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Thermoluminescence Characteristics of Different Types of Natural Marble and the Effect of Annealing Temperatures

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors designed the study. Author FK performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Both authors managed the analyses of study and managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

Aims: This paper presents preliminary results on the characteristics of different marbles from Libya and Jordan. Several samples were collected and analyzed using thermoluminesence (TL) technique.

Study Design: Study the effect of annealing temperature on the nature and the kinetics of TL trapping centers of natural marble was studied.

Place and Duration of Study: Samples: Department of Physics (Atomic Physics Lab's, The University of Jordan), between June and August 2016.

Methodology: Samples of high purity marble powder were annealed at 400-1100°C/1h. The natural sample revealed one peak at 380, 336, 344 and 364°C in the MLM, MLN, MLT and MLG, respectively, 265°C and high shoulder at 360°C in the MJB and 278, 356,350°C in the MJ-grey, MJG and MJW, respectively.

Results: Our results showed that anneal treatment at 400°C increased the sensitivity of 0.5 Gy

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radiation-induced TL peaks except for the glow peaks MLT and MLG where they showed significant decrease. On the other hand, annealing in air, at a temperature of 1100°C caused a collapse in the TL sensitivity. The additive computer glow curve de-convolution was used to evaluate the trapping parameters, namely the activation energy (E), order of kinetics (b), frequency factor (s) and lifetime (τ) associated with the dosimetric TL glow peaks of natural marble and annealed at different temperatures with beta irradiation.

Conclusion: Annealing produces changes in the sensitivity of all marble samples to ionizing radiation.

Keywords: Thermoluminescence; marble rocks; calcite; sunlight bleaching.

1. INTRODUCTION

Marble was used as decorative and a material for construction since ancient times. However, marbles are extremely sensitive to weathering conditions and degradation, and hence can have marked effects and limitations on their durability. Generally, marble is a metamorphic rock that can be present in different forms and many colors ranging from white to yellow, or brown, green or even black. The rock is metamorphic, i.e. it is formed from sedimentary rocks (limestone or dole-stone) by solid-state changes in mineralogy and texture because of changes in temperature, pressure and the effect of chemically active fluids [1]. The characteristic swirls and veins of many of the colored marble varieties are usually due to various mineral impurities such as clay, silt, sand, or iron oxide that were originally present as grains or layers in the limestone [1,2]. Pure white marble is, however, a result of metamorphism of a very pure (silicate-poor) limestone or dolomite protolith, green coloration is often due to serpentine resulting originally from high magnesium limestone or dolostone with silica impurities [3]. Various marble formations are known to correspond to different conditions of metamorphosis, which are a result of the presence of unlike defects and incorporation of certain trace elements to various concentrations.

Thermoluminescence (TL) is a technique by which several primary physical properties can be revealed where potential applications in the field of radiation dosimetry can be explored [4]. Several natural and synthetic samples may exhibit TL properties after subjecting to suitable conditions of thermal stimulation. For natural marble samples, however, the thermoluminescent properties depend on the background associated with the marble and calcite is, however, large and e.g., the orange-red emission has been observed in almost 100% of calcites analyzed [5,6] materials origin, history, impurities and composition [7–10]. Therefore, TL can be used to study the thermal and radiation histories and terrestrial age of the sample under investigation [11–15]. The TL It is therefore, reasonably acceptable to consider the TL 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 minimize possible inherent errors in the determination, we made a full study that involves the evolution of glow-curves and indicates changes on shapes resulting from thermal treatment which obviously affect the kinetic parameters such as: activation energies, frequency factors, and subsequently the effect of radiation dose on the TL response and variations of the experimental processes on the generated TL for different marbles. A comparison between the obtained results with other published data is made [1]. It is largely known that marble dating by TL, routines the dating implications from solar bleaching of TL of ancient marble were initiated by the studies of Liritzis and his co-workers [16-17]. It is well known that TL of marble drops by sun exposure. Polikreti et al. [1] observed that marble specimens exposed to sunlight show increased regenerated TL intensities after short or long period storage. This physical process, however, requires a previous study of the regenerated TL evolution with time as a necessary step to estimate the error induced in age calculations. Simultaneously, Galloway [18] performed an empirical study of luminescence around 360 nm from $\mathrm{CaCO_3}$ (limestone) concluding that the results do not behave in a way that could be exploited for dating.

The present work intends to contribute to the authenticity of marble from another view point. The approach is based on investigation of 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 TL technique is used to quantify the relationship between depth and annealing temperature.

To this end, TL characteristics related to trap structure and TL kinetic parameters, of natural marbles collected from different places and after irradiation using beta source, are measured and compared with values from the literature and the kinetic parameters are reported.

2. EXPERIMENTAL

2.1 Sample Preparation

Eight types of natural marble samples of different origin were used in this study. Four types were collected from different mountains in Libyan cities (Gharyan, Mizdah, Nalut, Tarhuna). Four other samples were provided by Geology Department, Faculty of Science, and The University of Jordan. The samples were originally from a large scale picked from Dab'a area specially Al-zumayla area, in the southern part of Jordan, where marble is extracted from quarries. Each type, however, was classified by the color (white, green, grey and brown). Details of all samples material are shown in Table 1. These samples were collected and stored in dark. They were crushed and grinded carefully with a mortar and pestle, washed for 10 min in 96% C_2H_5OH, and finally rinsed with distilled water and dried. The powder was sieved using a mesh of particle size less than ≤ 63 μm. Samples used in the measurements were shaped out in the form of circular discs with dimensions 5 mm diameter and thickness about 1mm., each of mass 20 mg, and pressed under a 1.0 ton pressure.

2.2 Annealing Processes

Prior to use of the TL technique, the samples were subjected to annealing in order to erase any previous history of filled defects, including those arising from irradiation (sun light) or tribo- and chemoluminescence, stabilizing the trap structure and restoring them to initial conditions. The samples were annealed for one hour in air and oven maintained at a temperature of 400°C. The samples were slowly allowed to cool to ambient room temperature (RT) [19].

2.3 Samples Irradiation

Samples irradiation was carried out at RT with a calibrated ^{90}Sr-^{90}Y source-β-particles emission source, using VINTEN Model 623 automatic dosimeter irradiator of nominal activity 1 mCi which, delivers to the samples dose at a rate of 2.87 μGy s^{-1}. This test dose was found suitable for stability conditions, repeated measurements and comparison purposes. The imparted test dose to the samples was 0.5 Gy was found to suitable to get conclusive results. All the TL measurements were performed using a linear heating rate of 2°C/s from room temperature up to 400°C.

2.4 Samples Readout

The glow curves were obtained by using a readout system of the type a Harshaw 3500 TL reader system USA. Read out was performed under the following parametric conditions: preheat temperature of 100°C/1h for 0s, readout temperature of 400°C for 200s and heating rate cycle of 2°C/s. These settings have been shown to provide an optimal glow curve free of superficial traps.

3. RESULTS AND DISCUSSION

If an irradiated thermoluminescent material with crystal structure is heated under control, in the glow curves obtained overlapping peaks and several peaks are observed which, according to band theory, correspond to different traps in the forbidden band gap of the crystal.

3.1 Natural TL Glow Curve Shapes

The natural TL glow curves of marble were studied on 48 samples of eight different types. Samples MLT, MJ-grey, MLG and MJG exhibits TL glow curve with larger intensity in comparison with their possible deteriorated counterparts. The TL glow curve of natural marble is shown in Fig. 1, and the variation of the TL glow curve as a function of different types is shown in Figs. 2-3. In all glow curves, the main single peaks and a height or shoulder overlapping with the black-body radiation were observed (Table 2). Except MLM, only single peak was observed around 380°C [1,18,20,21] (the exact temperature depends on type of marble), which overlaps with the black-body radiation. This result indicates that the traps related to the high temperature peak at 325°C were filled at first because their traps were all emptied, and the capture cross section of the carriers in the traps associated with this peak was much higher than the corresponding value for the other peaks [22].

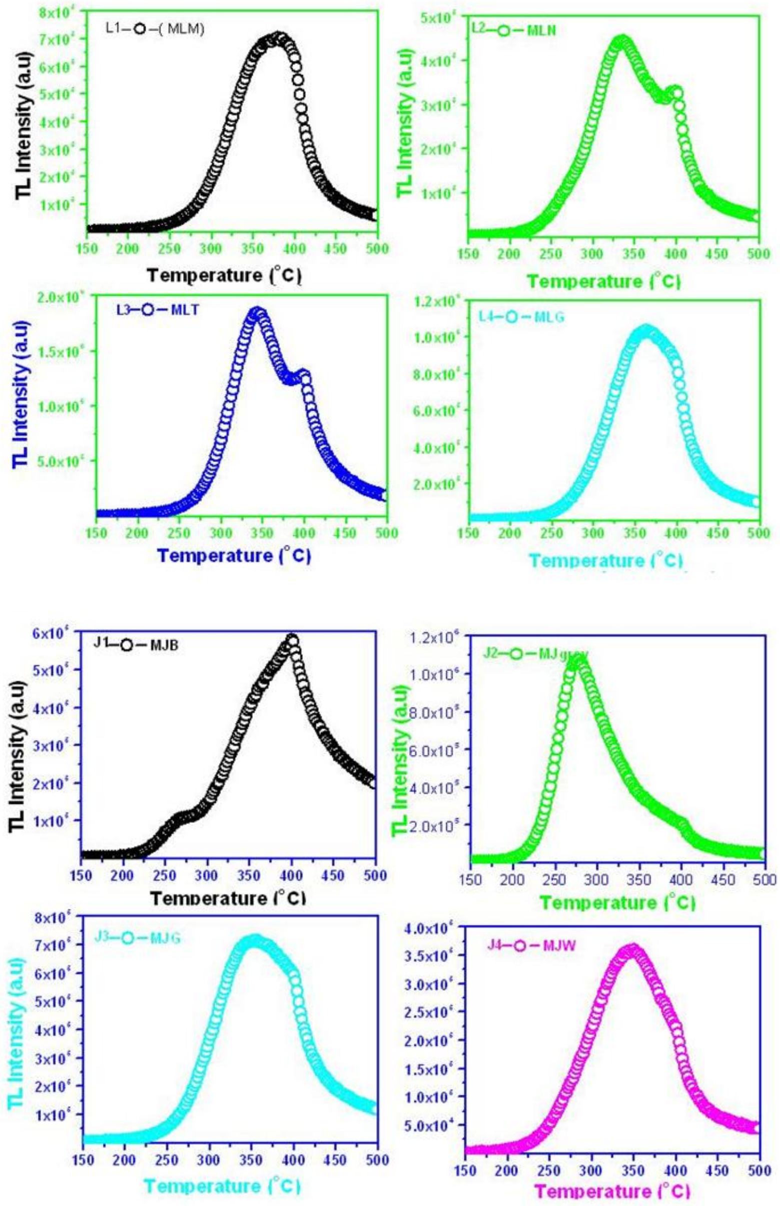

Fig. 1. Typical TL glow curves of Natural the powdered marble samples of this study (see Table 1)

3.2 Effect Annealing Temperature on TL Glow Curve Shapes of natural Samples

3.2.1 <u>Effect annealing on TL marbles without irradiation</u>

TL of the natural samples was annealed at 400°C/ 1h throughout the experimental work to erase the previous history of any geological information before the subsequent irradiation process. After that, the samples were allowed to cool in air, and then, the annealed aliquots were wrapped and stored in the dark. Because of the inhomogeneous distribution of impurities within the samples, they were oven annealed at 400°C/1h before the irradiation in order to homogenize the impurities. Therefore, all the trapped electrons and holes forming the natural TL were entirely removed, and the samples TL reading were very close to the background, as shown in Fig. 4 (a and b).

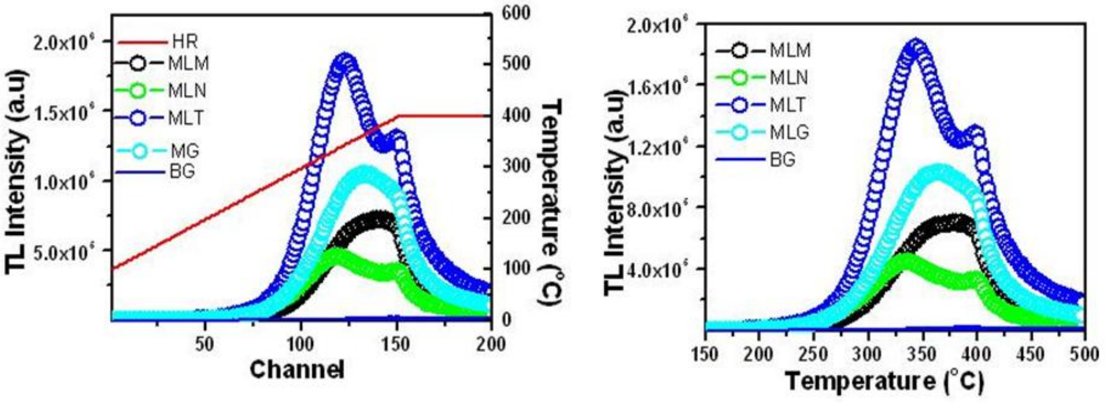

Fig. 2. Variations of glow curves of a natural Libyan marbles, glow curves are measured at a constant heating rate $2\mathrm{K}s^{-1}$.

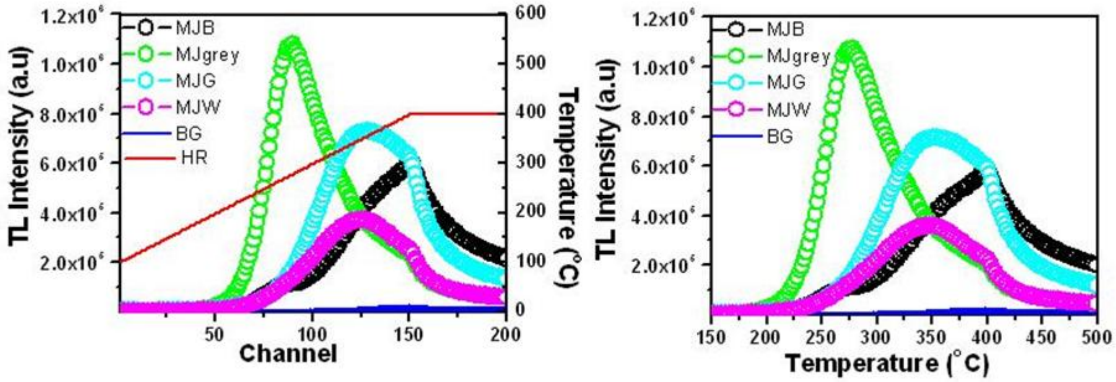

Fig. 3. Variations of glow curves of a natural Jordanian marbles, glow curves are measured at a constant heating rate $2\mathrm{K}s^{-1}$.

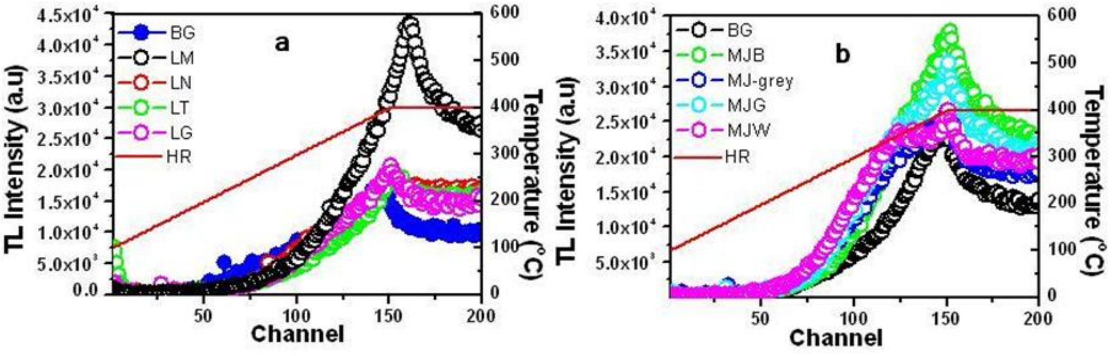

Fig. 4. Typical TL glow curves of all marble types of (a) Libyan marbles; (b) Jordanian marbles

3.2.2 Effects annealing on TL marbles with irradiation

For studying the effect of thermal treatment, the natural marble samples were annealed at 400 and 1100°C in a closed oven for a constant annealing time of 1 h, and followed by irradiation to a dose of 0.5 Gy. The effect of annealing temperatures on the glow curves of samples is shown in Fig. 5. However, the TL peaks above

400°C are not shown because they were small for all natural samples. For this reason, the TL peaks above 400°C for all marble samples were not taken into consideration. According to Fig. 5, the sensitivity of TL peaks does not change up to 400°C. Above 400°C, the sensitivity of all glow peaks for all marble sample rises continuously and then decreases, (except for MLG where is shows continuous increase). Annealing at 1100°C/1h caused a collapse in the TL sensitivity of all glow peaks for all marble samples, except for sample MLG. The glow curves MLN, MJ-grey and MJW consist of two regions. Region I(100-200°C) where the peaks can be easily separated and, region II (200 to 350°C) where a complex feature of several peaks exists. Generally, the glow curves presented in Fig. 5 before and after annealing give useful information on the properties of various types of defect present within the material. Features similar to those observed previously were noticed when the substrate temperature was varied up to 200^{o}C [23]. More specifically, the data reveals the detection of selective emission from new shallow defects states accompanied by perturbations in the defect concentration of other deeper trapping levels. The low temperature detected peaks structure centered on 110°C and 166°C for MLN; 155°C for MJ-grey; 125°C and 165°C for MJW and the variations observed at high-temperature (above 200°C) are two key features noted after thermal treatment. While, annealing at a temperature of 400°C/1h causes an increase of the height of the TL peaks of both marble types, for MJ-grey; MJW; MJG; MJB at 278, 350, 356 and 400°C by a factor of 2.4, 4.2, 1.1 and 1.5, respectively, and for MLM; MLN; MLT; MLG at 380, 336, 344 and 364°C by a factor of 1.2, 1.6, 0.7 and 1, respectively, as compared to unannealed samples. This behavior of samples annealed in a closed oven has been reported previously for a naturally-occurring calcite and marble by [23] as observed for MJ-grey. However, other results have been reported by other researchers [20,18,1,21] compared with natural samples.

Zimmerman [24] suggested that the sensitization of the 110°C peak in quartz, which had been attributed to the recombination of thermally-released electrons with hole centers, is due to the occurrence of a reservoir center, in which holes accumulated during the initial irradiation (pre-dose). The reservoir of holes is characterized by a high probability for capturing holes, and is too deep to release holes in the temperature range studied by the TL [25]. However, when the sample is heated up to at least 400^{o}C, the holes in the reservoir are thermally released into the valance band, and are eventually captured at a luminescence center. When the sample is subsequently irradiated with the same test dose, it will reveal an increase of sensitivity due to the presence of these additional holes in the luminescence centers. Franklin et al. [26] and Pagonis and Michael [27] attributed the increase in TL sensitivity to the ionizing radiation with annealing temperature of calcite and the sudden collapse of the sensitivity observed at higher annealing temperatures using the above-mentioned Zimmerman ``reservoir'' model [23]. The same researchers [26,27] suggested that a reservoir of holes is also present in calcite. This reservoir is filled before annealing by the presence of intrinsic hole defects in the crystal structure [27]. When the calcite sample is irradiated, the measured TL shows a small signal due to the small number of holes trapped in the luminescence centers. Upon heating the sample at elevated annealing temperatures, the intrinsic hole defects in reservoir are thermally released into the valence band, and are eventually trapped in the luminescence centers. Thus, the number of positively charged luminescence centers is increased, and the TL sensitivity rises. These results confirm that the sensitization process in our marble samples is due to annealing with irradiation.

Table 1. Characteristics of the eight marble samples

Sample	Description
MLG	Libyan marble from a Gharyan City (MLG)
MLM	Libyan marble from a Mizdah City (MLM)
MLN	Libyan marble from a Nalut City (MLN)
MLT	Libyan marble from a Tarhuna City (MLT)
MJB MJG MJ-grey MJW	Jordanian Marble (MJ) with different colors; a brown (MJB), green (MJG), grey (MJ-grey) and white (MJW)

Table 2. Position of peaks for different types of natural marble samples

Type	Position of traps [as peak and high shoulder] (°C)
MLM	380
MLN	336, 399
MLT	344, 398
MLG	364, 399
MJB	265, 355 and height peak overlapping with black-body radiation(~399°C)
MJ-grey	278 and small peak overlapping with black-body radiation(~399°C)
MJG	356 and height shoulder overlapping with black-body radiation(~399°C)
MJW	350 and height shoulder overlapping with black-body radiation(~399°C)

The collapse of the TL signal at higher temperatures has also been interpreted using the energy scheme of the Zimmerman pre-dose or "reservoir" model [26,27]. The charging electronic species in the deep traps would be lost by recombination during annealing. Therefore, the luminescence centers can no longer hold the charging electronic species. This case causes a collapse of the sensitivity to ionizing radiation.

A comparison between the TL natural glow curves and the effect of annealing temperatures of MJW and MLN is given in Table 3 and Fig. 6. (all samples are of white color).One main peak can be observed for natural of both at a temperature of about 335 and 350°C of MLN and MJW, respectively and they are very broad extending from 100 to 500°C. Annealing temperature at 400°C/1hcauses an increase of the height of TL peaks of both types, and it shifts towards high temperature at 354°C for MLN, with fixed position of MJW. The annealing temperature at 1100°C compound shows two prominent TL glow peaks at 110 and 158°C of MLN, with main peak at 332°C and also, for MJW shows two prominent TL glow peaks at 125 and 163°C, with fixed main peak at 350°C. Two peaks are generally observed in agreement with other researchers [23,28-30]. TL glow curves of MJW with larger intensity in comparison with MLN. This general overview, supported on total intensities using broad spectra filters, arises as a simple methodology to authenticate disputable marble objects.

3.3 Kinetic Parameter Analysis

Thermoluminescence analysis which governs the behavior of the glow curves contains inherent overlapping peak features and therefore, requires de-convolution of the total glow curve. Various peak components are extracted to reveal mechanisms dominating charge transfer and recombination processes. Data analysis, however, involves determining the trapping parameters based on available defect models and related techniques [31,32].

To understand the nature of the traps formed in natural marble samples under annealing and irradiation, we have employed the analysis of Kitis et al. [33] who derived expressions for the TL glow curve de-convolution (GCD) for 1st, 2nd and general orders of kinetics using the experimentally obtained maximum peak intensity (I_M) and the maximum peak temperature (T_M). The free parameters to be determined through non-linear curve fitting are then the activation energy (E) and the order of kinetics (b). In their analysis, the general order kinetics is generally given by:

$$I(T) = s'' n_o e^{-(E/kT)} \left[1 + \frac{s''(b-1)}{\beta} \int_{T_o}^{T} e^{-(\frac{E}{kT'})} dT' \right]^{\frac{b}{b-1}} \quad (1)$$

where: n_o= initial concentration (cm^{-3}) of trapped charge carriers at time *t=0* and initial temperature $T_o = 0K$.

s = a constant characteristic of the electron trap, called the pre-exponential-frequency factor or attempt-to-escape frequency” (s^{-1}). This parameter is proportional to the frequency of the collisions of the electron with the lattice phonons. Typically the maximum values of s correspond to the values of the lattice vibration frequency, i.e. 10^{12}−10^{14} s^{-1}, *s'* is the effective pre-exponential factor for general order kinetics ($cm^{3(b-1}s^{-1}$), $s'' = s' n_o^{(b-1)}$= an empirical parameter acting as an “effective” frequency factor for general-order kinetics (in s^{-1}), β = heating rate (in $K.s^{-1}$); assumed linear: $T = T_o + \beta t$, *E* = activation energy or trap depth (in eV);

b= kinetic order; *k*= Boltzmann constant (=8.617x10-5 $eV.K^{-1}$); and *T* = final temperature (in K).

Table 3. Position of peaks for comparison of MLN and MJW of a white marble samples

Type	Position of traps (°C)					Reference
	Natural	400°C	1100°C			
MLN	335	354	I_1:	110	158	[21,23]
			I_2:	332		
MJW	350	350	I_1:	125	163	[1,23]
			I_2:	350		[18]

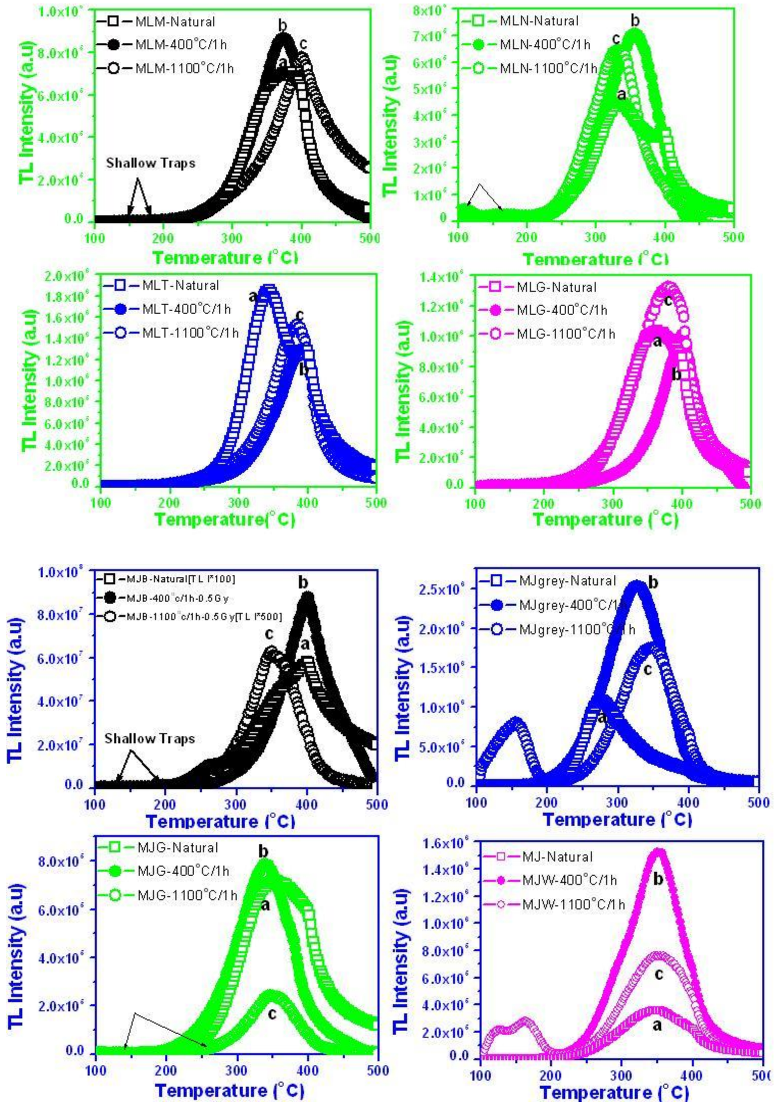

Fig. 5. Typical TL glow curves of both marble samples. (a) Natural glow curve; (b) Beta irradiated glow curves of annealed 400°C/1h samples; (c) Beta irradiated glow curve of annealed 1100°C/1h samples. Glow curves are measured at a constant heating rate 2Ks^{-1}

The frequency factor *s* and n_0 are therefore given by:

$$s=\frac{\beta E}{kT_M^2}\left[1+\frac{(b-1)(2kT_M)}{E}\right]^{-1}e^{\frac{E}{kT_M}} \qquad (2)$$

In this study, by fitting the experimental data of Fig. 5 with Eq. (2) using the common practice procedure of total computerized glow curve de-convolution (CGCD) to separate inherently overlapping features is an active area of interest and has become more important in view of its numerous applications, such as in: dating, dosimetry and defect studies. The method is based on solving equation (1) numerically using a standard software, e.g. Peak fit or Origin, we obtained the kinetic parameters (i.e. Ea and s) as a function of annealing temperature. Typical result of the fitting is shown in Figs. 7-9 for beta dose of 0.5Gyreveals the detection of the additional new defect states that were absent before annealing. The well-defined nature of the glow curve at 0.5 Gy is manifested by the perfect fit of the theoretical curve with the experimental data. Therefore, the TL kinetic parameters associated with the glow peaks in all the phosphors were obtained by CGCD method. The obtained kinetic parameters and peak temperatures at the maximum (T_m) are given in Tables (4-6). The incandescent background was subtracted from the TL analysis data to show traps, which were overlapping with black-body radiation.

The analyzed TL glow curves as shown in the figures consist of 3-6 glow peaks with small shoulders (the exact glow peaks depend on type of marble). The glow curves of MJ-grey, MLN and MJW exhibits 1-2 glow peaks, respectively at a temperature rang 100-200°C and prominent glow peak at samples annealed at 1100°C/1h. where they can be seen that all the peaks manifest a general order kinetic of order mixing with n_0 increasing and decreasing for some types (see Tables 4-6) as the annealing temperature increases which is an indication of increased number of defects and the frequency factor has decreased by an order of magnitude. The value of the activation energy as a function of annealing temperature is an indication that the shift in the energy level induced by defect clustering manifests itself through a change in the peak temperature. The peaks at (300-390) of J3(MJG) show a lifetime ranging from an hour to several months for natural and increases to several years with annealing temperature increase. This lifetime is very short as expected, considering that this produced by photo transferred TL [34-36] and the traps producing it are unstable. And show energy depths from 0.233 to 0.629 eV of natural, 0.815 to 1.757 eV for annealed at 400°C and 0.797 to 2.441 eV at 1100°C. It was found that the values of the kinetic parameters E, s, b and τ for TL glow peaks revealed changed for annealed samples.

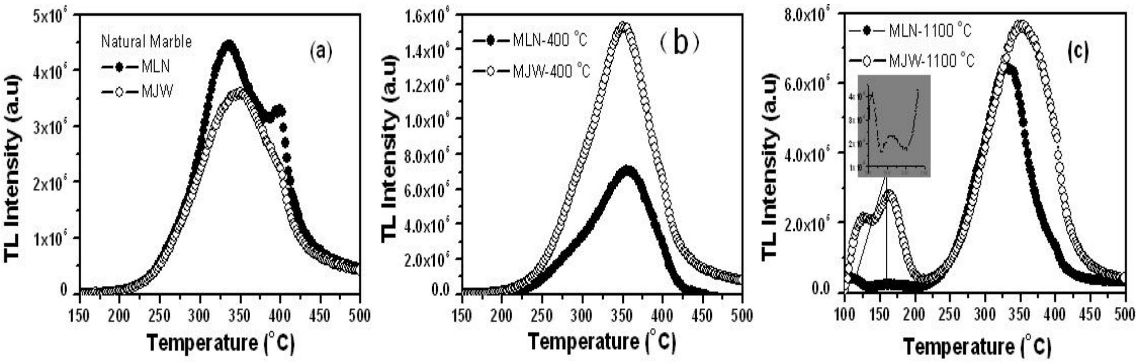

Fig. 6. Typical TL glow curves for different types of white marbles of MLN and MJW: (a) Natural glow curve and beta irradiated glow curves of annealed at: (b) 400°C/1h samples; (c) 1100°C/1h samples. Glow curves are measured at a constant heating rate 2Ks^{-1}.

Table 4. TL parameters for six characteristics of all Natural Marbles types; *E* the activation energy, T_m is the peak temperature, b kinetic order, w the FWHM, s the frequency factor and τ the lifetime

Samples	Ps	E(eV)	T_m(°C)	b	ω(°C)	s(s^{-1})	τ*
MJB	P1	1.342	260	1.00	42.58	5.367×1011	2.257×103y
	P2	1.831	284	1.63	44.02	4.900×1015	4.188×107y
	P3	1.860	320	2.19	57.15	7.412×1014	8.516×108y
	P4	1.900	355	2.01	59.93	1.874×1014	1.587×1010y
	P5	2.137	397	1.42	50.96	1.285×1015	2.252×1013y
MJ-grey	P1	1.509	271	1.27	44.53	1.112×1013	7.037×104y
	P2	1.642	302	1.41	48.42	2.777×1013	4.876×106y

Samples	Ps	E(eV)	T_m(°C)	b	ω(°C)	s(s^{-1})	τ*
	P3	1.940	337	1.51	47.85	1.258×1015	1.114×1010y
	P4	2.269	380	2.5	61.35	3.742×1016	6.977×1013y
MJG	P1	0.233	307	1.00	71.15	1.702	1.36h
	P2	0.482	328	1.75	57.46	293.846	5.087d
	P3	0.581	359	1.89	59.41	1.243×103	55.732d
	P4	0.629	398	1.00	50.09	1.719×103	8.628m
MJW	P1	1.032	277	1.00	57.81	2.267×108	32.441y
	P2	1.534	314	1.37	53.00	1.495×1012	1.379×106y
	P3	1.695	350	1.73	60.74	4.995×1012	2.113×108y
	P4	1.703	395	2.27	79.81	5.761×1011	2.498×109y
MLM	P1	1.097	318	1.00	61.24	1.651×108	552.867y
	P2	2.101	353	1.86	52.05	9.806×1015	7.315×1011y
	P3	2.343	393	2.15	57.00	6.243×1016	1.357×1015y
MLN	P1	1.159	266	1.00	50.26	6.367×109	158.406y
	P2	1.170	325	1.00	63.14	5.511×108	2.802×103y
	P3	1.361	361	1.00	53.24	5.18×109	4.882×105y
	P4	2.321	399	1.00	38.21	3.048×1016	1.185×1015y
MLT	P1	1.129	310	1.00	58.61	4.437×108	710.803y
	P2	1.766	335	1.12	44.76	4.796×1013	3.447×108y
	P3	1.984	359	1.16	43.94	7.58×1014	3.595×1010y
	P4	2.456	396	1.00	43.94	4.051×1017	1.668×1016y
MLG	P1	1.094	317	1.00	61.26	1.615×108	503.026y
	P2	1.874	353	1.62	53.99	1.314×1014	8.279×109y
	P3	1.898	394	1.96	66.64	2.055×1013	1.339×1011y

*: Lifetime measurements are determined at ambient temperature (26.5^oC), and scale is in years unless specified otherwise, with (h=hours, d=days and m=months).

Table 5. TL parameters for six characteristics of all Marbles types annealed at 400°C/1 h

Samples	Ps	E(eV)	T_m(°C)	b	ω(°C)	s(s^{-1})	τ*
MJB	P1	0.890	285	1.00	67.75	7.252×106	4.135y
	P2	1.603	329	1.00	46.77	2.703×1012	1.105×107y
	P3	2.266	364	1.23	40.46	1.088×1017	3.943×1013y
	P4	2.851	397	1.15	34.63	4.094×1020	7.322×1019y
MJ-grey	P1	0.882	303	1.00	71.36	3.219×106	83.357m
	P2	1.516	344	1.47	61.27	2.164×1011	47.439×105y
	P3	1.715	380	1.96	70.40	1.514×10112	67.773×104y
MJG	P1	0.815	308	1.00	77.11	6.581×105	30.402m
	P2	1.551	355	1.36	59.58	2.495×1011	1.597×107y
	P3	1.757	397	2.41	80.31	1.37×1012	85.173×108y
MJW	P1	1.101	289	1.00	56.55	6.049×108	176.201y
	P2	1.587	328	1.31	52.36	2.034×1012	79.024×105y
	P3	1.990	354	1.28	45.30	1.147×1015	8.478×1010y
	P4	2.244	385	1.67	50.84	1.794×1016	1.019×1014y
MLM	P1	0.916	292	1.00	67.25	9.874×106	8.318y
	P2	1.691	342	1.45	54.27	7.276×1012	12.427×108y
	P3	2.208	380	2.47	62.65	1.231×1016	3.682×1013y
MLN	P1	1.095	267	1.00	52.94	1.446×109	58.407y
	P2	1.636	295	1.33	45.95	3.791×1013	2.831×105y
	P3	1.797	323	1.38	47.18	1.805×1014	3.045×108y
	P4	2.106	352	1.49	46.09	1.173×1016	7.422×1011y
	P5	2.113	382	1.91	57.25	1.978×1015	5.774×1012y
MLT	P1	0.804	256	1.18	73.97	2.987×106	4.374m
	P2	1.233	305	1.00	53.58	4.832×109	3.671×103y
	P3	1.958	341	1.27	44.04	1.403×1015	2.006×1010y
	P4	2.378	372	1.49	43.70	4.941×1017	6.657×1014y
	P5	2.761	399	1.38	39.33	7.121×1019	1.287×1019y
MLG	P1	0.907	282	1.00	66.00	1.178×107	4.919y
	P2	1.736	328	1.65	54.08	3.882×1013	1.332×108y
	P3	1.931	365	1.25	47.91	1.949×1014	5.071×1010y
	P4	2.624	398	1.00	36.65	6.925×1018	6.6×1017y

*: Lifetime measurements are determined at ambient temperature (26.5^oC), and scale is in years unless specified otherwise, with (h=hours, d=days and m=months)

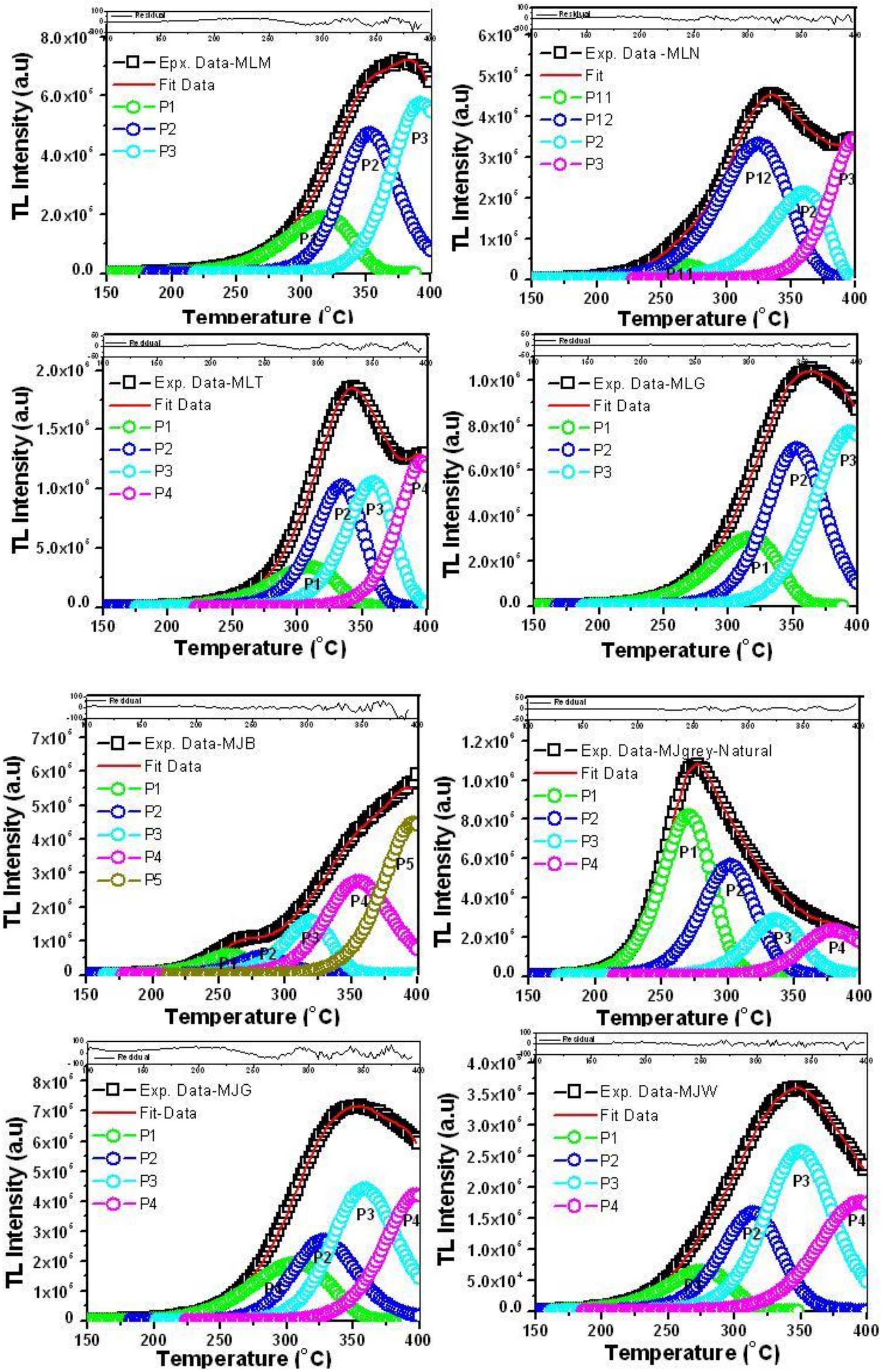

Fig. 7. D-convoluted glow curve of natural glow curves of all marble types

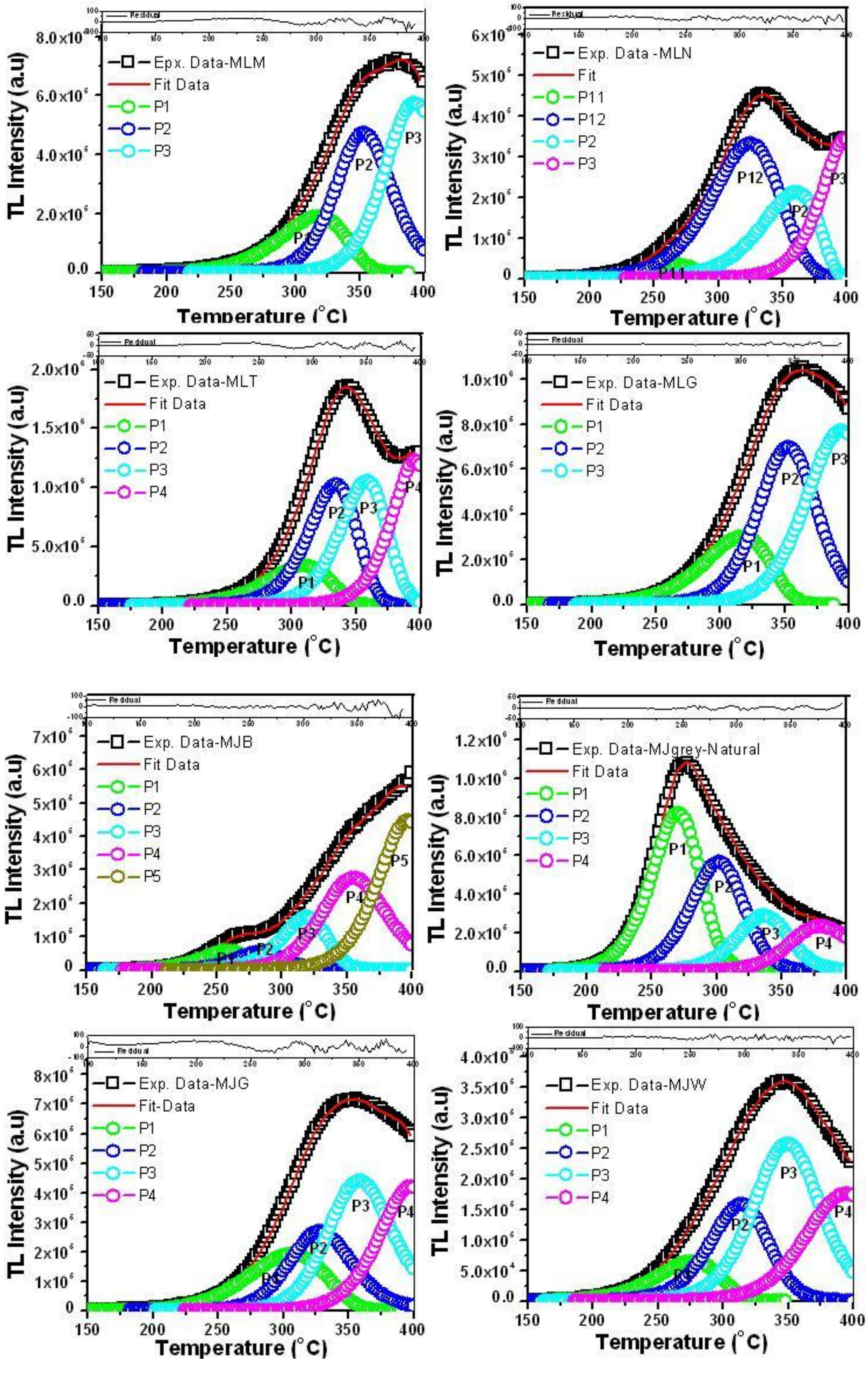

Fig. 8. D-convoluted glow curve of glow curves of all marble types irradiated with 0.5 Gy after annealed at 400°C/1h

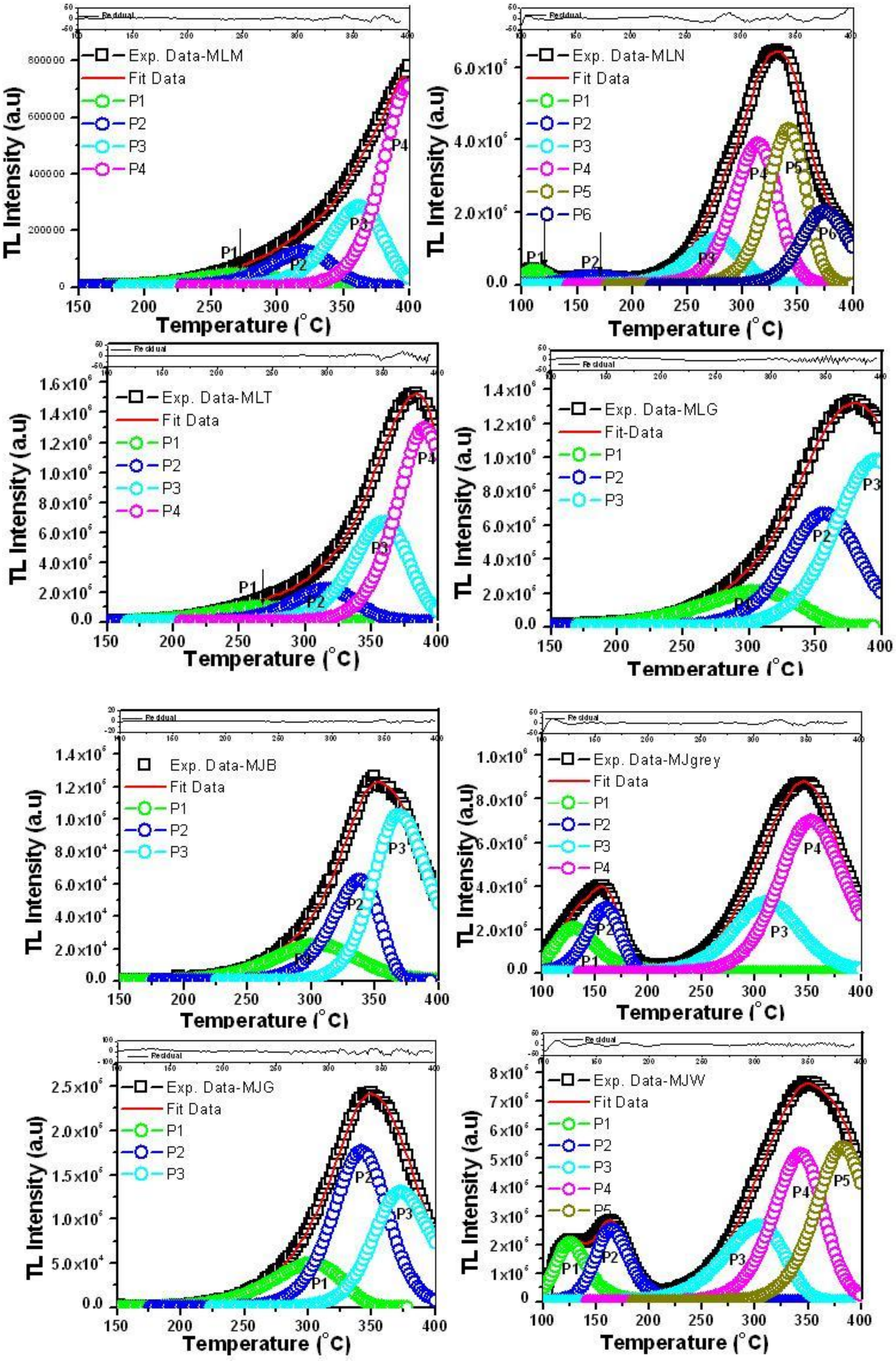

Fig. 9. De-convoluted glow curve of glow curves of all marble types irradiated with 0.5Gy after annealed at 1100°C/1h

Table 6. TL parameters for six characteristics of all Marbles types annealed at 1100°C/1h

Samples	Ps	E(eV)	T_m(°C)	b	ω(°C)	s(s^{-1})	τ*
MJB	P1	0.979	305	1.40	79.48	2.248×107	42.073y
	P2	1.744	338	1.00	43.75	2.636×1013	2.679×108y
	P3	2.559	369	2.5	53.00	1.662×1019	2.206×1016y
MJ-grey	P1	1.146	130	2.5	45.81	3.225×1013	6.917d
	P2	1.156	160	1.23	36.27	4.024×1012	2.125y
	P3	1.169	312	1.62	73.99	8.869×108	1.679×103y
	P4	1.523	353	2.04	74.07	1.535×1011	8.793×106y
MJG	P1	0.979	303	1.00	65.40	2.295×107	41.223y
	P2	1.893	342	1.56	50.69	3.672×1014	6.191×109y
	P3	2.441	373	2.45	55.50	1.41×1018	2.689×1015y
MJW	P1	1.479	126	2.5	35.20	9.692×1017	3.08m
	P2	1.569	165	2.20	37.31	2.033×1017	39.489y
	P3	0.981	304	1.00	67.66	2.534×107	40.335y
	P4	1.591	343	1.35	55.79	9.894×1011	1.902×108y
	P5	1.892	383	1.59	57.98	3.387×1013	6.458×1010y
MLM	P1	0.804	275	1.00	71.87	1.541×106	8.479m
	P2	1.399	321	1.22	55.67	6.718×1010	1.646×105y
	P3	1.874	362	1.23	48.30	7.87×1013	1.383×1010y
	P4	2.515	399	1.17	39.75	9.343×1017	7.132×1016y
MLN	P1	1.091	113	1.32	31.68	2.931×1013	21.68h
	P 2	1.112	165	2.5	55.41	7.625×1011	1.934m
	P 3	1.292	277	1.13	49.99	6.696×1010	2.613×103y
	P4	1.697	314	1.31	47.02	4.174×1013	2.741×107y
	P5	2.096	342	1.33	41.52	1.901×1016	3.117×1011y
	P6	2.371	374	2.02	51.68	3.698×1017	3.585×1014y
MLT	P1	0.772	266	1.00	72.62	1.02×106	3.705m
	P2	1.423	316	1.33	56.39	1.396×1011	2.007×105y
	P3	1.827	359	1.29	50.36	3.874×1013	4.548×109y
	P4	2.309	390	1.40	45.87	4.266×1016	5.335×1014y
MLG	P1	0.694	307	1.00	87.66	5.138×104	3.583m
	P2	1.530	357	1.60	65.31	1.491×1011	1.187×107y
	P3	1.701	396	2.00	76.97	5.391×1011	2.477×109y

**: Lifetime measurements are determined at ambient temperature (26.5^oC), and scale is in years unless specified otherwise, with (h=hours, d=days and m=months)*

4. CONCLUSION

Thermoluminescence of natural marble and the effect of annealing temperature and irradiation on the natural marble were studied. Annealing produces changes in the sensitivity of all marble samples to ionizing radiation. Annealing increases the intensity of all glow peaks except the peaks above 1100°C. The increase in TL producing efficiency depends on the annealing temperature and irradiation. The annealing procedure reveals change in the kinetic parameters E, T_m, s, b and τ of glow. Our results showed that the annealing process probably does change the nature of the trapping centers. Heating for 1h at 400°C followed by slow cooling to ambient room temperature are the optimum conditions for TL sensitivity enhancement in the systems investigated.

The dosimetric characteristics of annealed natural marble were investigated using TL technique. The radiation induced the 400°C, 350°C glow peaks of MJB, the 348°C, 344°C glow peaks of MJ-grey, the 3548°C, 350°C glow peaks of MJG, the 372°C, 400°C glow peaks of MLM, the 358°C, 332°C glow peaks of MLN and the glow peaks of another samples nearly stable with annealing at 400°C and 1100°C respectively. The kinetic parameters (E, s, τ values) were successfully calculated by de-convolution method CGCD. Dating marble is of major interest in quaternary and archaeological research, because marble is a constituent of a large number of materials. The lifetime of traps was successfully calculated. The calculation of these peaks could find useful application such as in TL dating.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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