PERGAMON

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Radiation Measurements 37 (2003) 87–94

Radiation Measurements

www.elsevier.com/locate/radmeas

Thermoluminescence characteristics of marble and dating of freshly excavated marble objects

K. Polikreti*, C.T. Michael, Y. Maniatis

Laboratory of Archaeometry, NCSR "Demokritos", Aghia Paraskevi, 153 10 Attiki, Greece

Received 21 February 2002; received in revised form 27 May 2002; accepted 27 May 2002

Abstract

This work explores the potentials and difficulties in thermoluminescence (TL) dating of marble objects, which have never been exposed to sunlight since their first burial, by applying a new procedure similar in approach to sediment dating. The idea is based on the observation that exposure to sunlight reduces the TL peaks of marble to a residual level. When the marble is buried after bleaching, radiation from the sample and soil, as well as cosmic radiation, refill the electron traps that have been emptied by the sunlight.

Using the additive dose method, an attempt has been made to date a sample of known age (2nd century BC) buried since antiquity. The peak at 290°C was selected as the most suitable for dating (activation energy 1.7–2.0 eV, minimum spurious effects, high intensity, linear response up to 50 Gy, bleachable down to the residual level in 1 h). This peak is well defined in most types of marble, common in antiquity (marble from Penteli, Paros, Naxos and Thassos). The age calculation gave 2570 ± 410 years, which is quite close to the archaeological age. Possible error sources, such as surface impurities and regenerated thermoluminescence, and ways to minimise them are discussed.

Keywords: Thermoluminescence; Dating; Marble; Calcite; Sunlight bleaching

1. Introduction

The thermoluminescence (TL) properties of calcite and limestone have been used for dating. Stalagmitic calcite (Wintle, 1978; Debenham and Aitken, 1984), secondary calcite (Franklin et al., 1988) or fossil shells (Ninagawa et al., 1992) dating is based on the formation of the material. In the case of heated Paleolithic limestones, dating is based on the last heating of the material (Roque et al., 2001).

In this study, we attempt to date a buried marble object by applying a procedure similar to sediment dating. The case study is a marble piece that has never been exposed to sunlight since its first burial. The dating of the piece was carried out according to the following rationale: if a marble artefact is exposed to sunlight at least for an hour, the intensity of the peak at 290°C drops to a residual level (Liritzis and Galloway, 1999; Polikreti et al., 2002), following a function behaving as a stretched exponential (Liritzis and Bakopoulos, 1997). If after bleaching, its surface is covered, i.e. it is buried for a long period of time, radiation from the soil radioactivity will refill the surface traps to a certain extent. Therefore, if a buried marble artefact, can be kept in the dark during and after its excavation, the date of its burial can be obtained. Theocaris et al. (1997) dated the limestone blocks of a megalithic monument using a similar approach. The additive dose method as applied to sediments will be also used here. Spatial inhomogeneity is not a problem in the case of white, well-crystallised marble, but there are several other sources of errors that have to be investigated and minimised.

Marble is a metamorphic rock, i.e. it is formed from a sedimentary rock (limestone or dolstone) by solid-state changes in mineralogy and texture as a result of changes in temperature, pressure and the action of chemically active fluids. Different marble formations correspond to different

---

* Corresponding author.
E-mail address: kpolikreti@ims.demokritos.gr (K. Polikreti).

1350-4487/03/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S1350-4487(02)00088-4

Table 1
High peak temperatures and ratios of peak intensities for marble samples from different quarries

Sample	Marble origin	Dolomite (%)	1st peak (°C)	2nd peak (°C)	ΔT (°C)	Ratio: 1st/2nd Peak
Calcitic						
THAL1	Thassos-Aliki		290	390	100	0.7
THAL2	Thassos-Aliki		293	395	102	0.6
THAL3	Thassos-Aliki		284	394	110	0.3
NXAP10Γ	Naxos-Apollon	7	290	372	82	1.0
NXAP1A	Naxos-Apollon		308	376	68	1.3
NXAP3B	Naxos-Apollon		286	376	90	3.5
NXAP4E2	Naxos-Apollon		284	372	88	3.0
NXDI4	Naxos-Distomo	40	292	379	87	2.0
NXML4	Naxos-Melanes		290	368	78	1.4
NXSP15	Naxos-Spedo	20	286	362	76	5.6
NXSP18	Naxos-Spedo		279	352	73	4.2
ITCR1	Carrara-Italy		305	352	47	1.1
ITCR2	Carrara-Italy		270	368	98	1.0
PALX2	Paros-Lychnites		286	350	65	4.1
PALX6	Paros-Lychnites		284	361	77	4.2
PE10	Penteli		283	344	61	2.0
PE9	Penteli		301	347	46	1.5
PEEP3	Penteli		290	332	42	1.1
PEEP4	Penteli		290	340	50	1.3
PEEP5	Penteli		299	326	27	1.0
PR1	Proconnessus		279	350	71	3.0
PR4	Proconnessus		287	350	63	1.0
YM2	Hymettus		298	374	84	1.9
YM11	Hymettus		290	350	60	1.4
KZRM	Kozani-Rymio		297	340	43	1.3
US1	Usak		301	355	54	1.0
DRMN	Drama-Monastiraki		297	373	76	1.0
Average			290	361	72	
SD			9	18	21	
Dolomitic						
AF1	Afrodisias	62	293	378	85	0.6
BL	Naxos-Volakas	57	320	388	68	3.7
THVA1	Thassos-Vathy	66	300	379	79	1.5

conditions of metamorphosis, which result in different defect and trace element concentrations. We could reasonably consider the thermoluminescence properties of marble to be similar to those of calcite. However, in an attempt to ensure the validity of the method for different types of marble and to minimise possible errors, we made and will present here a full study containing glow-curve shapes, activation energies, frequency factors, response to radiation dose and experimental data concerning regenerated thermoluminescence for a number of marbles.

2. Samples and experimental techniques

All the samples are of white, well-crystallised marble. They come from 15 ancient quarries in Greece, Turkey and Italy (Table 1). The samples are of calcitic ($CaCO_3$) or dolomitic ($CaMgCO_3$) nature and their maximum grain sizes vary from 0.5 to 3.0 mm. Thirty samples were used for the study of glow curve shapes and TL efficiency as a function of impurity content. A more detailed study for determining activation energies of traps, etc., was carried out on four selected representative samples: a dolomitic one from Thassos (Greece) and three calcitic ones from Pentelikon mountain, Naxos and Paros islands (Greece).

The ancient marble piece (lab code: VEEY8) used as a case study for dating, was excavated at ancient Vergina, Macedonia, Greece. The piece, measuring 2.5 × 3 × 10 cm, belongs to an architectural element from the ancient temple dedicated to the goddess Eukleia. It was found, among other pieces, at a depth of 0.6 m, in a destruction layer, dated by archaeologists to the 2nd century BC. The archaeological evidence attributes the collapse of the temple to abandonment due to population movements after the Roman conquest and not to a natural disaster, fire or earthquake (Vakoulis, 2000). The sample was collected in the dark and has been kept in the dark since then.

All the thermoluminescence measurements were performed using the aluminium foil technique (Michael et al., 1997, 1999). The powdered sample is spread with a small paint brush on aluminium foil discs (diameter: 1 cm and thickness: 8 μm) which have been covered by silicon grease. The heating rate was 14°C/s and a Schott KG5 (infrared absorption filter) was used. Normalisation of the peaks was done by a second run of TL after 5.2 Gy irradiation (beta source ^{90}Sr : 0.52 Gy/min). Maximum reproducibility of the peak intensities was achieved for grain sizes between 80 and 125 μm and this range was used in sample preparation. In order to avoid tribo-luminescence, the powdered samples were etched with acetic acid 0.5% for 1 min (Wintle, 1975; Göksu et al., 1988). The sample treatment and preparations were all performed under red light to avoid bleaching effects.

According to Bettinali and Ferraresso (1968) adsorption thermoluminescence is avoided in high vacuum ($< 10^{-3}$ mm Hg). Adsorption thermoluminescence is generated by the recombination of electrons trapped on oxygen atoms (which are adsorbed by the surface and diffuse through the bulk) with positive centres (Mn^{2+}) or holes. Given that the vacuum in our chamber is slightly lower than 0.06 mm Hg and that it is not possible to distinguish between TL and adsorption TL by optical filters, our measurements most probably contain an adsorption TL component.

The samples used in studying the TL efficiency versus ion concentration were treated according to a “heating–irradiating” protocol: 1 h heating at 500°C followed by irradiation of 5 Gy beta. The TL efficiency cannot be represented by simple TL intensity recordings, because these values are affected by bleaching and/or regeneration phenomena (several samples were small, exposed to sunlight for various time intervals and kept in drawers for months or years). A standard treatment was followed to ensure that the recorded intensity variation expresses the variation of sample sensitivity to beta irradiation.

Electron paramagnetic resonance (EPR) spectroscopy was used to measure the relative concentration of the Mn^{2+} and Fe^{3+} ions in the calcite or dolomite crystals of the marble matrix. The measurements were done using an EPR BRUKER ER-200 spectrometer (X-band, microwave frequency $f = 9.42$ GHz), at room temperature. A quantity of 220 mg of marble powder was used for each measurement. The instrument settings used are described by Mandi et al. (1992), Polikreti and Maniatis (2002) and used for standard marble characterisation and provenance investigation in conjunction with a large databank on ancient marble quarries.

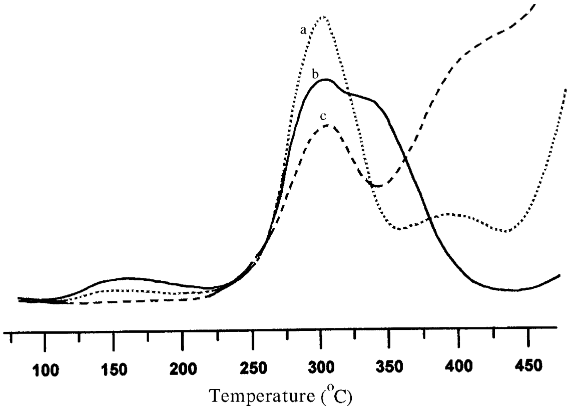

Fig. 1. Typical thermoluminescence curves for different types of marble: (a) White Naxian (Apollon quarry) (intensity multiplied by 5), (b) White Pentelic, and (c) White Thassian (Aliki quarry) (intensity multiplied by 5).

3. Results and discussion

3.1. General characteristics of the TL of marble

3.1.1. Glow curve shapes

The natural thermoluminescence of marble was studied on 30 samples of 15 different types, with various Mn^{2+} concentrations and grain sizes. Peak temperatures and intensity ratios are given in Table 1, while typical glow curves of marble are given in Fig. 1. Three peaks are generally observed in agreement with other researchers (Bruce et al., 1999): A peak at around 180°C, a well-defined intense peak at 285–300°C and a weak one at 325–390°C (the exact temperatures depend on type of marble), which overlaps with the black-body radiation.

Except for the samples from Thassos-Aliki which have the third peak at an unusually high temperature, and those from Penteli and Rymio-Kozani with the characteristic overlapping peaks (Fig. 1), all other shapes (including dolomitic samples) are similar to that of curve 1a (Naxian marble). However, the intensities of the TL peaks may vary greatly between different marbles (note the scale differences in the curves of Fig. 1). The intensity of the 290°C peak has been reported to be linear with Mn^{2+} concentration, as Mn^{2+} is considered the main recombination centre for calcites (assuming isolated activator centres, Medlin, 1968; Lapraz and Iacconi, 1976). The TL intensities for the samples of Table 1 (treated according to the heating—irradiating protocol of paragraph 2) versus Mn^{2+} concentration are given in Fig. 2. A linear trend of TL intensity with Mn^{2+} concentration is obvious, although large variations from linearity are observed. This scatter is inevitable given the fact that beside Mn^{2+} concentration, there are other structural and mineralogical variations between the samples used in Fig. 2. The concentration of Fe^{3+}, for example, which is a typical

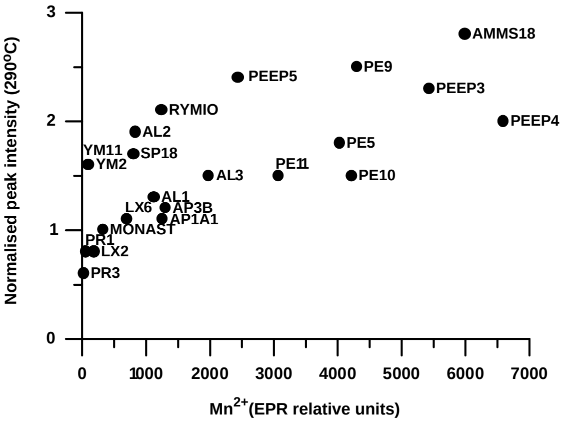

Fig. 2. Correlation of thermoluminescence intensity with Mn^{2+} concentration measured by EPR, for samples from different quarries.

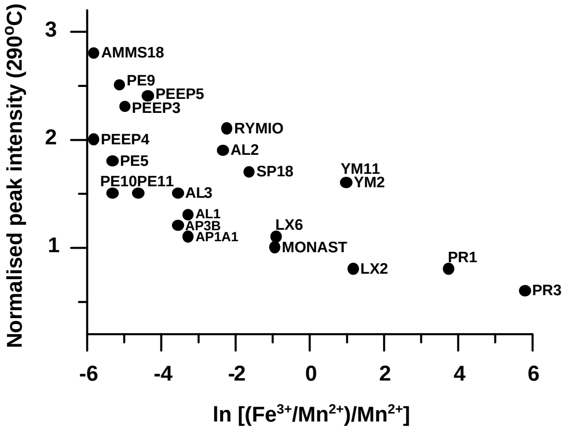

Fig. 3. Correlation of thermoluminescence intensity with Fe^{3+} to Mn^{2+} ratio measured by EPR, for samples from different quarries.

luminescence quencher (Medlin, 1963, 1968), also varies a lot between these samples. The quenching effect of Fe^{3+} is obvious in Fig. 3, where the TL signal intensity decreases with relative Fe^{3+} concentration. The simultaneous presence of Fe^{3+} and Mn^{2+} and their opposing effects, lead us to the use of the normalised (Fe^{3+}/Mn^{2+})/Mn^{2+} ratio, as the most suitable formula to express the overall quenching result with respect to Mn^{2+} concentration.

3.1.2. *Activation energies*

In our attempt to find a TL peak suitable for marble dating, we calculated the activation energies and corresponding lifetimes of the observed peaks. Our target was to calculate the age of "burial", i.e. the date of "first covering of the marble piece by soil". Peaks originating from traps with lifetimes on the scale of tens of thousands of years are thus suitable for this archaeological piece.

The activation energies (E) and frequency factors (s) were calculated by two methods: initial rise and peak shift with heating rate (McKeever, 1985) and the results are given in Table 2. Four samples were used, originating from the most important ancient quarries (Pentelikon mountain, Thassos Vathy (dolomitic sample), Naxos Melanes and Paros Lychnites).

The peak shift method gives higher energy values in general, probably due to thermal quenching. The dolomitic sample from the Thassos–Vathy quarry gives larger activation energies than the calcitic samples. Crystal lattice differences and in particular the presence of Mg^{2+} probably favours the formation of deeper traps.

The peak at 180°C shows a lifetime ranging from several days to several years. This lifetime is very short as expected, considering that this peak is produced by phototransferred thermoluminescence (Lima et al., 1990; Liritzis et al., 1996; Bruce et al., 1999) and the traps producing it are unstable. The peak at 290°C shows energy depths from 1.70 to 2.00 eV and lifetimes from 10^5 to 10^8 years. Finally for peak at 350°C, the energy depths calculated range from 1.87 to 2.30 eV and the lifetimes from 10^7 to 10^{12} years. This peak has been used for calcite dating in the past (Wintle, 1978; Debenham and Aitken, 1984). However, we consider the peak at 290°C more suitable for dating, as it is better defined and more intense than the 350°C peak. Other disadvantages of the 350°C peak are that it showed supralinearity for doses above 50 Gy for the dolomitic sample, and it has been reported to be susceptible to spurious signals (Roque et al., 2001).

3.1.3. *Regenerated thermoluminescence*

Marble samples exposed to sunlight show increased TL intensities after short or long period storage. Such self-regeneration phenomena (similar to recuperation of OSL) have also been observed in other materials (Charalambous and Hasan, 1983), for samples both in powder and crystal form. A study of the regenerated TL evolution with time was necessary in order to estimate the error induced in age calculations. Thus, homogenised powder from 5 different types of marble was exposed to natural sunlight for 5 days (for the TL to reach the residual level) and the thermoluminescence was measured after 10 min, 10 days, 1 month and 3 months. The samples were kept in a dry, dark drawer, at room temperature.

Fig. 4 shows the thermoluminescence intensity versus time after bleaching for the peak at 290°C. The intensity shows an increase with time in the first month after bleaching, which can be from about 20% of its residual dose up to 100%, depending on the type of marble. The regenerated thermoluminescence seems to reach a plateau after about 3 months, for all marble types. Since the peaks of both the natural and the regenerated thermoluminescence occur at the same temperature, the phenomenon involves the same traps as the irradiation-induced thermoluminescence. A possible

Table 2
TL parameters for four characteristic marble types; T_m is the peak temperature, E the activation energy, s the frequency factor and t the lifetime

T_m(°C)	Initial rise method			Peak shift with heating rate		
	E (eV)	s(s^{-1})	Lifetime (yr)	E (eV)	s(s^{-1})	Lifetime (yr)
PESP5	*Penteli*					
170	1.08	1×10^{12}	18 days	1.11	6×10^{11}	89 days
285	1.70	1×10^{15}	1×10^{6}	1.82	3×10^{16}	4×10^{6}
348	1.87	9×10^{14}	1×10^{9}	1.94	2×10^{17}	6×10^{7}
THVA2	*Thassos*					
200	1.30	5×10^{13}	4	1.40	5×10^{15}	2
295	1.75	2×10^{15}	4×10^{6}	1.97	2×10^{17}	2×10^{8}
378	2.10	1×10^{16}	6×10^{11}	2.30	2×10^{18}	7×10^{12}
NXML5	*Naxos*					
185	1.14	2×10^{12}	83 days	1.18	8×10^{12}	10^{2} days
290	1.72	2×10^{15}	1×10^{6}	1.78	1×10^{15}	3×10^{7}
368	1.98	1×10^{15}	3×10^{10}	2.03	2×10^{16}	2×10^{10}
PRLX2	*Paros*					
184	1.03	2×10^{11}	11 days	1.10	1×10^{12}	36 days
286	1.70	10^{15}	3×10^{5}	1.69	1×10^{15}	8×10^{5}
350	2.01	10^{16}	2×10^{10}	2.11	2×10^{16}	5×10^{11}

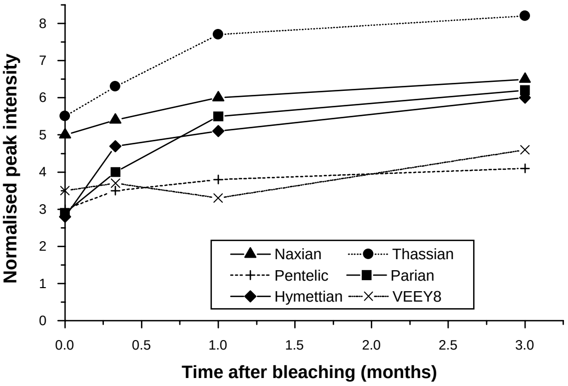

Fig. 4. RTL versus time after bleaching for 5 days in natural sunlight, for various marble types (peak at 290°C normalised by weight).

explanation is that, during bleaching, the photo-evicted electrons are retrapped into short- or mid-term centres. The regenerated thermoluminescence is then produced by their recombination with the photo-luminescent centres via a tunneling process.

Regeneration rates also seem to be quite high for marble surfaces exposed to sunlight for long periods. For a specimen exposed to sunlight for 8 years, the regeneration TL is in the range between 33% and 60% of the remaining TL (depending on the sample distance from the surface) after 6 months storage.

This regeneration phenomenon complicates dating, since it starts as soon as the sample is buried. An extra error is thus added to the calculated age, which can be significant especially for "young" samples. From Fig. 4 we can estimate an upper limit for this additional TL intensity, which is 100% of the value of the residual level (for the Parian sample). These problems and possible solutions are discussed in the dating application presented below.

3.2. *Application of the method to dating of a buried marble object*

The marble piece we attempted to date was broken off from an architectural piece, in the middle of the 2nd century BC, when the Temple of Eukleia tumbled. The piece ($2.5 \times 3 \times 10$ cm^3) was excavated in the dark and since then kept in a black plastic bag. It shows an ancient, almost flat, ground surface and three other broken surfaces, created when the piece broke off. All surfaces were thoroughly washed with water at first, dried in air, etched with hydrochloric acid 0.5N (for 5 min), ground by sandpaper and etched again (HCl 0.5N for 5 min). This treatment was considered absolutely necessary, as the ancient surface was quite uneven with bumps up to 1 mm, and the removal of soil from the depositions was difficult. Finally, a surface layer of approximately 2 mm was removed.

The dating procedure used here is the one normally used for sediment dating. The event that sets the TL clock to zero is the exposure to sunlight, as it is in the case of

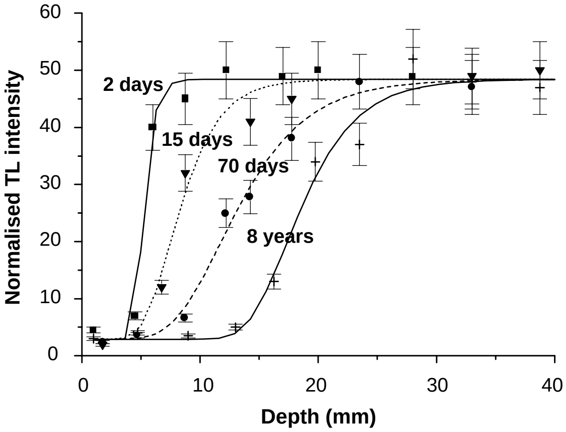

Fig. 5. Thermoluminescence versus distance from the marble surface for various exposure times (Pentelic marble). TL intensities are normalised by a monitor beta dose.

sediments. Even 1 h of exposure is enough to bleach the TL of marble (peak at 290°C) down to its residual level (Liritzis and Galloway, 1999; Polikreti et al., 2002). The TL will re-accumulate if the exposed marble piece is buried and the calculated age will be the time elapsed since the "first burial". This "first burial" of course is not an exact moment and may represent as much as a whole year or more. We also assume that the burial period is undisturbed and continuous.

To ensure that the clock really started from zero, we have to ensure that even at a depth of 2 mm (the surface layer we removed) the TL intensity has reached the residual level at the moment of "first burial". Fig. 5 is a study of TL with depth for different exposure time intervals (Polikreti et al., 2002). It can be seen that two days of exposure are enough to minimise the TL to a residual level, up to a distance of 3 mm into the marble surface. Since the ancient surface of VEEY8 has certainly been exposed to sunlight for a few years, we can securely suggest that when the piece broke off, i.e. at the starting moment of burial, the TL in the first 3 mm layer was equal to the residual.

The profile of TL with depth of VEEY8 was also obtained (Fig. 6). The TL is practically the same throughout the marble piece. This can be explained again by Fig. 5. If the freshly broken surface of VEEY8 has been exposed to the sun for at least 3 months, the TL would reach the residual level at a depth of approximately 1 cm.

Another conclusion of Fig. 6 is that the contribution of beta irradiation from the ground is negligible in a depth of 2 mm (the surface sample of Fig. 6 is actually 2 mm deep because we have removed a surface layer of this thickness). We can thus ignore beta irradiation in the calculations for the annual dose.

3.2.1. *Total absorbed dose*

The additive dose method was used on a surface chip 0.5 mm thick.

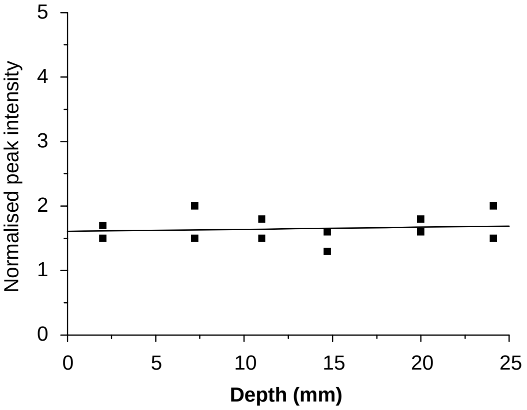

Fig. 6. Thermoluminescence versus distance from the marble surface for the dated marble piece. TL intensities are normalised by a monitor beta dose.

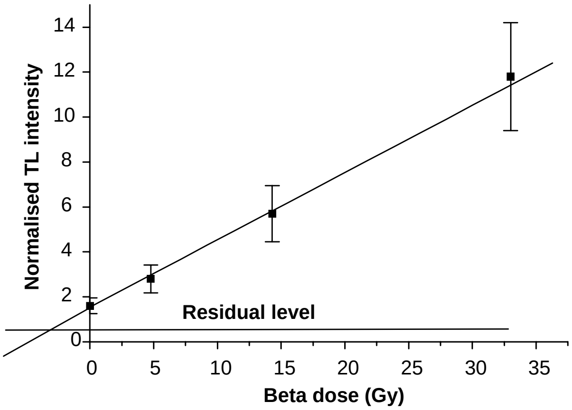

Fig. 7. Build-up curve for the sample taken from the marble surface. The residual level is also shown.

Aliquots from the chip (prepared according to the procedure described in paragraph 2) were irradiated and a build up curve was obtained for the peak at 290°C (Fig. 7). The response to irradiation is linear up to 50 Gy. No supralinearity or predose effect was observed. The age was calculated by the well-known equation:

$$\text{Age} = \frac{\text{Total absorbed dose}}{\text{Annual dose}}.$$

The *Total absorbed dose* was calculated from the interception point of the build-up curve and the residual level (Fig. 7) (Aitken, 1985). The residual level was obtained after exposure to sunlight for 5 days, with the average of four measurements giving 0.5 ± 0.1 (normalised intensity), a value equal to 25% of the natural TL.

The calculations gave: Total absorbed dose = 3.49 ± 0.50 Gy.

3.2.2. Annual dose

The annual dose is a sum of the contributions from surrounding soil radioactivity, the cosmic ray dose and the radioactivity due to U, Th and ^{40}K in the marble piece. The surrounding soil dose rate and cosmic dose rate was measured in situ, at 1.04 mGy/year with a portable scintillometer (calculated for 4π geometry). Gamma attenuation in the sample and effects on gamma dose induced by differences in matrix composition between soil and calcite, have been neglected. As long as the outer 2 mm layer of the sample is discarded we do not need to take the beta contribution from the soil into account.

$$D_{\text{environment}} = 1.04 \pm 0.06 \text{ mGy/yr}.$$

The radioactive elements concentration in the marble were evaluated with alpha-counting (U $= 103 \pm 42$ ppb, Th $= 0.1 \pm 0.1$ ppm). For ^{40}K concentration, an average taken from 169 marble samples, analysed with neutron activation analysis was used (Mandi, 1993). This value is 51 ± 2 ppm. According to the radiation dose–rate data of Adamiec and Aitken (1998) the dose per year from the marble itself was calculated:

$$D^{\text{a}}_{\text{marble}} = 0.319 \pm 0.033 \text{ mGy/yr},$$

$$D^{\text{b}}_{\text{marble}} = 0.019 \pm 0.003 \text{ mGy/yr}.$$

Finally,

$$D_{\text{marble}} = 0.320 \pm 0.039 \text{ mGy/yr}.$$

The k-value was taken equal to 0.28 ($\pm$0.12), which is the mean value taken from 36 values given in the bibliography for calcites, stalagmitic calcites and limestones (Wintle, 1978; Debenham and Aitken, 1984; Theocaris et al., 1997; Roque et al., 2001). The annual dose was then calculated : annual dose $= 1.358 \pm 0.072$ mGy/yr.

The values of total absorbed dose and annual dose was put in Eq. (5) and the age was calculated : age = 2570 yr. The calculation of the total error according to propagation of errors gave ±410 yr. The preliminary age evaluation is very satisfying, given that the archaeological date lies in the 2nd century BC.

However, the calculated error does not include regeneration effects. Also, the level of regenerated TL shown in Fig. 4 is ambiguous, due to the lack of data after prolonged exposure to sunlight, for this particular type of marble. We certainly have evidence that the real age is younger than the one calculated and the error due to regeneration depends on marble type, but it is too early to calculate a precise regeneration error. Assuming that Fig. 4 can give us an idea of the maximum regeneration level, we can have a rough estimation of the induced error. This maximum level for VEEY8 is up to 30% (0.16 ± 0.05 thermoluminescence units), a value which adds a 16% correction to the calculated age. In other types of marble, regeneration effects may be stronger and the shift in the final age larger, but this has to be tested during the dating procedure.

4. Conclusions

The TL of marble was studied systematically for the first time, taking into account the different types of marble, in order to find a stable but bleachable peak, well defined in all types of white marble and suitable for dating. The peak at 290°C satisfies all the above, with activation energies from 1.7 to 2.0 eV and a time period of 1 h needed to reach the residual TL under exposure to sunlight.

The aim of the study was to develop a methodology for dating the moment of burial of an ancient marble object. The rationale is similar to that in sediment dating: the zeroing mechanism is exposure to sunlight and the zero moment is the time of “first burial”. The results are very encouraging, as the calculated age—range (1st–4th centuries BC) matches the archaeological age (2nd century BC).

A few requirements are necessary for the method to be valid. First, the marble surface to be dated should have been exposed to sunlight for a period long enough to reduce the TL to the residual level. This period depends on the crystallisation, transparency and homogeneity of the marble to be dated. To ensure that despite these deviations the methodology can be used, the full profile of TL with depth should be taken and compared with reference curves for the same type of marble. The characterisation of the type and provenance of marble is therefore an important requirement. Second, the burial conditions must be undisturbed and suitable for a more or less precise annual dose determination (i.e. not in a grave among bones or built in a wall foundation, etc.). Third, a thorough cleaning of the surface is essential to avoid soil impurities.

Finally, the problem of regenerated TL can produce overestimations of age that can be very serious for certain types of marble, and a study of the regenerated TL versus time must be done for each sample.

References

Adamiec, G., Aitken, M.J., 1998. Dose-rate conversion factors: update. Ancient TL 16 (2), 37–50.

Aitken, M.J., 1985. Thermoluminescence Dating. Academic Press, New York.

Bettinali, C., Ferraresso, G., 1968. Adsorption TL of CaCO3. In: McDougall, D.J. (Ed.), Thermoluminescence of Geological Materials. Academic Press, London, pp. 143–152.

Bruce, J., Galloway, R.B., Harper, K., Spink, E., 1999. Bleaching and phototransfer of thermoluminescence in limestone. Radiat. Meas. 30 (4), 497–504.

Charalambous, S., Hasan, F., 1983. Regenerated thermoluminescence. Phys. Lett. 95A, 259–262.

Debenham, N.C., Aitken, M.J., 1984. Thermoluminescence dating of stalagmitic calcite. Archaeometry 26 (2), 155–170.

Franklin, A.D., Hornyak, W.F., Tschirgi, A.A., 1988. Thermoluminescence dating of Tertiary period calcite. Quat. Sci. Rev. 7, 361–368.

Göksu, H.Y., Pennycock, S.J., Brown, L.M., 1988. Thermoluminescence and cathodoluminescence studies of calcite and MgO: surface defects and heat treatment. Nucl. Tracks Radiat. Meas. 14 (3), 365–368.

Lapraz, D., Iacconi, P., 1976. On some luminescent and optical properties of synthetic calcite single crystals. Phys. Status Sol. A 36, 603–615.

Lima, J.F., Trzesniak, P., Yoshimura, E.M., Okuno, E., 1990. Phototransferred thermoluminescence in calcite. Radiat. Prot. Dosim. 33 (1/4), 143–146.

Liritzis, I., Bakopoulos, Y., 1997. Functional behavior of solar bleached thermoluminescence in calcites. Nucl. Instrum. Methods Phys. Res. B 132, 87–92.

Liritzis, I., Galloway, R.B., 1999. Dating implications from solar bleaching of thermoluminescence of ancient marble. J. Radioanal. Nucl. Chem. 241, 361–368.

Liritzis, I., Guibert, P., Foti, F., Schvoerer, M., 1996. Solar bleaching of thermoluminescence of calcites. Nucl. Instrum. Methods Phys. Res. B 117, 260–268.

Mandi, V., 1993. Provenance determination of the marble of ancient monuments with the techniques of electron paramagnetic resonance spectroscopy and neutron activation analysis. Ph.D. Thesis, Department of Chemistry, University of Athens (in Greek).

Mandi, V., Maniatis, Y., Bassiakos, Y., Kilikoglou, V., 1992. Provenance investigation of marbles with ESR spectroscopy: further developments. Acta Archaeol. Lovaniensia Monogr. 4, 213–222.

McKeever, S.W.S., 1985. Thermoluminescence of Solids. Cambridge University Press, Cambridge.

Medlin, W.L., 1963. Thermoluminescence in calcite. J. Opt. Soc. Am. 53, 1276–1285.

Medlin, W.L., 1968. The nature of traps and emission centers in TL rock materials. In: McDougall, D.J. (Ed.), Thermoluminescence of Geological Materials. Academic Press, London, pp. 193–223.

Michael, C.T., Zacharias, N., Maniatis, Y., Dimotikali, D., 1997. A new technique (foil technique) for measuring natural dose in TL dating and its application in the dating of a mortar containing ceramic fragments. Ancient TL 15 (2–3), 36–42.

Michael, C.T., Zacharias, N., Polikreti, K., Pagonis, V., 1999. Minimising the spurious TL of recently fired ceramics using the foil technique. Radiat. Prot. Dosim. 84 (1–4), 499–502.

Ninagawa, K., Adachi, K., Uchimura, N., Yamamoto, I., Wada, T., Yamashita, Y., Takashima, I., Sekimoto, K., Hasegawa, H., 1992. Thermoluminescence dating of calcite shells in the Pectinidae family. Quat. Sci. Rev. 11, 121–126.

Polikreti, K., Maniatis, Y., 2002. A new methodology for marble provenance based on EPR spectroscopy. Archaeometry 44 (1), 1–21.

Polikreti, K, Michael, C.T., Maniatis, Y., 2002. Authenticating marble sculpture with thermoluminescence. Ancient TL, in press.

Roque, C., Guibert, P., Vartanian, E., Bechtel, F., Schvoerer, M., 2001. Thermoluminescence—dating of calcite: study of heated limestone fragments from Upper Paleolithic layers at Combe Saunière, Dordogne, France. Quat. Sci. Rev. 20, 935–938.

Theocaris, P.S., Liritzis, I., Galloway, R.B., 1997. Dating of two Hellenic pyramids by a novel application of thermoluminescence. J. Archaeol. Sci. 24 (5), 399–405.

Vakoulis, Th., 2000. Marble quarries in ancient Macedonia and investigation of provenance for the marble. Ph.D. Thesis, University of Thessaloniki, Greece.

Wintle, A.G., 1975. Effects of sample preparation on the thermoluminescence characteristics of calcite. Mod. Geol. 5, 165–167.

Wintle, A.G., 1978. A thermoluminescence dating study of some Quaternary calcite: potential and problems. Can. J. Earth Sci. 15, 1977–1986.