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A new mathematical approximation of sunlight attenuation in rocks for surface luminescence dating

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The attenuation of sunlight through different rock surfaces and the thermoluminescence (TL) or Optical stimulated luminescence (OSL) residuals clock resetting derived from sunlight induced eviction of electrons from electron traps, is a prerequisite criterion for potential dating. The modeling of change of residual luminescence as a function of two variables, the solar radiation path length (or depth) and exposure time offers further insight into the dating concept. The double exponential function modeling based on the Lambert–Beer law, valid under certain assumptions, constructed by a quasi-manual equation fails to offer a general and statistically sound expression of the best fit for most rock types. A cumulative log-normal distribution fitting provides a most satisfactory mathematical approximation for marbles, marble schists and granites, where absorption coefficient and residual luminescence parameters are defined per each type of rock or marble quarry. The new model is applied on available data and age determination tests.

1. Introduction

The principle of dating buildings made of carved rocks (marble, limestone, sandstone, and granite) by luminescence (TL or OSL) is the prerequisite of complete solar bleaching of luminescence traps with depth from top surface [1–5].

Complete eviction of electrons from traps of crystalline minerals is desirable although a residual unbleachable (residual) luminescence component often remains. Quartz and feldspars in monolayer are bleached within minutes of sun exposure, but in rocks it needs dozen of minutes to zero the signal due to overlying layers. The direct optical transition to the conduction band (photoionization) gives rise to the near-exponential dependence of bleaching efficiency on photon energy [6].

Theoretical calculations define the penetration depth of solar radiation that comply with experimental data i.e. a complete absorption at around 4–5 mm. However, reservations are made for the penetration as exposure time indicates slow bleaching at greater depths [1,4,7–10]. For calcitic rocks the bleaching is much slower in the order of hours to several dozens of hours, where a residual luminescence level is reached. The latter serves as the initial level upon which radiation growth builds up [3,11].

Making use of the TL/OSL (thereafter L from luminescence) drop as a function of exposure time [2] (with the assumption that the rate of trapping due to natural environmental radiation is negligible in comparison to the rate of detrapping due to bleaching),

$$L = R + C\exp(-\lambda_0 t) \quad (1)$$

as well as, the Beer–Lambert Law for L drop per depth, and combining these two a double exponential function is produced [10,12] giving the L curves versus depth and exposure time:

$$L = R + Ce^{-\lambda_0 t e^{-kx}} \quad (2)$$

where R is the residual luminescence, C the bleached luminescence (geological minus residual), λ_0 is the time constant (time^{-1}) of the exponential decrease of luminescence as a function of time at surface, k_x is rate of decrease of solar radiation in time at surface ($x=0$) or at depth x within the rock, with units (1/length), also called as attenuation coefficient of solar radiation (Beer–Lambert Law, see Section 4). These coefficients and constants refer to certain type of material and an electron trap i.e. TL peak or OSL component.

However, this equation is not the most appropriate, instead a cumulative log-normal is proposed.

Both, the bleaching of luminescence for various rock types of archaeological origin as a function of depth and exposure time, and the modeling with a double exponential and an error function distribution, are critically assessed.

2. Sample preparation, measurement condition and equipments

The processed luminescence data derive from various sources.

Regarding the bleaching with depth in various marbles [10,13] all TL measurements were performed using the aluminum foil while

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a Littlemore Type 711 TL reader was used. The heating rate was 14 °C/s and a Schott KG5 (infrared absorption filter) was used. Normalization of the peaks was done by a second run of TL after 5.2 Gy irradiation (beta source Sr-90:0.52 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. The sample treatment and preparations were all performed under the red light to avoid bleaching effects.

In other marble/limestone data [3,7,11] sample preparation and measurements followed standard procedures [3,11]. All aliquots (washed with 0.5% acetic acid, $\varphi < 40$ μm) were exposed to solar simulator (SOL) (1 h of SOL-6 h of sunlight). The TL measurements were carried out with a homemade TL reader, employing filters BG 39 of 4 mm and HA 3. The heating rate was 5.6 °C/s and the beta source a Sr-90 of 4.4 Gy/min. Normalization of the prominent TL peak at 280 ± 5 °C was made on the low TL peak at ~130 °C performed with a second monitor beta dose (ratio of their integrated signal).

For luminescence measurements on granitoids [8,9] with conventional standard devices, a large portions of rocks were crushed using a jawcrusher in combination with a mill. To avoid machine damage due to large grains, the material was sieved and fractions larger than 315 mm were rejected. The remaining material, unsorted with regard to mineral composition or grain size, was fixed on steel discs with the aid of silicon spray. Similarly prepared aliquots were used for spectral measurements with a TL/OSL spectrometer. Other measurements were taken with granite slices of 189 mm × 189 mm × 6 mm, that completely replaced the normally used sample tray of an ELSEC OSL 9010 reader system. To enhance the sensitivity and allow stimulation with an infrared laser diode, the commercial version was modified. A temperature-controlled infrared laser diode (84,024 nm) delivers approximately 5 mW/cm^2 onto the aliquot, any blue emission of the laser diode is blocked by means of a R62 filter (Hoya). The signal-to-noise ratio was improved and was about 6.5 times higher when compared to a Riso TL-DA-12 reader.

For other granitic samples [14], sub-samples for luminescence measurements were taken by drilling cores from the rock surface using a diamond tipped coring drill, 6 mm internal diameter. One millimeter thick slices were then cut from the cores using a low speed diamond tipped saw. By examining the luminescence sensitivity and signal, it was found necessary to wash the surface slices in 10% HCl for 10 min and etch in 45% HF for 10 min, to remove the weathering products. From the surface slices would be used to obtain the burial age, and so it is important that the OSL signal is unaffected by the effects of burial (e.g. weathering products, diffusion of impurities, etc.). No acid treatment was necessary on inner slices. Measurements of the whole rock slices were made in an automated Risø TL/OSL reader equipped with blue LED (~50 mW/cm^2 at 470 ± 30 nm) and IR laser (~500 mW/cm^2 at 830 nm) stimulation sources. Luminescence was detected by 9 mm of U-340 filter, and the reader is fitted with an internal 90Sr/90Y beta source delivering 0.024 Gy/s. Individual grains of quartz from the soil samples were measured using the single-grain attachment to the Risø TL/OSL reader. This unit uses a stimulation source consisting of a 532 nm laser delivering about 40 W/cm^2 to 180–212 μm grains mounted in one hundred holes, 300 μm diameter by 300 μm deep, drilled in the surface of a 10 mm diameter aluminum sample disc. Detection optics is the same as in the standard reader, and the beta source in this unit delivers 0.10 Gy/s. A single-aliquot regenerative-dose (SAR) protocol was used for the measurement of the equivalent dose De for all samples.

For schists from Styra dragon houses [4] small sized samples were removed from firm contacts between two joining blocks with the aid of an hammer and chisel, gently and efficiently hit to detach a piece with the undisturbed original block surface. Two OSL readers (model TL/OSL – DA – 15) were used (based at CETI and NCSR Demokritos) operating at identical conditions, simulation was made under blue LEDs light source ($\lambda p \sim 470$ nm, FWHM 30 nm), equipped with a calibrated 0.075 Gy/s 90Sr/90Y β-ray source (Bøtter-Jensen et al., 2000) delivering 4.5 and 6.25 Gy/s, respectively, for the two sets. Heating was carried out using a heating rate of 1 °C/s, in order to avoid thermal gradient, using a 7.5 mm Hoya U-340 ($\lambda p \sim 340$ nm, FWHM 80 nm) filter. The De was determined on recovered traces of quartz from calcareous schists The single aliquot regenerative-dose (SAR) protocol, was used in order to estimate the equivalent dose using blue OSL. The blue OSL signals were measured in the continuous wave OSL (CW–OSL) mode for 50 s at 125 °C with the laser held at 90% power. The background OSL levels measured after 45–50 s exposure were subtracted from the initial luminescence intensity (0–1 s) of the decay curves obtained. Each disc was exposed to infrared radiation for 100 s at 125 °C before the blue stimulation, in order to reduce the malign influence of feldspars grain to the signal.

3. Solar penetration in various rocks materials

3.1. *Calcitic*

Regarding marble it is found that the drop at the top of marble under solar simulator (SOL-2) is ~85% for 75 min, while it reaches plateau at ~40 h; at the depth 2 mm the luminescence drops down to 30% in 40 h; at 4 mm drops to 70% in 40 h, at 8 mm there seems a fall around 20%, and for 16 mm and 140 h at SOL-2 it does appear within the errors a drop to ~75% [7]. The former upper layers imply that the bleaching of marble causes drop of luminescence within dozens of minutes to hours, taking into account, however, the residual signal caused by SOL exposure. The deeper layers indicate that solar penetration goes deep but bleaching of TL/OSL is very slow as a function of time exposure; the longer exposure time the deeper bleaching occurs that in some marble may reach 30 mm [10,13].

Examples of bleaching of luminescence for different daylight hours for marble schists from the Dragon Houses at Styra (Euboea, Greece) with presence of traces of quartz show that about 80% reduction occurs within 20 h of sun exposure [4]. Geological luminescence commences occasionally immediately after 1–2 mm depth from surface of the two marble schist slabs in contact, so that particular care is required in powder acquisition exerting gentle friction. Obviously calcite in calcareous schists obviates a complete quartz resetting clock in a short time as it occurs for sole monolayer of quartz grains an observable effect in granitic surfaces, too [1,14]. Higher sun exposures ensure a complete bleaching in concordance to earlier literature accounts for granites [1,8,14] and marbles [7,11].

In another marble schist the surface exposed to sun for 2 h, and the geological OSL levels off at about 1.5 mm [4]. Further tests on two flat surfaces were exposed to sunlight for 20 min and five successive layers were removed each of thickness 200–250 μm and OSL readings were taken [4]. The non-zero remaining signal implies insufficient sun exposure. However the cutting and carving and placing of such large slabs to the walls by ancient masons surely took much higher duration to ensure a complete bleaching of upper surface layers and reset of luminescence traps to zero.

3.2. *Granite/sandstone/basalt*

In a bleached TL plot for basalt (Egypt), it is shown that for single aliquots on brass discs exposed to sun for 10–1000 min the bleaching is quite fast remaining 60% within 24 h. While, for sandstone from Oseirion, Abydos, Egypt the residual TL was 70% after sun exposure of 8 h. The geological TL curve does differ from the bleached residual TL, and this is an another indication of the dose-plateau test concept for De determination in the case of calcitic rocks [5,11].

In granitic slices, instead of powder, and blue and IR stimulation, for three rock types – granite, metamorphic and ultramafic – bleaching of 1 mm slices under SOL shows a drop in dose for ultramafic within 100 s but large errors, for granite within 100 s and for metamorphic the same [14].

Further measurements on luminescence at surfaces has shown for granites that the prerequisite rule of deep and efficient bleaching below the rock surface combined with a shallower origin of IRSL emission seems to be fulfilled [9]. Surely, as shown above, longer exposures lead to sunlight penetration to deeper layers. Vafiadou et al. [14] shows that the 14 days daylight penetration in granite, for blue and IR stimulation compared to the geological dose of the rock, reaches a depth of 5 mm and goes even deeper. In fact for blue stimulated data the mean dose of 18 Gy at about 15 mm into the rock is still only 50% of the dose measured before light exposure (33 Gy). In the case of IR stimulation data the mean dose at 15 mm is consistent with the previously measured dose before light exposure of 18 Gy.

Lastly Sohbati et al. [12] have also shown that for beach rocks (granites) bleaching with depth reaches the inner geological dose at $\sim$5 mm for corrected IR signal, and that light attenuation is 90% at 3–4 mm depth.

However, the complete bleaching of luminescence in surface layers of rocks varies with the attenuation coefficient μ and light exposure time, and at any rate this depth seems to lie between 1 and 5 mm depending on the particular rock opaqueness.

The above examples indicate that the fast (within minutes) solar bleaching of luminescence of quartz grains in a monolayer is not applied to solid rocks, due to polymineral phase and lack of loosening, both making solar radiation intensity to attenuate. Moreover, it is proved that solar radiation bleaches luminescence in rock surfaces, and the percentage of signal diminution depends on the exposure time, material structure (rock density, mineralogy, defects, pores, and cracks), penetration depth and energy spectrum.

4. Light transmission and modeling: a short overview

Bleaching of luminescence for various exposure times as a function of depth is used to model the attenuation of sunlight based on the *Beer–Lambert* law of transmission—absorption is proportional to the light path length and to the concentration of absorbing species in the material. Attenuation or transmission loss is an exponential function of the path length through the medium.

Attenuation decreases the intensity of electromagnetic radiation due to absorption and scattering of photons, (it does not include the decrease in intensity due to inverse-square law geometric spreading that applies for point sources, though one may regard the sun as a point source)

Therefore, calculation of the total change in intensity involves both the inverse-square law and an estimation of attenuation over the path. The primary causes of electromagnetic radiation attenuation in matter are the photoelectric effect, compton scattering and, for photon energies of above 1.022 MeV, pair production. For sunlight spectrum involving photons of a few eV these are not applicable but the attenuation causes are described below. The solar spectrum that causes electron eviction of luminescence traps covers a wide range of wavelengths including UV—Visual and IR or $300<\lambda<1500$ nm.

The propagation of light through the rock-medium is based on internal reflection from rough and irregular surfaces even at the molecular level of the minerals that cause light to be reflected in many random directions. This light scattering depends on the wavelength of the light being scattered. Thus, attenuation results from (a) the incoherent scattering of light at internal surfaces and interfaces in the form of grain boundaries, (b) microstructural defects, (c) pores, (d) selective absorption of specific λ in a manner similar to that responsible for the appearance of color, (e) multi-photon absorption, and (f) reflection and transmission of light waves that occurs because the frequencies of the light waves do not match the natural resonant frequencies of vibration of the objects. All non-metals materials exhibit at least a small amount of subsurface transmission and some materials exhibit a much higher amount of scattering e.g. skin, wax, and marble. Complex transport of photons phenomena in materials have employed various models and such a review is given by Carter [15].

Primary material considerations include both electrons and molecules as follows: (1) at the electronic level, for the UV or visible ranges, and (2) at the atomic or molecular level (mostly determine transmission of longer λ in the IR or far IR). Since different atoms and molecules have different natural frequencies of vibration, they will selectively absorb different frequencies (or portions of the spectrum) of infrared (IR) light.

When the size of the scattering center (or grain boundary) is reduced below wavelength of the light being scattered, the scattering no longer occurs to any significant extent and this gives rise to increased transparency (e.g. fine grained clear marble). The latter occurs to some marbles rather than in granites and less homogeneous rocks.

Thus, intensity of the light (radiant power) changes as it passes through the rock surface. In the Beer–Lambert Law the fraction of the light absorbed by each layer of material is the same and the Law deviates at high densities/concentrations. This deviation is not dealt with here, but the choice of error function seems to counteract this drawback

For particular photon energy and absorbing material, the absorption coefficient μ is a constant having the unit reciprocal length. Its value does, however, change from one material to another, and it also depends, for a given absorbing material, on the energy of the radiation. For low-energy photons, whose removal occurs principally through the photoelectric effect, the absorption coefficient μ is large.

As it is shown here the Double Exponential (DE) functional shape [10,12,13], is produced in a quasi-manual manner and provides a reinforced 'false' best fitting to all data, instead a particular type of error function (erf) is most appropriate.

In fact, in some case (see Section 6.6) the average residual or remaining TL after sun bleach of marbles and the geological TL values are pre-defined manually with a hand calculator and introduced to fitting software for the DE fitting. In all four available statistical packages known (Matlab, TableCurve 2D, Origin and Profit) of processing fittings up to 11 variables, none can provide a DE with the four variables R, C, λ and k be unknown of Eq. (2). We have overcome this inadequacy applying a cumulative log-normal distribution fitting.

Data of luminescence loss with depth due to solar bleaching as a function of exposure time are taken from so far available published sources, whereas their sample preparation and dose calculation techniques has been described above:

(a) Marble: [7,10,13].
(b) Marble schists: [4]
(c) Granites:[9,12,14].

5. Data analysis and the new *erf* approximation

5.1. Cumulative log-normal fitting

The data regarding the shape of luminescence (either TL or OSL) drop due to sun bleaching or solar simulator for the marbles, schists and granites derived from the published sources have been examined for a best mathematical expression to describe their variation. In fact, searching for appropriate functions and based partially on the Lambert–Beer law but modeling variation of relevant luminescence phenomena too the error function (erf) was found, by trial and error, to offer the best simulation [16,17]. In fact, the distribution of residual TL signal, after bleaching, as a function of depth *x*, follows the cumulative logarithmic normalized distribution, while attributing to coefficients a physical meaning.

The general equation of the cumulative log-normal distribution is Eq. (3).

$$F_X(x;\mu,\sigma)=\frac{1}{2}erfc\left[-\frac{\ln x-\mu}{\sigma\sqrt{2}}\right] \quad (3)$$

But for our purposes taking into account Eqs. (1) and (2), we introduce a different form (Eq. (4)) i.e., adding the residual (constant) term α, the *b* in place of *C* and reorganizing the difference in the nominator as ln of ratio (*x*/*c*).

$$TL(x;a,b,c,d)=a+\frac{b}{2}erfc\left(\frac{-\ln\left(\frac{x}{c}\right)}{d\sqrt{2}}\right) \quad (4)$$

where *a* is the residual luminescence, *b* is the geological minus residual, *c* is the transition depth of the residual TL curve and *d* is a non-dimensional factor, most probable a measure of the dispersion of the un-bleached traps around the transition depth. From our research until now, this *d* factor seems to be uncorrelated with exposure time or transition depth.

6. Data analysis of marbles, marble schists and granites

Here, the processed data of the various published sources are given fitted by L-N error function distribution of residual TL/OSL after exposure to solar radiation as a function of depth. Due to more available homogeneous data on sun exposures in marbles rather than granites or schists a fuller elaboration is focused on the former.

6.1. Marble schist [4]

A 2 h solar transmission caused bleaching as a function of depth increasing and reaching a saturation level at around 1.5 mm Data were DE fitted, as well as, with log-normal (L-N) distribution (Fig. 1)

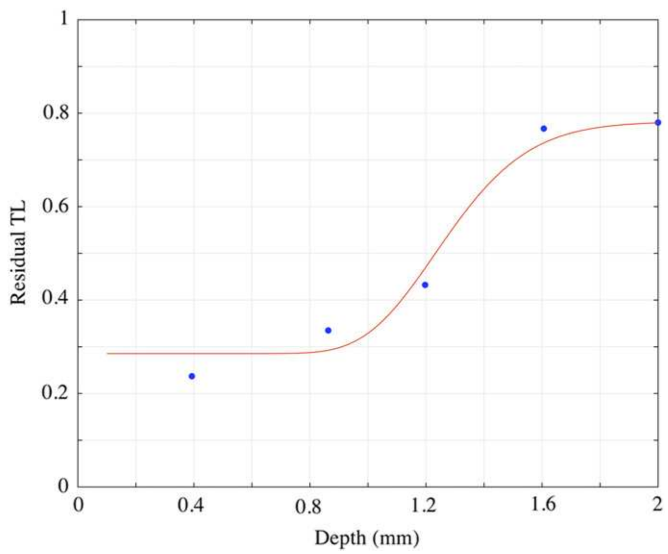

Fig. 1. Cumulative Log-Norm fitting. $a=0.2855$, $b=0.4963$, $c=1.2789$, $d=0.1247$ and $r^2=0.9802$ (DF Adj $r^2=0.924$), FitStdErr=0.069, for marble schist.

A series of experiments on marbles with different exposure times in relation to the residual luminescence and bleaching depth has been reported as part of a thesis [10]. The re-processing of these data with the new *erf* fitting and DE is given below along with the respective parameters.

6.2. Penteli and Naxos marbles [10,13]

For both Penteli and Naxos (Apeiranthos) marble quarry exposed to sun for 2, 15, 70 days, 8 and 10 years for former and 4, 70 days and 300 years for the latter, fittings by DE and log-norm exhibit similar respective trends, with L-N giving the best. Figs. 2–5 present some representative ones.

6.3. Granite [8,9]

DE fit is not possible because no pre-defined exposure time, *t*, is given, but L-N is shown in Fig. 6. Parameters are given in the figure caption.

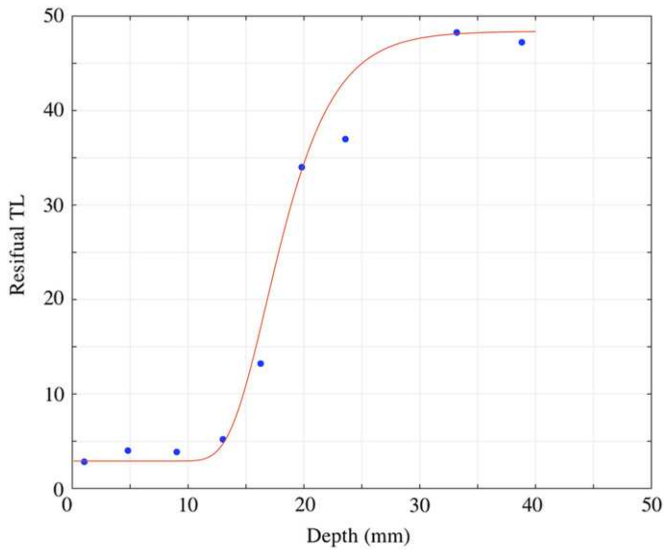

Fig. 2. Penteli marble: DE fit (Eq. (2)) by Matlab of 8 years exposure with *R*, *C* and *t* equal to 2.9, 45.5 and 2920, respectively, and pre-defined.

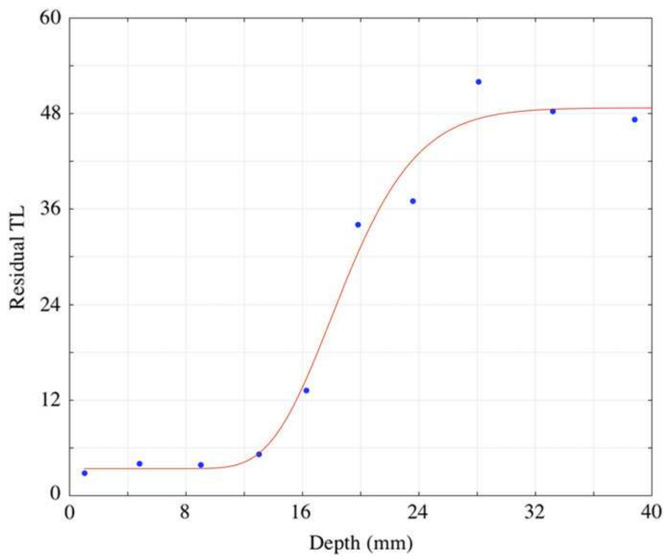

Fig. 3. Cumulative Log-Norm fitting of Fig. 2. ($a=3.41$, $b=45.31$, $c=18.93$, $d=0.2094$, $r^2=0.966$, Adj $r^2=0.97$, and FitStdErr=3.32).

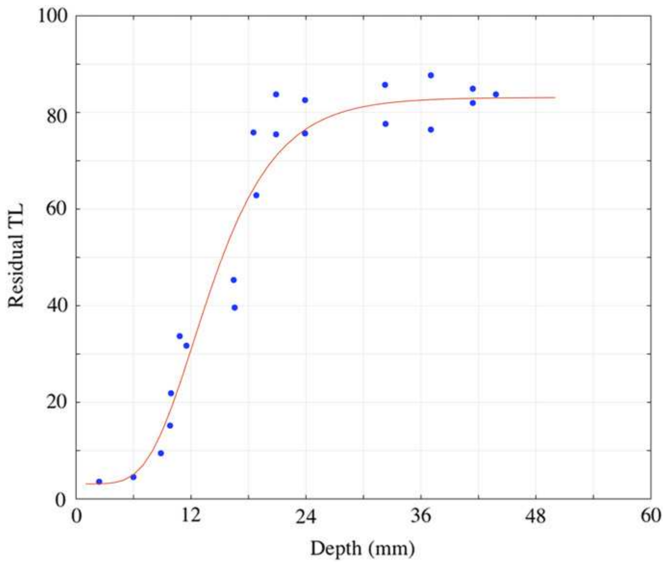

Fig. 4. Naxos marble, exposure for 300 years: DE fitting with matlab for *R*, *C* and *t* equal to 3.1, 80 and 109,500 days, respectively.

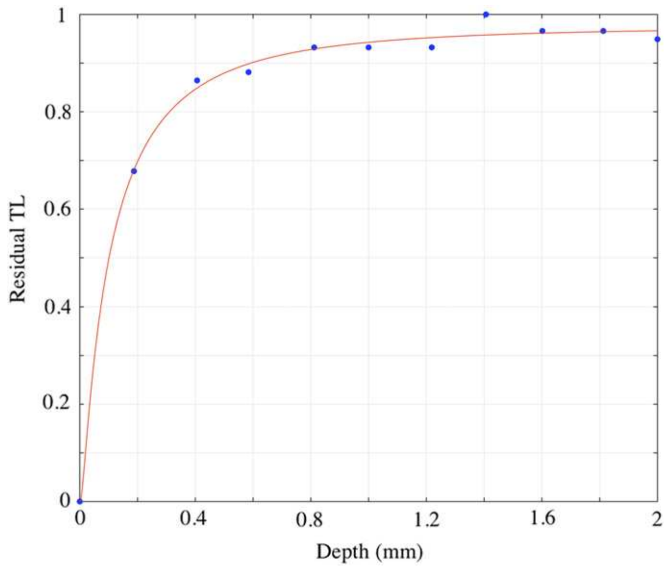

Fig. 6. Cumulative Log-norm fitting on granite [8,9] data. ($a=-5.78e-05$, $b=0.97$, $c=0.097$, $d=1.26$, Adj $r^2=0.99$, and FitStdErr$=0.02$).

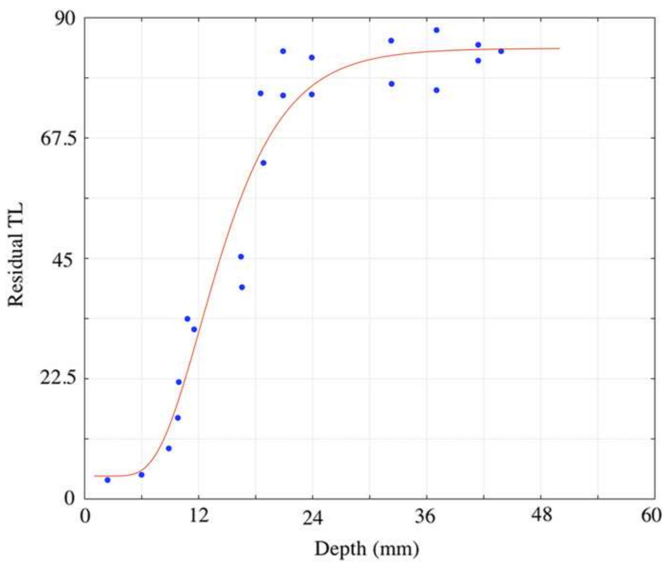

Fig. 5. Cumulative Log-Norm fitting of Fig. 4.

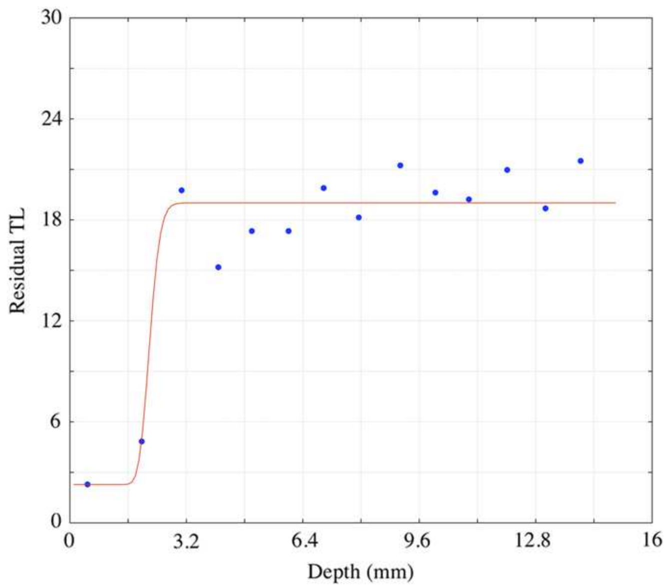

Fig. 7. Cumulative Log-Norm fitting of granite [14] data.

6.4. *Granite [14]*

For a sample from prehistoric settlement at Mykonos island MYK-R (granite) probed by IR exposed to daylight for 14 days the L-N fit is given in Fig. 7. Similar applies for blue light stimulated luminescence as well as for ultramafic rock.

6.5. *Granite [12]*

For another granite sample No. 099902 (Metamorphosed granite) the Cumulative log-norm fits on granites is given by Fig. 8.

6.6. *Brief remarks on modeling residual luminescence of above rocks*

The quoted DE fit of residual TL of marbles by Polykreti [10] can be used only by pre-defined values of variables *R* and *C* taken from the experimental data, whereas λ and k are computed by the matlab and Eq. (4). Moreover, λ and k are not constant for all DE fittings (see, Table 1). It appears that the coefficients are sensitive to mathematical fitting procedure rather than light wavelength.

Regarding the granite data by Sohbati et al. [12], they do not follow the DE by Polykreti [10], and Polykreti et al. [13] but they construct another DE instead (Eq. (5)) for the corrected natural luminescence signals (L_n/T_n), without *R* (of Eq. (2)), and in place of the product $\lambda.t$, a general coefficient is set:

$$L/T = Ce^{-ae^{-kx}} \tag{5}$$

This simplified DE expression can though be solved using MATLAB software for unknowns the *C*, α and *k* (see, Table 2).

In granite sample 099902 with more data points and commencing geological luminescence saturation, cumulative log-norm fitting was successfully applied (Fig. 8) giving residual OSL=1.66 and

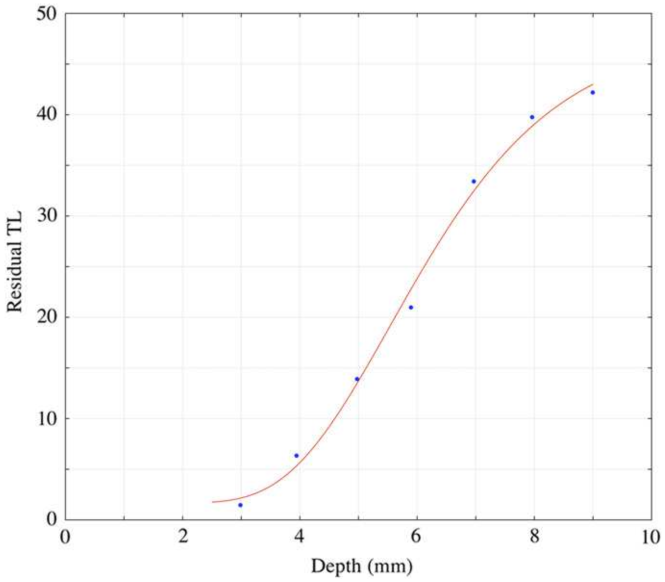

Fig. 8. Sample 099902—Metamorphosed granite [12] data.

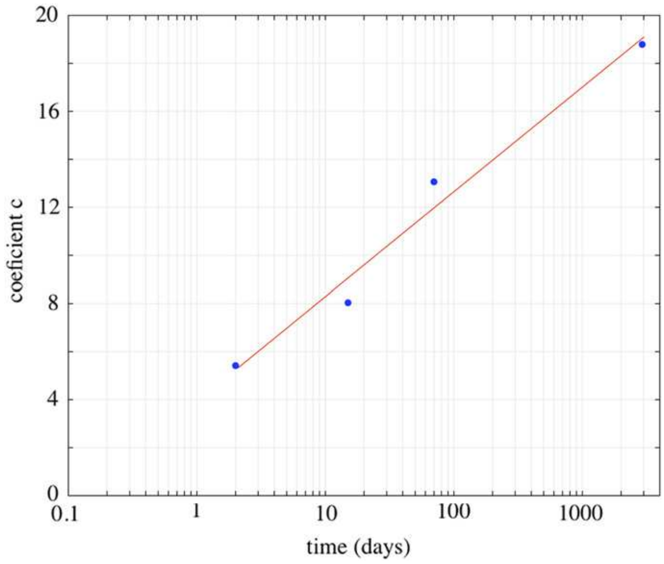

Fig. 9. Coefficient *c* of Eq. (4) (transition depth of the cumulative log-norm distribution) as a function of exposure time (days), *x*.

Table 1
Variation of coefficients λ and k based on DE fittings for marbles as obtained by Ref. [10] and present study of cumulative log-normal distribution.

Sample/time	λ (days^{-1}) Polykreti	λ (days^{-1}) Present	κ (mm^{-1}) Polykreti	κ (mm^{-1}) Present
Penteli 2 days	1816	1412	1.6	1.58
Penteli 15 days	2	1.867	0.4	0.44
Penteli 70 days	0.3	0.27	0.25	0.25
Penteli 8 years	–	0.062	–	0.301
Penteli 10 years	0.06	0.062	0.31	0.31
Naxos 4 days	1.7	1.65	0.69	0.68
Naxos 70 days	0.3	0.46	0.5	0.61
Naxos 300 years	0.0001	0.00012	0.167	0.212

Table 2
Fittings on [12] data for granite.

Sample	Variable		
	C	*a*	*k* (mm^{-1})
099902 From Sohbati et al.,	60	16	0.51
099902 present study with $C=60$ predefined	60	10.87	0.41
099902 present study all unknown	50	17.45	0.52

Geological OSL=46. These values may be more representative if more data points were available. For all experimental data we rely on the attached measurement errors (around $\pm 10\%$) that in turn give large uncertainties.

7. Bleaching by variable sun exposure time

Further, the Cumulative Log-Normal Distribution of Eq. (4) is applied on same materials given above in Section 6, but exposed to variable exposures to investigate its possible representation per rock type. A typical fitted curve is obtained representative of this marble. Use of this fit is made to reconfirm the sun exposed time of another similar marble.

Here the only available large amount of data set of same Penteli marble quarry treated on various conditions is used. The fittings determined the coefficients *a, b, d* of cumulative log-normal distribution which, as it is expected, are not correlated with either, the time exposure (2, 15, 70 days and 8 years) or the depth variation. However, coefficient *c* (transition depth) deduced from Eq. (4) exhibits a linear dependence on time when plotted against, the exposure time ln (days) denoted as *t* (Fig. 9).

For the latter the fitting of Fig. 9 is:

$$f(x) = p1t + p2 \quad (6)$$

With coefficients: $p1=1.894$ ($1/p1=0.52$ attenuation coefficient), $p2=3.932$, Goodness of fit, *R*-square: 0.978. Hence, this is one way to compute transition depth *c* that can be described by Eq. (7):

$$c = p2 + p1\ln(days) \quad (7)$$

Furthermore, by taking the average of *a*, *b* and *d* computed values of fittings with cumulative Log-Norm for the data 2, 15, 70 days and 8 years (2920 days) which are: $a=3.33\pm0.92$, $b=44.8\pm0.89$, $d=0.2359\pm0.097$; then the generalized Eq. (4) becomes:

$$TL = 3.33 + 22.4\,erfc\left(\frac{-\ln(\frac{x}{c})}{0.3336}\right) \quad (8)$$

Eq. (8) represents the general equation for Penteliko Marble and can be used in any future study of this material. It should be noted that the standard deviation of the mean values for *a*, *b*, and *d* coefficients are higher than the luminescence measurement errors.

Both Eqs. (8) and (7) – the linear relationship between *c* and *time* – imply that residual TL depends on *path length* (depth below surface) and *time exposure*.

Fig. 10 demonstrates the experimental data for Penteliko marble (circles) and the Cumulative Log-Norm curves of Eq. (8) with values of transition depth *c* as they were calculated from the Cum. Log-Norm. fitting while Fig. 11 demonstrates the same data with Fig. 10 except that the *c* values are calculated from Eq. (7).

In spite of high *R*-square=0.978 for Eq. (7), it is not good enough, along with Eq. (8), to provide a very good fit (see Fig. 10).

Furthermore, we may suggest that the slight deviation between the cumulative Log-Norm curves in Figs. 10 and 11 may be due to the dependency of coefficient c of Eq. (8), which even if it seems to be very linearly correlated with log (time), the phenomenon is more complicated implying random transport of photons in matter through pathways and cascade phenomena.

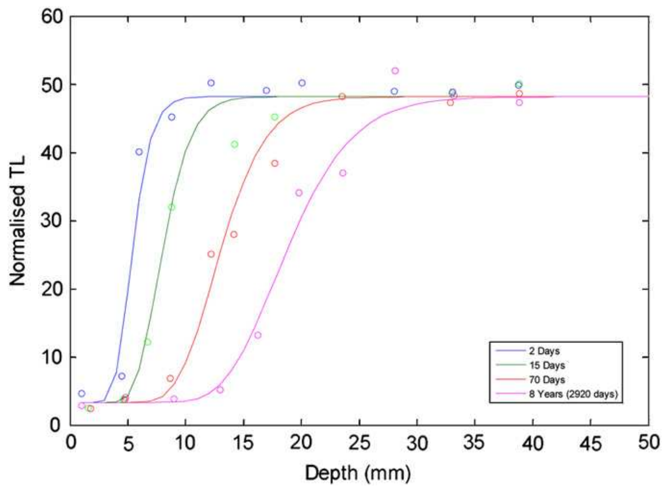

Fig. 10. Experimental data (dots) [10,13] and fittings by Eq. (8) (solid curves). Values of coefficient c calculated from Log-Norm Fitting.

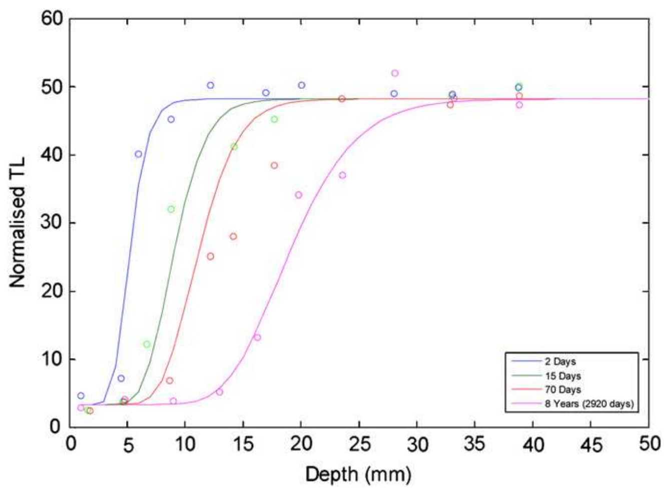

Fig. 11. Experimental marble data (circles) and respective curve fittings (solid curves) of Eq. (8) and for c derived from Eq. (7) and the known ages.

8. Further implications of L-N fitting

8.1. Inflection point

Our cum. L-N distribution best fitting approximation is moreover exploited regarding the construction of a representative functional behavior of luminescence bleaching per time and penetration depth, of the studied material with the particular mineralogy, grain size, opaqueness, etc.

In addition we examine the variation per time and depth of the inflection point of residual luminescence as a function of depth making use of the first derivative of the log-normal distribution (Fig. 12).

The 'inflection depth' point is defined as the depth at the peak of 1st derivative, which is linearly related to the neperian logarithm of time in days (Fig. 13).

The fitting of Fig. 13 is

$$f(x) = p1\,\ln(\text{days}) + p2 \tag{9}$$

with coefficients (95% confidence bounds): $p1=1.787$, $p2=3.606$, goodness of fit: R-square: 0.9875. The reverse ratio of slope $1/p1=0.56$ is the attenuation coefficient for this marble, evident also from Eq. (7) with a ratio 0.52 and errors around 10%.

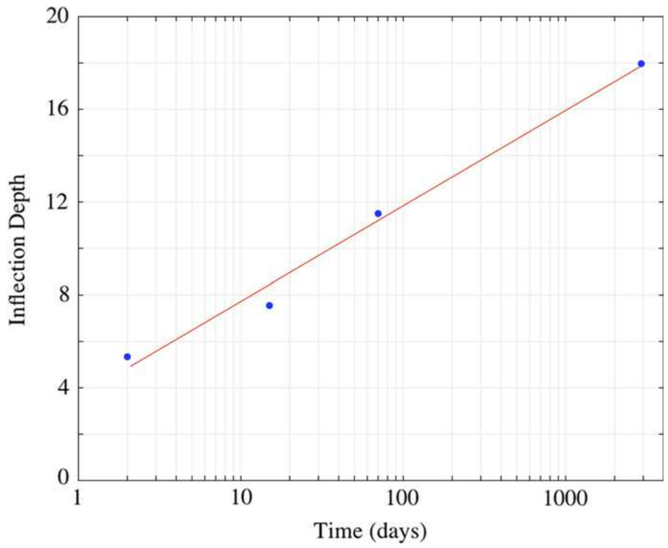

Fig. 13. Variation of the "inflection" point versus time for Penteli marble.

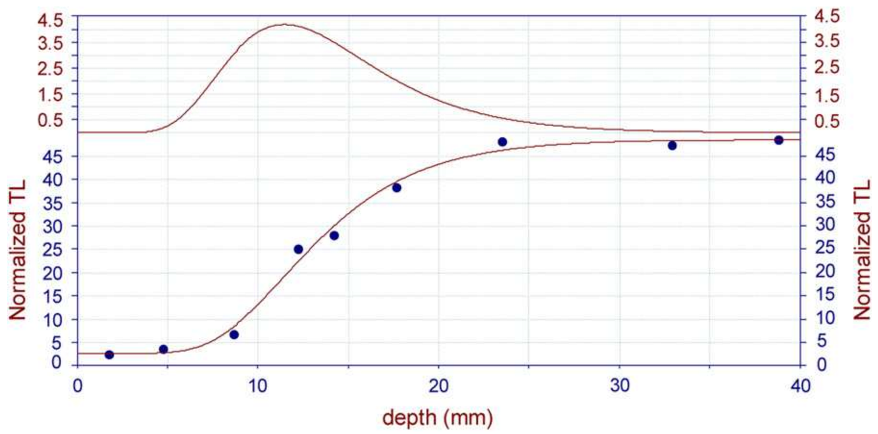

Fig. 12. Residual luminescence of marble (Penteli, Attica, Greece) bleached for 70 days under sunshine (circles), the cum. log-norm fitting (solid curve through points) and its 1st derivative. L-N data: $a=2.706$, $b=45.81$, $c=13.06$, $d=0.35$, Adj $r^2=0.986$, and FitStdErr$=2.05$.

Coefficient c also has units of distance (depth) and distance is the inflection point, too. Thus, Eq. (9) resembles Eq. (7) and obviously Figs. 9 and 13.

Accordingly, the above proposed fitting (model) is applied to date two marble types (Penteli and Naxos).

9. Application of fittings on Penteli marble exposed to Sun for 10 years: reconfirm its dating

Use of the generalized fit for Penteli marble quarry (Eq. (8) and Section 6) is made to date another Penteli sample exposed to sun for 10 years. The experimental points and respective L-N fit for the 10 years sun exposure are shown in Fig. 14.

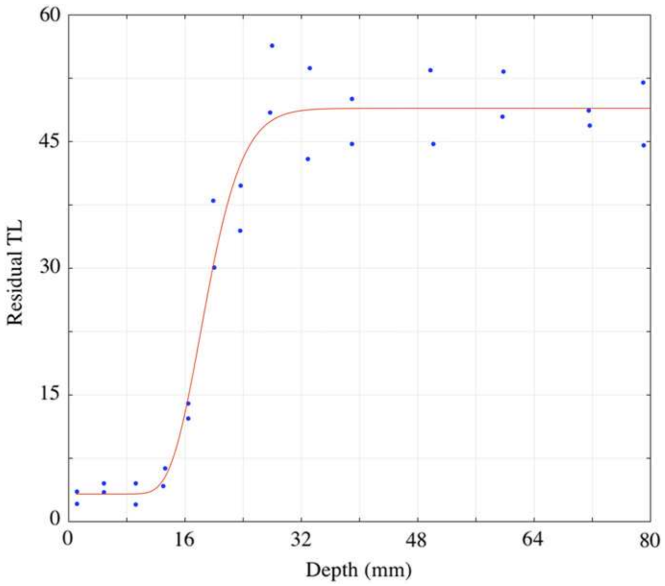

Fig. 14. Residual luminescence data with depth and fitting by Eq. (4) (cum. Log-norm), for the Penteli marble.

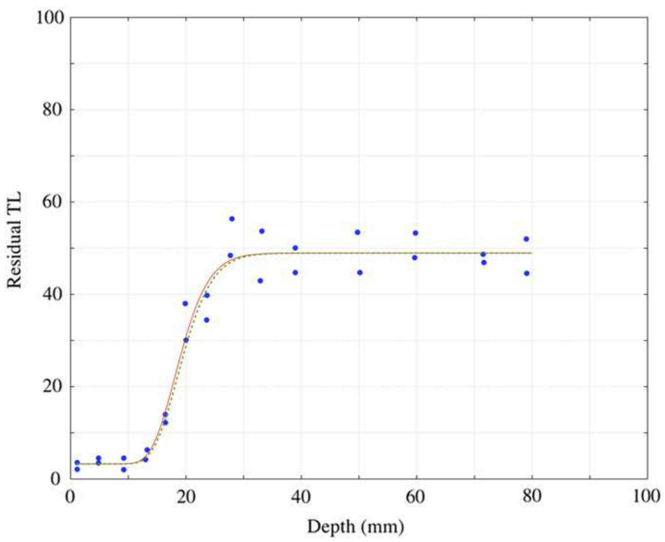

Fig. 15. Marble of Penteli, residual TL versus depth for 10 years sun exposure (blue circles). The solid red curve is for $c=18.9$ (from fitting of Fig. 13), dashed green curve is for $c=19.4$ as predicted from Eq. (7). L-N data: $r^2=099$, DF Adj $r^2=0.96$, FitStdErr=4.02, $a=3.27$, $b=45.67$, $c=18.93$, $d=0.21$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

An interesting observation is that coefficients a, b and d are within the bounds computed earlier taking the error of the mean as a rule of thumb extracting approximate data errors from original sources (Eq. (8)).

Fitting the 10 years data with Eq. (8) and $c=18.9$ found from Fig. 14 and for $c=19.4$ from Eq. (7) along with the original data is shown in Fig. 15. This way Eq. (8) modeling for this marble is tested for validity on the 10 years data too in a similar manner in Fig. 10.

The second curve for $c=19.4$ predicted from Eq. (7) will show if this value is reliable, thus Eq. (8) model will be applied alone without further fitting of the data. We show below that since c could be computed, from time exposure, then Eq. (8) is used to construct theoretical curves for this marble for any sought age.

Eqs. (7) and (8) rely on the 2, 15, 70 days and 8 years exposure data. Making use of the found modeling the 10 years exposure can be confirmed, that is, the exposure time (i.e. age) of an outdoors marble monument exposed steadily to light since construction, can be obtained.

Thus, in a retrospective procedure the surface luminescence dating can be realized taking as 'unknown' the 10 years curve with following steps and procedures: (a) by fitting with Eq. (8) (Fig. 14) of data, then (b) use of coefficient $c=18.9$ on Eq. (7) and solve for time t, which is found equal to 7.44 years, and (c) from the variation of inflection depth point (Eq. (9)) versus depth the depth of the 1st derivative peak is defined for data of Fig. 14 (similar to Fig. 12), equivalent to 18.11 mm depth. Eq. (9) then solved for time gives 9.1 years or very close to the actual age of 10 years, with standard deviation for the fit around 2 years, in contrast to earlier found uncertain age by Polikreti of 6 ± 5 years [10].

10. Application of the proposed model on a Naxian marble: further authenticity and dating tests

The last test concerns an application to a marble cross of St. Apostoles church in Apeiranthos, Naxos island dated to 1698 A.D. by inscription. A comparison of the new functional treatment is made, first with the above treated Penteli marble, and then with the original study [10]. Figs. 16 and 17 represent sun exposed pieces for 4 and 70 days to determine absorption. A measurement on sample taken from face on side of marble

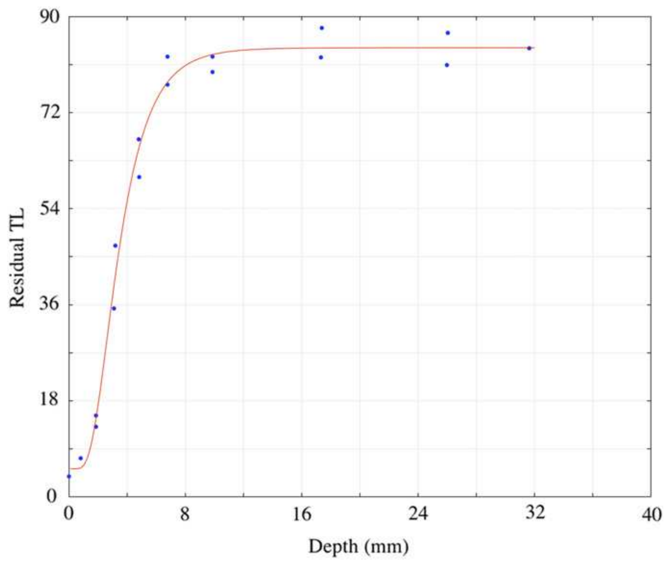

Fig. 16. Data and fitting with log-normal distribution of Naxian marble and sun exposure of 4 days. ($r^2=0.989$, Adj $r^2=0.986$, FitStdErr=3.53, $a=5.27$, $b=78.92$, $c=3.37$, and $d=0.503$).

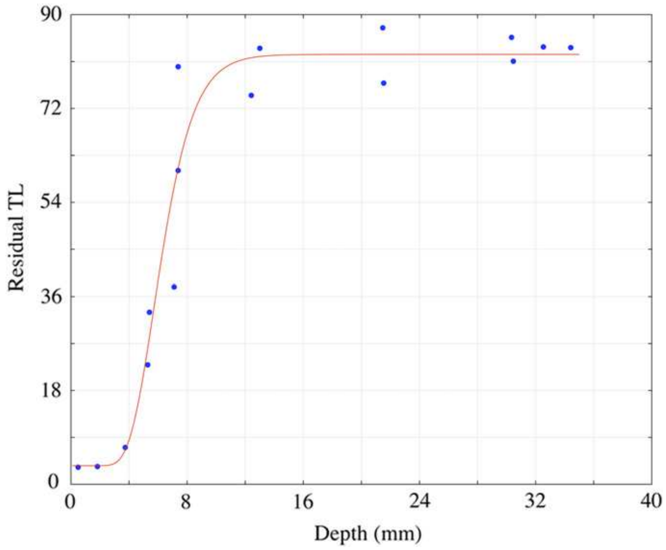

Fig. 17. Log-normal fitting for Naxian marble cross after 70 days exposure to sun. (r^2=0.94, DF Adj r^2=0.923, FitStdErr=8.67, a=3.57, b=78.8, c=6.22, and d=0.288).

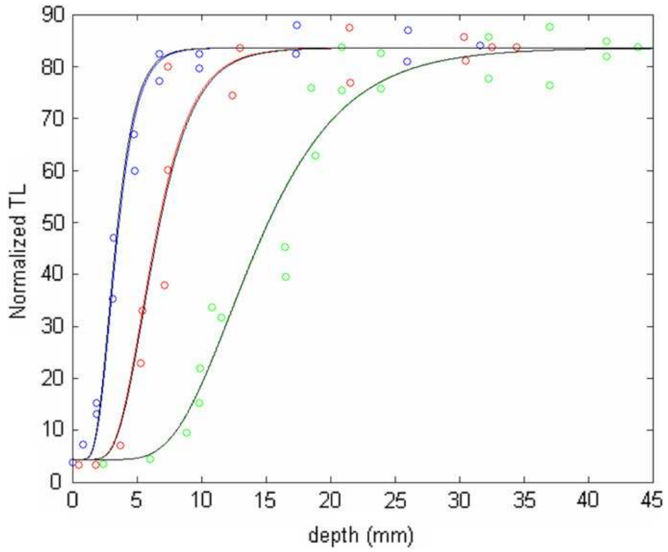

Fig. 19. Data (circles) for Naxian marble cross at 4 days (left), 70 days (center) and known 301 years (right), and the solid colored curves are for respective c found from the fittings of Figs. 16 and 17. Black solid curves not discernible are for c computed from Eq. 11. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

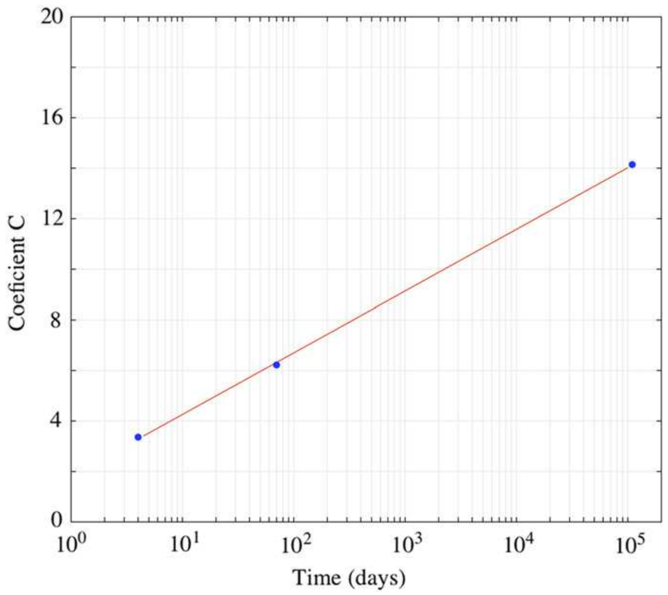

Fig. 18. Semi-logarithmic plot of c variation versus time for 4, 70 days and 301 years known age Naxian marbles (Figs. 5, 15 and 16).

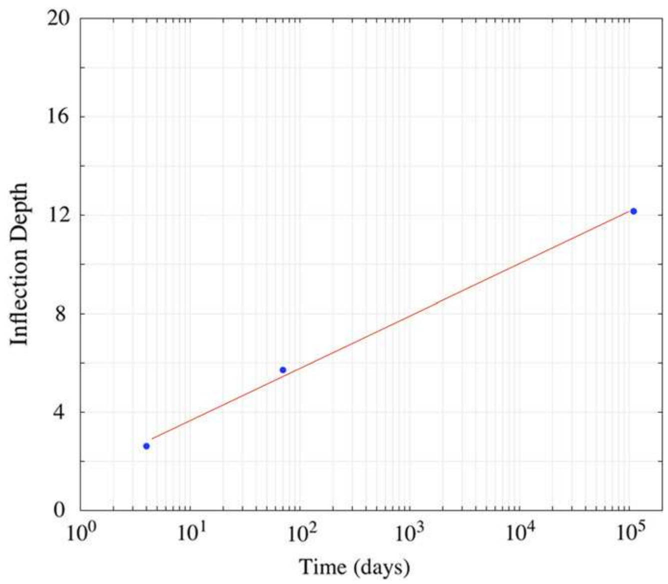

Fig. 20. Variation of "inflection" point with exposure time for Naxian marble. Linear fitting of data points.

plaque exposed to sun steadily since 1698 A.D. is already demonstrated in Fig. 5 (measurements are taken in 1999 A.D. therefore the expected exposure time or the age is 301 years).

The cumulative log-normal does a proper fit to these data reinforcing our earlier conclusion. Due to lack of more exposure time data, use of all these three (4 days, 70 days and 300 years) residual TL curves is made. The average values of a, b and d are: $a=4.37\pm0.89$, $b=79.2\pm0.60$, $d=0.38\pm0.1102$, where, a is residual TL of the particular TL peak, and b the intensity of geological TL minus residual. Coefficient d as we mentioned before is a non-dimensional factor.

Therefore, final equation for this type of marble is:

$$TL(x,c)=4.37+39.68\,erfc\left(\frac{-\ln(\frac{x}{c})}{0.5374}\right) \tag{10}$$

The variation of coefficient c versus time is shown in Fig. 18.

The relationship between c versus time (Fig. 18) is similar to that found earlier for Penteli marble:

$$c=a+b\ln(\text{time}) \tag{11}$$

where a=1.82 and b=1.059 and the goodness of fit measured as r^2 is 0.9997. The a-value is in units of path/time and c in units of path length. Attenuation coefficient of this material is 1/1.059=0.94 (±10%).

Fig. 19 demonstrates the comparison of experimental data, theoretical curves using Eq. (10) and for c derived from the initial cum. Log-Norm fitting, and the theoretical curves using Eq. (10) but for c calculated from Eq. (11) for the known ages.

The excellent convergence between predicted and experimentally found c resulting in an overlapping cumulative log-normal fitting reinforce the new procedure.

10.1. Variation of inflection point versus exposure time

The variation of inflection point versus time for the three sets of Naxian marble data is shown in Fig. 20.

The variation of 'inflection point' as a function of sunlight exposure time for Naxos marble cross, shown in Fig. 20, appears to be linearly correlated with ln(time), same as with Penteli marble.

10.2. Determination of the age of Naxian marble

The known age of 301 years for the sample derived of the surface of marble cross, has been calculated to 204 years based on the double exponential approach accounting for measurement errors around $\pm 10\%$ [10].

The new fitting requires a fair amount of simulated curves (more than three) to get accurate parameters, much like for Penteli marble tests. Here use of the three sun exposed curves for the Naxian sample is unavoidably made. The age is calculated in four cases making use of the proposed cum. L-N fit, the variation of c and of the inflection point, versus exposure time.

10.2.1. Case A: application of Eq. (11) for c value of cum. log-norm fitting (Fig. 5)

Solving for time (t) (age) of Eq. (11) for $c=14.14$ (computed from the cum. Log-norm Fig. 5), the age is equal to 309 years.

10.2.2. Case B: equation using 'inflection point' of Fig. 5 (L-N fit of 300 years) and applied to Fig. 20

From the equation of the inflection point of the cum. L-N fit as a function of time, for inflection depth $=12.14$ (value found from 1st derivative of Naxian marble, Fig. 5), an age of 279 years is made. The standard deviation of the fit of Figs. 5 and 20 is around $\pm 10\%$. As one of the three points of inflection points equation includes the sought age the obtained date is close to the real one.

10.2.3. Case C: use of c value from cum. log-norm fitting (Fig. 5) and linear fit for data of the two curves (4 and 70 days)

The two c values resulted from the log-normal fit (Eq. (10)) of the 4 and 70 days exposure times, define another linear equation. Then the c of the third curve (of 300 years) making use of this linear relation of two points only, gives an age of 531 years. Two data points on exposure time are not enough to provide a reliable accuracy.

10.2.4. Case D: use of a new 'inflection point' equation of 4 days and 70 days and solved for 'inflection point' of Fig. 5 Naxian marble

Use of the 'inflection point' versus time relationship for only the two 4 days and 70 days of sun exposure data curves (Fig. 20), then making use of this relation, the inflection point of Fig. 5 (i.e. the 300 years sun exposed Naxian marble), gives an exposure time or age of 70 years. Here again, two data points on inflection relationship are not enough to provide a reliable date.

The age results from the above four cases lead to the conclusion that in order to have an accurate dating result we need as many as possible curves for several exposure times, say more than four.

11. Comparison between the coefficients in Naxos and Penteli marbles

The cumulative Log-Normal fitting provide satisfactory results for both marble quarries. For Penteli marble, where simulation experiments of residual TL versus depth and exposure time were adequate, the age of an old marble was accurately computed. For Naxos marble the only two experimental simulation residual TL curves gave less accurate ages.

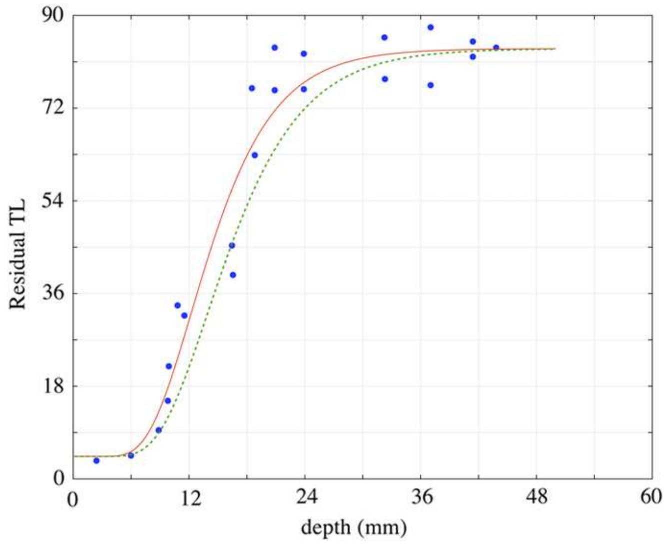

Fig. 21. TL residual versus depth for 300 years data exposure time (circles), the log-normal fit (red) and a theoretical curve for 2000 years exposure (dashed), for the Naxian marble cross. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The cumulative Log-Normal fitting can make accurate fitting of residual TL versus two variables; the *solar penetration depth* and *exposure time*, in various rock types, having the general shape of Eqs. (4) and (7).

As c (transition depth) value depends logarithmically from time – the depth is logarithmically related to exposure time (or the age) – the present modeling method cannot clearly distinguish ages as we go to higher exposure times. Indeed, for 300 years old TL residual curve (Naxos marble—Fig. 5) an expected theoretical curve is calculated for 2000 years exposure time. (Fig. 21), making use of Eqs. (10) and (11). Apparently the two fits are separated, but the spread of errors rising thereof – luminescence measurements and determination of sampling depth – is high alerting for more accurate techniques expecting to occur via OSL readings and sampling depth cutting.

The ability to separate time exposures of some days from some hundreds of years makes the new approach suitable for authenticity tests. It appears that the difficulty of separating between two ages is first due to the very nature of the phenomenon but also due to the errors in sampling depth and luminescence readings.

12. Conclusion

Our new type of functional fitting approximation of solar radiation bleaching and penetration into rock surfaces differs from the double exponential proposed by Polykreti [10] and Sohbati et al. [12]. The latter applied double exponential fitting without reasoning this choice, the found values are apparent but without rigorous justification. The former author provides the basics of double exponential based on Lambert–Beer law of attenuation, followed later by Sohbati et al. [12]. In fact Polykreti [10 p. 210–211] admits the lack of good fit of double exponential with the experimental data trying to explain them. Both groups obviously followed same approach for determination of age and attenuation coefficient.

We here have produced a generalized approach for the bleaching of luminescence signal as a function of depth for every surface rock, promoting the functional behavior of cumulative logarithmic-Normal distribution type of error function and attributing to the variable coefficients a physical meaning. The construction of a particular equation unique for each material exposed to sunlight versus depth and exposure time has been tested on various rock types and data sets inhering variable errors, that at the end offers a new way to surface luminescence dating and authenticity. The residual TL/OSL at top surface layer for $CaCO_3$ of marbles is discernible while for granite and quartz is anticipated near zero.

For ancient walls made by limestone/ marble the solar penetration can reach depths of 5–10 mm, a useful sampling depth for dating of face wall, provided that sampling is made properly during excavation avoiding exposure to sunlight. Otherwise, sampling from internal contacts between two overlied blocks, solar penetration ensures complete zeroing only in the first 1–3 mm from surface. Incomplete bleaching from variable solar exposure may be determined applying the dose-plateau test [18].

For granites, the complete bleaching of luminescence in top layers of rocks varies with the attenuation coefficient μ and light exposure time, and at any rate this depth seems to lie between 1 and 5 mm depending from the particular rock opaqueness.

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