Authenticating marble sculpture with thermoluminescence

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Abstract: *Several attempts have been made in the past to develop a methodology for authenticating marble artifacts and monuments. They have been basically focused on understanding the weathering alterations in the chemical composition of the surface. The present study presents a new approach which concentrates on the bleaching of the thermoluminescence, occurring when the marble surface is exposed to sunlight. Exposure to sunlight reduces the TL peaks of marble to a certain low level, with similar bleaching rates for samples from different geological formations. The effect of sunlight is reduced with depth from the surface of marble. An equation-model describing the combined dependence of TL intensity on exposure time and depth from the surface of the marble is proposed. The potential of using this model as an authenticity test for artifacts continuously exposed to sunlight is proved with applications on ancient and modern pieces.*

Introduction

The need for a scientific technique to detect forgeries of marble sculpture is getting very urgent because of the continuous appearance of doubtful cases, involving large amounts of money and historical importance. The scientific community however, have not been able yet, to develop a reliable methodology. The problem arises from the fact that the bulk of a marble piece is a stable geological material and dating techniques, would give the geological rather than the historical age.

Authenticity approaches in the past, focused on the surface alterations, depositions, gradual change of ion concentration etc.

One of the most usual approaches involves testing of the disputed artefacts under ultra-violet light, where they should phosphoresce either in purple in case they are authentic, or in amber in case of forgeries (Young and Ashmole 1968). Unfortunately the results of the technique have not been scientifically documented and interpreted and consequently they are not reliable. Furthermore they depend strongly on the condition of the marble surface, past treatments (cleaning, varnishing, consolidating or even taking plaster copies).

Most researchers, on the other hand, study the gradual change of ion concentration from the surface to the marble interior (Margolis and Showers 1988, Ulens et al. 1995). However, these changes are not easily quantifiable due to their complicated formation procedures and unfortunately they can be produced artificially in the laboratory (Heller and Herz 1995). Furthermore, the reports on gradual ion transportation inwards and outwards from the bulk of marble, have not been verified on ancient samples.

The present work intends to contribute in the authenticity of marble from another point of view. Our approach concentrates on the defects existing in the marble since geological times. Exposure to sunlight anneals these defects up to a depth depending on the exposure time. The technique of Thermoluminescense is used to quantify the relationship between depth and exposure time and an equation model is proposed, which discriminates ancient from modern surfaces exposed to sunlight for a considerable period of time.

The results presented here are a first step towards the development of a new full methodology for solving authenticity problems of marble artefacts under all conditions.

Experimental methods and techniques

All the thermoluminescence measurements were performed by using the aluminum foil technique (Michael et al. 1997, Michael et al. 1999). The powdered sample is spread with a small paint brush on aluminium foil discs (diameter of 1cm, thickness of 8μm) and covered by silicon grease. The technique ensures good heating contact between sample and heater plate and increases reproducibility even in high heating rates. Another advantage is the reduction of chemiluminescence, since the measurements can be performed under vacuum. The heating rate was 14°C/sec and a BG39 (infrared absorption filter) was used. Normalisation of the peaks was made by dividing with a monitor beta dose (^{90}Sr: 0.52 gray/min).

The effects of mechanical treatment (Wintle 1975, Goksu et al. 1988) have been proved to be disastrous in calcite dating and several remedies have been proposed (Wintle 1975, Bangert and Henning 1979), the pressure exerted is the main cause (Maniatis and Mandi 1992). In order to avoid tribo-luminescence (in this case new traps created on the grain surfaces by grinding), the powdered samples were etched with acetic acid 0.5% for 1 min.

Maximum reproducibility of the peak intensities was achieved for grain sizes between 80 and 125μm and this range was used in sample preparation. The reproducibility of the peak temperature was calculated at ±1°C and of peak intensity at 22%.

All measurements and sample preparations were performed under red light. The use of a solar simulator was avoided since several researchers report that the presence in the light source of a strong ultraviolet component gives risk of removal of residual TL or phototrasfer phenomena (Aitken 1985, McKeever 1986). All samples thus were exposed to natural sunlight, in June, October and November in Athens.

The specimens for the TL profile measurements were cylinders of diameter 20mm and length 60mm approximately, drilled out in red light. After cleaning them with HCl, 0.5 N they were exposed to natural sunlight. Following that, thin (1-1.5mm) slices parallel to the exposed surface were cut from the surface to the interior of the specimens and cleaned again with HCl, 0.5N.

Results and Discussion

The natural thermoluminescence of marble was studied on thirty four samples from fifteen different quarries, with various Mn^{2+} concentrations and grain sizes. Mn^{2+} is considered the main recombination center for calcites (Medlin 1968, Lapraz and Iacconi 1976, Calderon et al. 1984, Down et al. 1985). Typical glow curves of marble are given in Figure 1. Three peaks are generally observed in agreement with other researchers (Bruce et al. 1999) and their energy depths were measured with the initial rise method and peak shift with heating rate (Mc Keever 1985): a) A peak produced by photo-transferred thermoluminescence (Lima et al. 1990, Liritzis et al. 1996, Bruce et al. 1999) at around 180°C, b) a well defined and stable peak at 285-300°C (lifetimes from 10^5 to 10^8 years) and c) a very stable (lifetimes from 10^7 to 10^{12} years) peak, of low intensity at 325-390°C, which overlaps with black body radiation. This peak has been used for calcite dating in the past (Wintle 1978, Debenham and Aitken 1984). However, our experiments showed that the peak at 290°C is quite suitable for monitoring the changes of thermoluminescence of marble due to bleaching and as it is better defined than the 325-390°C peak was used in this work.

The relative intensities between the two high temperature peaks vary for different types of marble. The ratio observed in curve 1a corresponding to Naxian marble is the most common one.

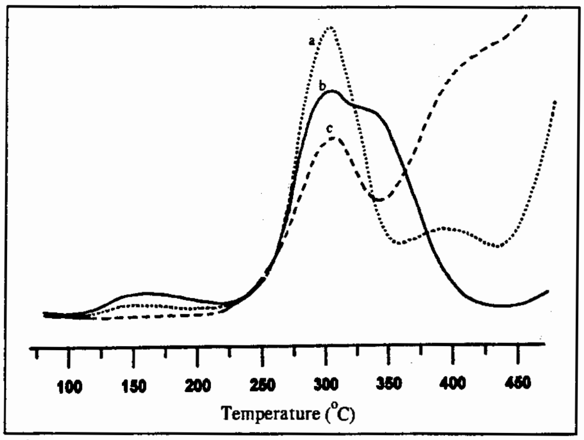

Figure 1.

Typical thermoluminescence curves for different types of marble:

- *a) White Naxian (Apollon quarry) (intensity multiplied by 5)*
- *b) White Pentelic*
- *c) White Thassian (Aliki quarry) (intensity multiplied by 5).*

Bleaching of thermoluminescence was observed in all types of marble exposed to sunlight. Marble slabs ($4x4\ cm^2$, 4 mm thickness), were exposed to sunlight for different time intervals. The resulting plot for the peak at 290°C is shown in Figure 2 (Parian marble, Lychnites). The experiment was repeated with samples from four different quarries with different grain sizes and Mn^{2+} concentration. The peak at 290°C, shows the same behaviour in all quarry samples: After 20 minutes of exposure, the peak loses 80% of its initial intensity. The reduction in peak intensity continues at a lower rate, until 60min when it reaches the lowest level which remains practically constant even after a prolonged exposure (residual TL) say 3 months. The intensity of the residual level is usually 11 to 18% of the natural thermoluminescence.

The data in all cases can be fitted by the sum of two exponential functions (Polikreti et al. 1996, Liritzis et al. 1996). One with a time constant of 0.09-0.16 min^{-1} and a second one with a time constant of 0.001-0.002 min^{-1}(Table 1). The phenomenon can be explained by the existence of two different types of electron traps in the $CaCO_3$ lattice. Electrons in these traps have different escape probabilities. Those with the higher probabilities of escape are evicted from their traps easily and cause the high bleaching rate observed at the first 20 minutes.

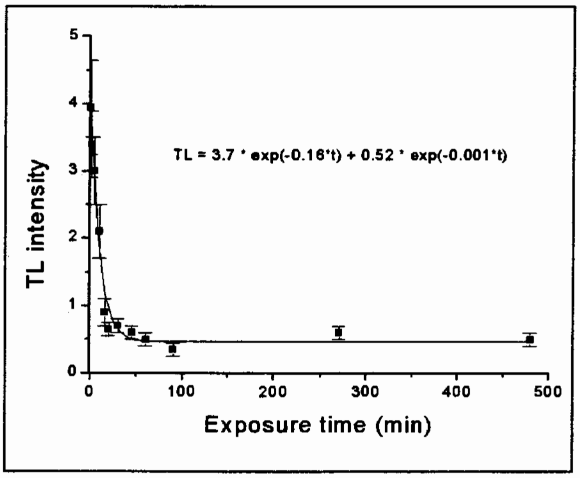

Figure 2.
TL intensity versus exposure time (white Parian marble, Lychnites). TL intensities are normalised with a second glow.

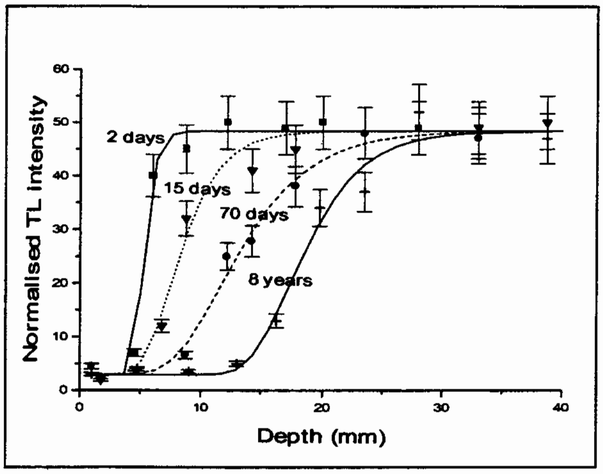

Figure 3.
Thermoluminescence versus distance from the marble surface for various exposure times (Pentelic marble). TL intensities are normalised with the second glow.

For a detailed study of thermoluminescence versus distance from the surface, the TL profiles of thermoluminescence with depth were drawn for three specimens from a quarry from Pentelikon mountain. They were exposed to natural sunlight for 2, 15 and 70 days (Fig. 3). Another profile, of a surface exposed for 8 years (the date of last use of a modern marble quarry) was also drawn. All curves show an initial part near the exposed surface where thermoluminescence is minimum and then an almost linear increase, up to a maximum value which corresponds to the natural (geological) thermoluminescence of the particular marble piece.

In an attempt to find an equation describing the curves of Figure 3, the following assumptions were adopted:

Theoretical Approach

To simplify the calculations, we assume that the decrease of TL versus time is represented by an exponential term plus a constant. This simplification does not introduce major errors since the second exponential term fades very slowly (Tab. 1). According to this assumption TL at two different depths d and d+x, which correspond to exposure times t_d and t_{d+x} will be:

$$\begin{aligned} TL_d &= R + C\exp(-\lambda_d t_d) \quad \text{(a)} \\ TL_{d+x} &= R + C\exp(-\lambda_{d+x} t_{d+x}) \quad \text{(b)} \end{aligned} \qquad (1)$$

where R is the the residual TL, C the geological minus residual TL and λ_d the time constant at depth d If the two TL intensities are equal, then:

$$\lambda_d t_d = \lambda_{d+x} t_{d+x} \qquad (2)$$

Now we can assume that the marble matrix, is an homogenous and isotropic material, where the intensity of a light beam passing through it, decreases according to Lambert - Beer law:

$$I_{d+x} = I_d \exp(-kx) \qquad (3)$$

where I_d, I_{d+x} are the beam intensities at depths d and d+x and k(mm^{-1}) is a constant depending on the wavelength of sunlight radiation and the transparency of marble (i.e. density, texture, grain size and accessory minerals).

Assuming that the total number of sunlight photons or the total energy E ($=I\cdot S\cdot t$), needed to decrease natural TL to a certain intensity is the same for the two depths d and d+x, we have:

$$E = I_{d+x} \,.\, S \,.\, t_{d+x} = I_d .\, S \,.\, t_d$$

where S is the cross-sectional area.

Hence from eq. 3,

$$t_d / t_{d+x} = \exp(-kx) \qquad (4)$$

and combining with eq. (2) we have:

$$\lambda_{d+x} = \lambda_d \exp(-kx) \qquad (5)$$

Introducing eq. 5 to eq. 1(b) gives (for d=0) a double exponential equation:

$$TL_x = R + C \exp(-\lambda_o\, t \exp(-kx)) \quad (6)$$

where λ_o (day^{-1}) is the time constant for the TL exponential decay versus exposure time at the marble surface.

Application on the experimental data

Equation (6) was used as a fitting function on the experimental data of the TL profiles with depth, for 2, 15, 70 days and 8 years (Fig. 3). Average values for R (2.9 r.u.) and C (45.5 r.u.) were calculated from the data. The fitting seems satisfactory, however the calculated constants k and λ_o (Tab. 2), appear to decrease with increasing exposure time (although the λ_o errors are very large).

This behavior indicates that the equations describing the phenomenon are much more complicated than assumed. The coefficient k for example, depends actually on wavelength, a fact that could introduce an error, given that marble absorbs strongly at the ultraviolet region (Vaz et al. 1968), which is also the critical region for TL bleaching. On the other hand, calcite crystals show decreased optical absorption after they have been subjected to ultraviolet irradiation (Vaz et al. 1968). These data agree with our experimental results showing that k decreases with exposure time.

As for the time constant λ_o, it is expected to decrease for longer exposure times, since the average solar radiation intensity in 100 years is smaller than that of 70 days of sunny weather, due to weather variations. However, taking meteorological data into account, i.e., multiplying the exposure time by a factor representing the mean solar radiation intensity for the particular period the experiment took place, introduces very small corrections, which give results within the experimental errors. The large errors for λ_o, could be reduced if we increase the number of experimental points in the linear part of eq. 6. For technical reasons, it was not possible to have more than 2-3 slabs every 3-5 mm, at this first stage.

Time-Depth model for authenticity testing

In order to avoid the problems occuring due to the variations of k and λ_o, without loosing the correlation of the phenomenon with time, the inflection point of the double exponential function was found:

$$t = (1/\lambda_o) \exp(kx_{ip}) \quad (8)$$

where x_{ip} is the inflection point, in which the TL is calculated: $TL = R + C/e$.

Equation (8), from now on refered to as "time-depth model", can be used to calculate the exposure time for a certain measured depth x_{ip}, by using "effective" values of k and λ_o, characteristic for each type of marble. These values can be calculated from fitting with equation (8) at least three experimental (t, x_{ip}) pairs.

The model can be used as an authenticity test according to the following procedure: Three TL profiles are drawn, corresponding to specimens exposed for known times. The x_{ip} depths are estimated for each profile, with the use of the double exponential function (Eq. 6). Fitting the (t, x_{ip}) pairs by the time-depth model (eq. 8), gives "effective" values for k and λ_o. Then an unknown exposure time can be calculated by measuring the corresponding x_{ip} depth. This can be done for every piece of the same marble type.

For Pentelic marble, the effective values of k and λ_o calculated by treating the data of Figure 3 as described above are: k = 0.67 (±0.02)mm^{-1} and λ_o = 53 (±15)day^{-1}.

Figure 4 shows the behaviour of depth x_{ip} with exposure time. The effective values lie within the range calculated from the fitting by the double exponential (Table 1).

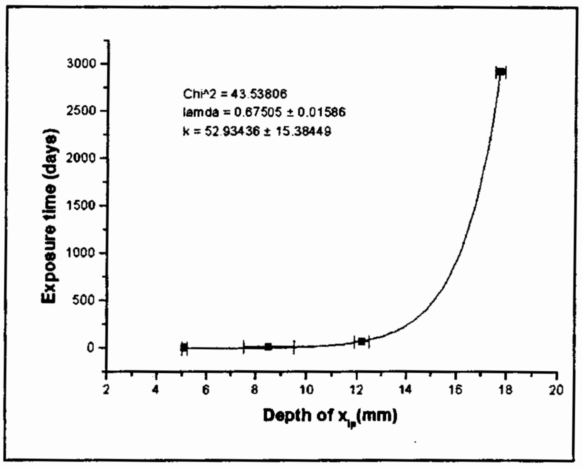

Figure 4.
Time - Depth model for Pentelic marble (x_{ip} is the inflection point of eq. (6), lamda and k as in eq. (8))

For another type of marble, different effective values are expected for k and λ_o, as they depend on marble transparency and solar radiation intensity. For a Venetian piece of marble identified as Naxian (Polikreti and Maniatis 2001) for example, effective values of k and λ_o are: k = 1.021 (±0.002)mm^{-1} and λ_o = 9.8 (±0.3)day^{-1}. The resulting larger k value is in agreement with the lower transparency of Naxian marble compared to that of Penteli.

Table 3 shows some depths of x_{ip}, for typical exposure times calculated by eq(8), for Pentelic and Naxian marbles. This table shows the potential of the method as an authenticity test and approximate dating method. According to Table 3, the method gives broad age ranges for marble objects exposed to sunlight. For example, an object made of Pentelic marble with a x_{ip} depth calculated at 24 mm, is given an age of 300 to 1000 years (1000-1700 AD). The range resulted by assuming an error for x_{ip} equal to 1mm, which is the maximum error value calculated in all studied cases (Tab. 2). Similar ranges can be assigned to objects made of Naxian marble.

In order to evaluate the efficiency of the proposed model in actual problems, we attempted to "date" a small, worked parallelepiped block abandoned in an ancient quarry and a modern quarry front, both from Pentelikon mountain. The piece bears toolmarks (point chisel), securely identified as "ancient". The modern front shows an almost white surface, with traces of loose depositions.

The inflection points for the ancient and the modern profiles (Fig. 5a and b) were calculated at $x_{ancient}$ = 25.0 (±0.5) mm and x_{modern} = 20.50 (±0.05) mm. These depths, according to the model correspond to $t_{ancient}$=1103 (±656) years (300-1500 AD) and t_{modern}= 53 (±23) (errors calculated by propagation of errors procedure). The results confirm that the proposed methodology can easily distinguish ancient from modern marble surfaces, exposed to sunlight for long periods.

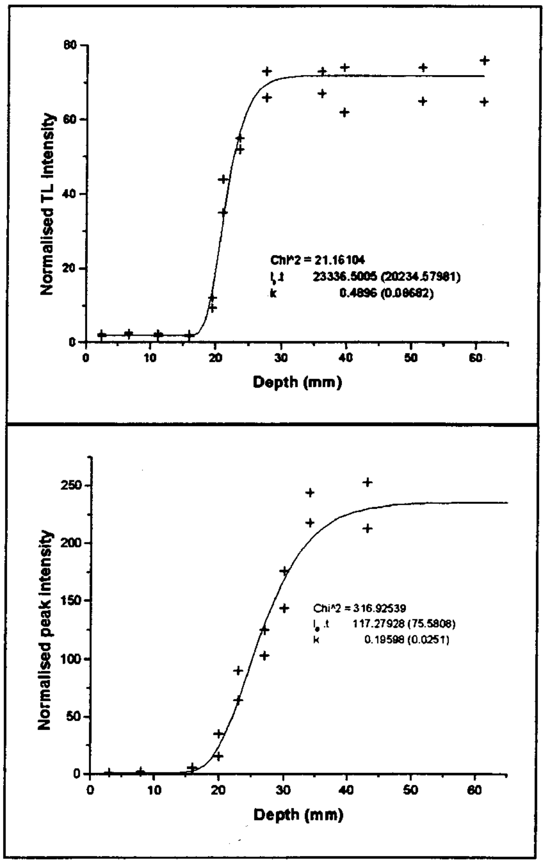

Figure 5.

TL profiles for two Pentelic marble surfaces (intensities normalised with a second glow, λ_o.t and k as in eq. (6)):

a) a piece bearing ancient toolmarks (x_{ip} = 25mm) and

b) a modern quarry front (x_{ip} = 20.5mm)

Conclusions

The natural thermoluminescence of marble and the effects of natural sunlight irradiation on the surface of ancient marble monuments were studied. Bleaching rates and dependence of thermoluminescence on depth were calculated for different types of marble.

The results lead to a time-depth model for samples continuously exposed to sunlight. This model is still in a preliminary form but it could lead to a method for testing the authenticity of disputable marble monuments. In its initial form it can distinguish between samples exposed to sunlight recently from those exposed since antiquity. If the studied marble piece is homogenous and the sources of error are minimised, the method can give a really narrow age range.

Table 1.
Maximum Grain Size (MGS), Mn^{2+} concentration (in relative units, measured by EPR spectroscopy), residual TL and fitting function of the TL decrease versus time, for different types of marble.

Sample description	**Mn^{2+} (r.u.)**	**MGS (mm)**	**Residual TL (% of natural)**	**Fitting function**
White, Pentelic	2012	0.6	14	$1.90\,e^{-0.10x} + 0.37\,e^{-0.001x}$
Whitish, Naxian	860	3.0	18	$0.80\,e^{-0.14x} + 0.40\,e^{-0.001x}$
White, Parian	184	1.0	14	$3.7\,e^{-0.16x} + 0.52\,e^{-0.001x}$
White, Thassian, dolomitic	685	1.6	11	$10.10\,e^{-0.09x} + 2.6\,e^{-0.002x}$

Table 2.
λ_o and k calculated by eq. (6) and inflection points by eq. (8) (Pentelic marble).

Exposure time (days)	***λ_o (days^{-1})***	***k (mm^{-1})***	***x_{ip} (mm)***
2	1816 ± 4611	1.6 ± 0.5	5.1 ± 0.1
15	2 ± 2	0.4 ± 0.2	9 ± 1
70	0.3 ± 0.2	0.25 ± 0.05	12.2 ± 0.3
8x365	0.1 ± 0.1	0.31 ± 0.08	17.7 ± 0.2

Table 3.
The x_{ip} depth calculated by the time–depth model for typical exposure times.

Exposure time (years)	***x_{ip} for Penteli (mm)***	***x_{ip} for Naxos (mm)***
10	18.1	10.3
100	21.0	12.5
500	23.8	14.1
1000	24.8	14.8
2000	25.9	15.4
3000	26.5	15.8
5000	27.2	16.4

It is a first time that bleaching of defects in marble by the sunlight as a function of time and depth was studied in detail. The results are leading to the development of an authenticity test for ancient marble artefacts that gives reproducible numeric results, close to the real ages. The model has, of course, to be improved in order to include artefacts exposed to sunlight and then buried for long periods. This will take into account the expected increase in TL intensity due to the natural irradiation from the radioactive elements of the ground, a standard procedure in TL dating. This modification will extend the application to complicated exposure histories such as exposure, burial and exposure to sunlight again. These natural processes are very difficult to be reproduced by forgers.

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Reviewer
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