL system. Ancient TL, 8, 2, 10-11.

[10] Aitken.M.J (1985) Thermoluminescence dating. Academic Press, London.

[11] McDougall.D.J (ed.) (1968) Thermoluminescence of geological materials. Academic Press, London, pp.678.

[12] Medlin..W.L (1968) The nature of traps and emission centers in thermoluminescence rock materials. In Thermoluminescence of geological materials, (McDougall.D.J, ed). Academic Press, 193-224.

[13] Kirsh.Y, Townsend.P.D and Shoval.S (1987) Local transitions and charge transport in thermoluminescence of calcite. Nucl. Tracks Radiat. Meas., 13, 2/3, 115-119.

[14] Graig.H and Graig.V (1972) Greek marbles: determination of provenance by isotopic analysis. Science, 176, 401-403.

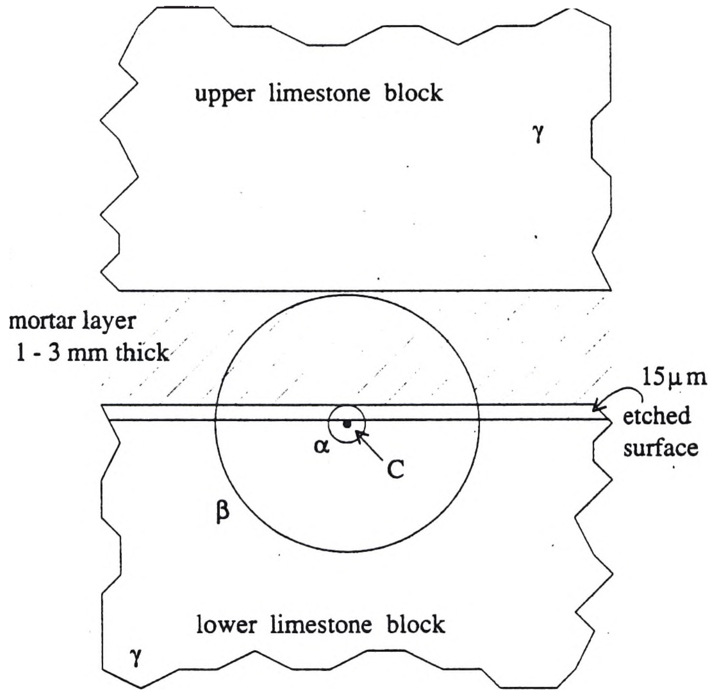

Figure 1 Schematic illustration, of the natural radiation dosimetry relevant to the dating process. The calcite for thermoluminescence measurements is taken from the surface of the lower block after a layer of about 15 μm thickness has been etched off the surface to ensure that clean calcite is used. A grain of the calcite used for dating is indicated by *C* in the diagram (~30 μm diameter). It has been irradiated by alpha particles from within a sphere α of radius equal to the alpha particle range (~30 μm), that is primarily from alpha activity in the lower calcite block; by beta particles from within a sphere β of radius equal to the beta particle range (~1.5 mm), that is from a hemisphere within the lower calcite block and from a hemisphere within the mortar, by gamma rays from both limestone blocks and the surrounding environment, and by cosmic rays.

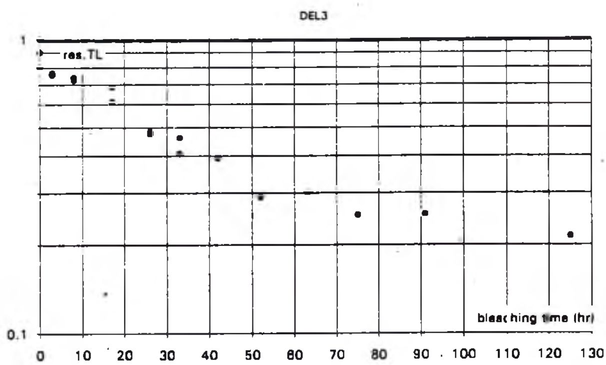

Figure 2 Reduction of thermoluminescence after exposure of a sample from Delphi (monument of Rhodean's chariot, 304 B.C.) to sunlight for different times against the bleaching time in hours.

Figure 3. View of Hellenikon pyramid, in Argolid.

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DATA UNALTERED

                3 DEL3-.
1.220E-1        5 DEL5-'------.                                  A
5.677E-1        8       E94N-I
5.827E-1       10  LIG94-.   I
2.265E-1       13   E94S-'-. I
4.635E-1        1     DEL1-'-I
6.444E-1       11       BLH1-'-.
8.021E-1        2         DEL2-'---.
1.108E+0        9      E93/1-.     I----------.
6.597E-1       12       BLH4-'------'         I
1.857E+0        4           DEL4-             I---.
9.049E-1        7          DEL8R-'------------'   I-
2.254E+0        6                        DEL8W-'
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DATA UNALTERED                                                   B

                5 E93/3-.
1.134E-2        7  E93W-'---.
1.247E-1        6    ETL5-. I-----.
4.914E-2        8    E93S-'-'     I
4.028E-1        3            MTL3-'-.
4.644E-1       10              E93E-'-.
5.004E-1        9                E93N-'-.
6.059E-1        2                  MTL2-I
6.285E-1        1                   LIG-'---.
7.455E-1        4                      ETL6-I
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Figure 4 a) Dendrogram of TL parameters for first phase, b) Dendrogram of TL parameters of second phase (see text).