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PROBING LUMINESCENCE DATING OF ARCHAEOLOGICALLY SIGNIFICANT CARVED ROCK TYPES

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ABSTRACT

The thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) dating of crystalline materials, first applied to calcites (limestone buildings), has been extended to carved megalithic monuments made of granites, basalt and sandstones derived from archaeological sites. Various applied criteria for potential dating included pulsed blue light stimulation, different preheating and solar simulator bleaching, while the single (and multiple) aliquot regeneration and additive dose procedures were used for equivalent dose determination. The decay curves of signal loss follow a power law, n^{-p}; for blue stimulation the signal loss of quartz and feldspar is better approached by an exponential law, 1-aln(n).

KEYWORDS: luminescence, dating, rocks, bleaching, dose, OSL, TL, fading, IR, stimulation

INTRODUCTION

The eviction of electrons from electron traps in crystalline materials via thermal agitation or light stimulation and their refilling from ionizing radiation is the basis for zero set luminescence clock of TL and OSL dating methods (Liritzis 1995, 2001; Liritzis et al, 1997a, 2002; Aitken, 1998; Murray and Roberts, 1997; Wintle and Murray, 2006; Vafiadou et al, 2007, Roberts, 1997). A variant of TL and OSL has already been developed for dating large carved limestone blocks (megalithic, cyclopean) of Greek monuments (Liritzis, 1994, 2000; Liritzis and Galloway, 1999, Liritzis and Vafiadou, 2005). The progress in TL dating and optical stimulated luminescence (OSL) dating of sediments (Mejdahl, 1986) led to the extension of this mechanism to other rock types of archaeological significance.

The rationale of this new version is described below: This dating technique (coined optical thermo-luminescence) concerns the inter-block surfaces of the limestone building blocks and relies on the Optically Sensitive Electron Traps (OSET) responsible for TL in the surface layer of the carved limestone block having been bleached by sunlight, prior to the blocks being incorporated into the structure. The exposure time of the surface to sunshine (to a depth that ranges from about 0.5 mm for limestones to 4 mm for some marbles) depends upon the efficiency and time for the stone masons to put any block in the appropriate place overlaid by another. From the moment that any surface is no longer exposed to sunlight, then the OSET are filled by electrons produced by the ionization caused from nuclear radiation of natural uranium, thorium, rubidium, potassium, and the cosmic radiation. These isotopes are present in the limestone and the soil surrounding the sampling point.

The extension of this idea to the dating other carved rock types from ancient (particularly prehistoric) monuments, such as, granite, basalt and sandstone, lead us to investigate their potential dating. Extensive TL and OSL measurements were carried out. The OSL probes the OSET (blue light probes quartz and feldspar, the IR stimulation probes only feldspar), while the TL probes the Thermally Sensitive Electron Traps (TSET) but the OSET as well.

The age of a carved rock made a monument is found from the relationship,

AGE = equivalent dose (ED) / annual dose-rate,

where the ED measures the total exposure to radioactivity accumulated by the sample, and the ‘dose-rate’ is the (assumed constant) annual rate of exposure. The ED increases with time in proportion to the number of trapped electrons. In the laboratory, the trapped electrons can be evicted by heating (TL) or by monochromatic light (OSL) (usually green with quartz or infrared with feldspars). These electrons recombine with luminescence centers to emit light of a characteristic wavelength, the intensity of which is measured.

The 'dose-rate' comprises of the alpha, beta and gamma radiation doses from the natural radioisotopes of uranium, thorium, potassium, rubidium and the cosmic radiation, as well as the environmental gamma ray dose-rate (i.e. $kD\alpha+D\beta+D\gamma+Dc$), where k is the sensitivity ratio of alpha to gamma rays in inducing luminescence.

The OSL method has been improved with the introduction of the 'single aliquot technique' and similar approaches and relevant correction procedures, which uses one disc prepared from the sample to carry out all the measurements to determine ED (Duller, 1994; Galloway, 1993; Liritzis et al., 1994, Murray and Wintle, 2000). The criterion applied to examine their suitability for use in dating projects is twofold;

a) bleaching of luminescence after exposure to sunlight or solar simulator, and
b) growth of luminescence with irradiation (following the regeneration and additive dose techniques).

Both these criteria were investigated with detailed luminescence and radiation measurement tests on a variety of rock types.

The identification of mineral present was made by XRD, while, quartz and feldspar, were also identified by probing with IR and blue LED. For dating purposes, the single aliquot regeneration and additive dose techniques were applied, followed by sensitivity change corrections from preheat and read, for the equivalent radiation dose determination.

SAMPLE PROVENANCE AND SAMPLE PREPARATION FOR TL AND OSL

Six rock samples derived from ancient carved monuments were processed. Two granites, EGOS-7 (black and white) and EGMYK (red, black and white grains); one sandstone (EGOS-6); one basalt (EGBAS), (all of Egyptian origin), and two calcites (limestones), ITH-4 (Ithaca, Greece) and EGKH-2 (Abydos, Egypt).

Initially the flat surface layer of the samples was cleaned with dilute hydrochloric acid (30%) followed by gentle file brushings to remove a layer of 0.5-0.7 mm from limestones and up to 3 mm for the others (Liritzis et al., 1997b). For granites, solar penetration assures bleaching to at least 15 mm, where 50% of the geological dose remains, measured by blue and IR stimulations (Liritzis, 2001). For the calcites, powder of 2-10 um was prepared using the fine grain method (Zimmerman, 1971), with prior wash at 0.5% acetic acid. For granites and sandstone powder of 80-150 um grain size was selected. The obtained grain powder was deposited onto brass disks and disk aliquots of 1.5 mg/cm^2 were prepared.

Normalization was made with a test beta dose. The TL integral of a discrete glow-peak was used to normalize the disk over the same mass. The background was obtained by a second readout. The TL analyzer is a Littlemore Co type 711 reader, with the glow-oven evacuated down to 0.1 Torr and high purity N_2 flowing during measurement. The light emission was detected by an EMI QA PM tube and glow-curves were stored in a PC via a 1024-channel ADC card operating in the MCA mode. The heating strip was nicochrom 0.8 mm thick, with a Cr-Al thermocouple fixed on it. The heating rate was 5°C/sec, and the irradiator was a ^{90}Sr-^{90}Yt beta ray source delivering 0.6 Gy/min.

The OSL is a home-made (Edinburgh) system comprising of blue, green and IR diodes shining on the sample disk in the middle of the plate (Galloway, 1992; Liritzis et al., 1996). Disks were prepared from grains with the aid of non-luminescent silicone.

One sample of every rock type was tested for anomalous fading. These samples were EGOS-7 (granite, building), EGOS-6 (sandstone), EGBAS (basalt) and ITH-4 (calcitic wall). The experimental procedure was as follows:

- For the TL measurements one aliquot from every sample was bleached under a UV lamp, and irradiated with 20Gy of beta dose. The aliquot was measured, a background was obtained, irradiated again with the same dose and kept in a dark place for 20 days. Then the sample was measured again, with one extra measurement for background. Finally, a cycle of 10 irradiations with 20Gy (five for samples ITH-4 and EGOS-7) and measurements was performed in order to check the changes on the sensitivity of the samples were made.
- For the OSL measurements, one aliquot from every sample was bleached under a UV lamp and irradiated with 20Gy of beta dose. The aliquot was measured using IR and Blue light, irradiated with the same dose, preheated at 200°C for 10s and kept in a dark place for 20 days. Then the sample's IR and Blue stimulated luminescence was measured again. Finally, a cycle of 6 irradiations with the same dose and readouts with IR and Blue were made to check the changes on the sensitivity of the samples. Before every measurement the sample was preheated at 200°C for 10s. The readout with IR were performed for 100s at 125°C and with heating rate 5°C/s, and with Blue for 50s at 125°C and with heating rate 5°C/s.

EXPERIMENTAL RESULTS

EGOS-6, sandstone

XRD

It is a fragile rock of brownish color with obvious large crystals up to 1 mm diameter. XRD have shown 99-100% quartz,

OSL measurements

a) Bleaching

Fig. 1 shows the bleaching of the EGOS-6 by blue LEDs after a dose of 190 sec beta (20Gy). It bleaches quite fast; 20% of the natural signal remains after 100 seconds. IR stimulation shows only a small response (the background is around 75 counts), which implies predominant quartz. The minimal presence of feldspar was checked also with the single aliquot added dose procedure; no change in counting rate was observed. After a 20 Gy irradiation with a beta source, following 18 repeated preheating and reading cycles with 0.1 sec of blue

LEDs, the signal was unusually constant - as though preheating (220^{0}C, 60 sec) is compensating for loss of signal due to bleaching (Fig.2).

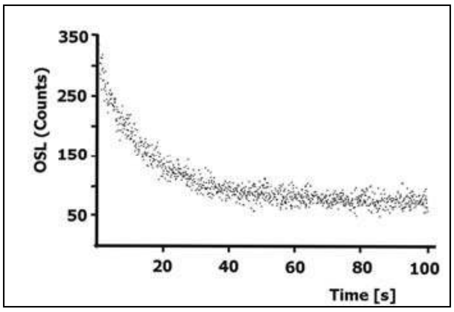

Fig.1 Bleaching of EGOS-6 by blue LEDs (sample irradiated with 20 Gy beta source, following the preheat/read sequence of fig.2).

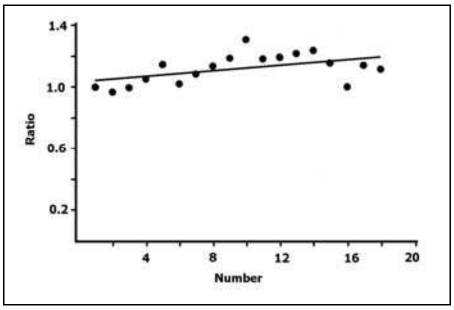

Fig.2 After a 20 Gy irradiation with a beta source, following 18 repeated preheatings and readings with 0.1 sec of blue LEDs, the signal was unusually constant.

b) Dose growth and equivalent OSL dose determination.

Fig. 3 shows the regeneration procedure of single aliquot with blue LED. The measurement time was 0.1 sec. Following the regeneration technique, the equivalent dose (ED) was 1.96±0.16 Gy. The additive dose procedure gave a similar dose. The ED was twice re-measured for another aliquot further extracted from the surface. The ED values obtained were 44±3 Gy and 24±1.5 Gy. These two higher values imply grains from deeper layers, where incomplete bleaching has occurred. The extracted grains were 80-150 microns. No etching was performed, thus the alpha particle dose was included in the annual dose rate component. This is because the sandstone was primarily composed of granular phase, and the grains contained natural radioactivity (k-value assumed = 0.1). The dose-rates were measured by a gamma spectroscopy (Hp Ge) and a plastic scintillator. The estimated age is 1300±570 years B.C

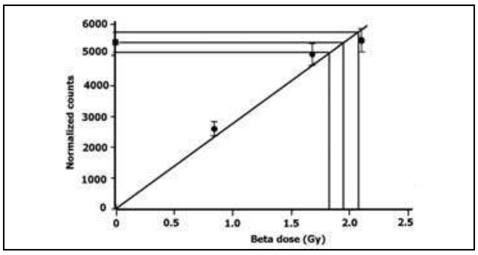

Fig.3 EGOS-6. Regeneration procedure of single aliquot with blue LED. The measurement time was 0.1 sec and the ED=1.96±0.16 Gy.

c) Anomalous fading (AF) results.

Method		Sensitivity Change (%)	Signal Change Before and after the 20 days (%)	AF
OSL	Blue	13±1.3	8±1.2	N
	IR	11±9.77	71±12	Y

Table 1: Anomalous fading (AF) results for sample EGOS-6 for OSL measurements

From Table 1 we can conclude that the signal in IR fades about 60%, but the change in signal in blue after 20 days is less than the sensitivity change percentage which indicates no fading.

TL measurements

a) Bleaching

Brass disks of single aliquots were exposed to daylight between 2 and 60 hours. 70% of TL remains after 8 hours of sun exposure. The geological TL signal does differ from the TL remaining after exposure to daylight; the longer bleaching the lower TL (Fig.4).

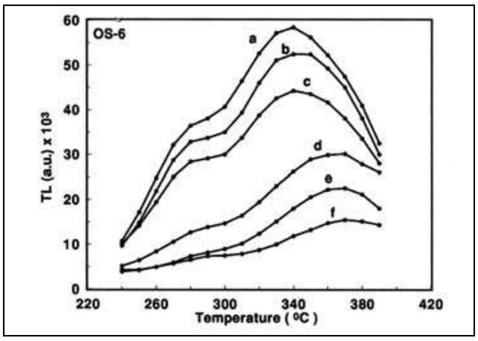

Fig.4 EGOS-6. Bleaching of TL after exposure to sunlight, a) geological TL, b) 2 hrs c) 8 hrs, d) 16 hrs, e) 24 hrs, f) 60 hrs.

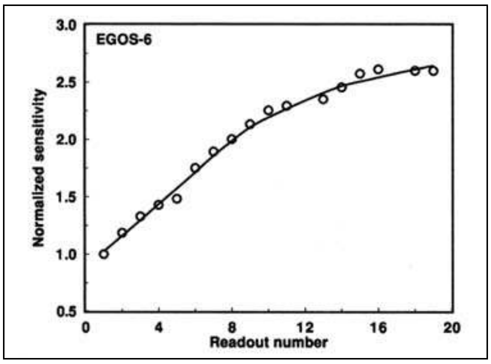

Fig.5 EGOS-6. TL sensitivity changes as a function of readout cycles (to 400^{o}C). The increase is rapid (more than a factor of 2) for the 10 cycles, becoming lower towards the 20th cycle (by a factor of 2.7)

The variability of bleach in different parts of the glow shapes is noticeable. Furthermore, an aliquot was exposed to successive readout cycles. The TL sensitivity increases substantially as a function of the readout cycle. The increase is rapid (more than a factor of 2) for the 10 cycles, becoming lower towards the 20th cycle (by a factor of 2.7) (Fig.5).

b) Anomalous TL fading results

Method	Sensitivity Change (%)	Signal Change Before and after the 20 days (%)	AF
TL	5.0±0.5	8.6±0.6	N

Table 2: Anomalous fading (AF) results for sample EGOS-6 for TL measurements

The difference in the sensitivity change and the signal change of only 3% (Table 2) is in the margin of systematic error, which indicates no fading.

EGMYK, granite (pink+black+white grains)

XRD

Granite mainly of pinky minerals (pink quartz), which cover large areas, and less, light grey and black opaque minerals. It consists by about 40% quartz, 30% K-feldspar (microcline, $KalSiO_3O_8$), Na-feldspar (albite, (Na, Ca) $Al(Si, Al)_3O_8$) 10%, biotite-phlogopite 15%, and some amphibole 5%.

OSL measurements

a) Bleaching

Fig.6 shows the bleaching by blue LEDs. The granite bleaches a little more slowly than sandstone EGOS-6. The fast bleaching of the OSET is 87% within one and half-hours. However, the large reduction of around 78% occurs in the first 500 seconds. IR stimulation of dosed (with 200 sec beta, approx. 0.25 Gy/sec) single aliquot granite indicates a significant feldspar presence.

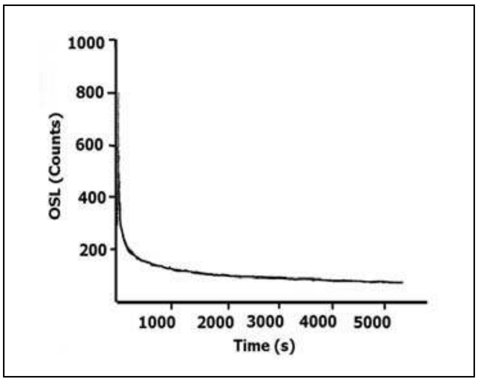

Fig.6 EGMYK. Bleaching by blue LEDs.

b) Dose growth

Fig.7 shows the corrected additive dose growth for a single aliquot by blue LED stimulation. This provisional ED=41±7 Gy is a natural TL with a dating significance. It is interesting to note the competing mechanisms between bleaching and phototransfer taking place simulta-neously; bleaching dominating at first, phototransfer dominating later (Fig.8).

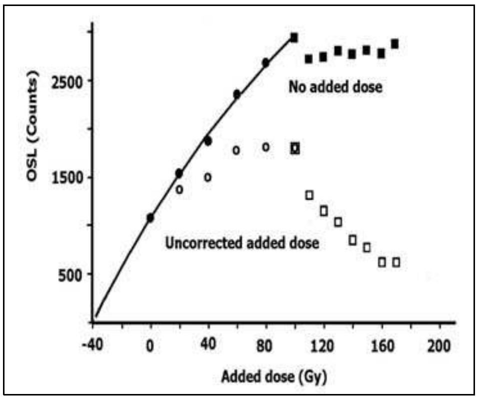

Fig.7 EGMYK. Corrected additive dose growth of a single aliquot by blue LED stimulation. Provisional ED=41±7 Gy.

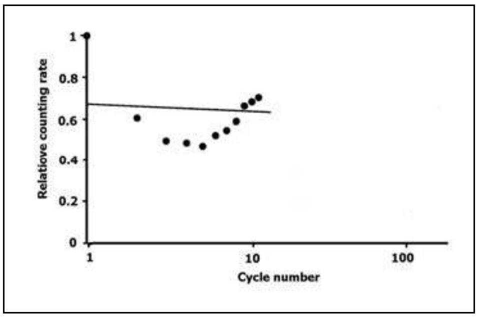

Fig.8 EGMYK after 3 hours SOL and 100 Gy, preheating for 300 sec at 220°C and 0.1 sec blue shine per cycle. It is interesting to note the competing mechanisms between bleaching and phototransfer taking place simultaneously; bleaching dominating at first, phototransfer dominating later.

EGOS-7 granite (black+white grains)

XRD

Granite with predominant white, grey and black color minerals, including less pink-brown ones. XRD have shown about 40% quartz, 25% biotite and phlogopite, 25% albite and 5% microcline (K-felsdpar) and 5% amphibole.

OSL measurements

a) Bleaching

EGOS-7 bleaches more slowly than is usual for quartz due to predominance of feldspar. Bleaching with blue LEDs shows that the luminescence falls to 50% after 150 sec of continuous exposure (Fig.9), a little slower that the sandstone EGOS-6. The SOL bleached samples for exposures up to 13 hours (or around 78 hours sunlight equivalent) are not completely zeroed. Instead, it remains a residual ED=1.3±0.4 Gy (for 600 sec at 220°C). Because for 5.5 hrs and 7 hrs SOL the residual ED falls from 1.3±0.5 Gy to 0.7±0.3 Gy, it would be expected for 13 hrs a further drop to zero which is not, this may imply a long duration SOL induced luminescence. The present results support the notion that SOL bleaching does not bring ED as close to zero for IR as for blue stimulation. However, the higher SOL exposure seems to induce luminescence, e.g. ED=3.5±0.4 and 4.9±0.3 Gy of 15 hours SOL bleaching and IR reading.

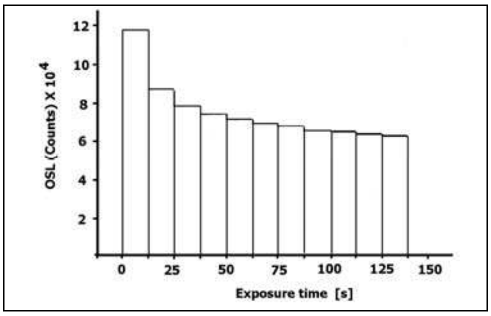

Fig.9 EGOS-7, natural signal. Bleaching by blue LEDs.

b) Dose growth and ED determination

Blue stimulation

To test for the reduction of OSL signal during preheat and read by blue light cycle, a prerequisite step for the correction procedure, a single aliquot was administered 20 Gy with a beta source. It was followed by 18 repeated preheats (60 sec at 220^{0}C) and reading (0.1 sec) with blue LEDs. The function of signal loss is of the form ratio = 1 - aln(n), where a=0.276±0.006, which is characteristic of feldspar (Fig.10). The single aliquot additive dose and the regeneration with saturating exponential fit gave ED between 5 to 7 Gy. Further three ED measurements gave an average ED=12.9±2 or a net ED=12.9-1.3=11.6±2 Gy.

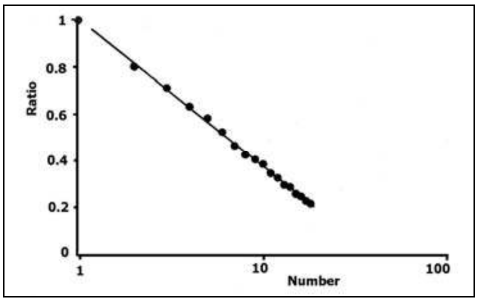

Fig. 10 EGOS-7 added 20 Gy and repeated preheat and read cycles by blue LEDs. The ratio is characteristic of feldspar, 1-aln(n).

IR stimulation

The decay ratios for correction of single aliquot additive dose measurements were determined, for repeated cycles of 300 s preheating at 220^{0}C and 1 s IR exposure.

Our earlier investigations of microcline and orthoclase (feldspar from basalt) had shown that they followed an exponential law. Further investigations give evidence that the behavior of this material is better approximated by a power law, n^{-p} (thereafter p-relationship), where p=0.572±0.05. The p-relationship gives a more constant corrected luminescence for no-added dose - the test of good correction.

The SOL bleached samples for 5.5 hours gave residual ED=1.1±0.9 Gy, and 9 ED measurements (8 with the additive dose and 1 with the regeneration) were made with average ED=12.4 Gy, applying the p-relationship and saturating exponential fitting. The net ED=12.4-1.1=11.3±1.3 Gy.

The variable EDs between blue and IR are probably due to partial bleaching of some grains. We favor an overall average value and the ED with IR stimulation because IR probes only feldspar, the blue probes both minerals and the functional loss of signal applies to two instead of one mineral, and granite consists mainly of feldspar.

Stimulation by pulsed blue LEDs

The pulsed stimulation by blue LEDs is on for 14 us, during which luminescence is emitted, and after the end of the light pulse the luminescence falls in intensity with a lifetime dependent on the processes in the crystal. These spectra indicated presence of feldspar different from microcline (Fig.11) and orthoclase, with no significant quartz. Indeed, the EGOS-7 has a mixture of albeit, microcline, quartz, biotic, actinolite as XRD has shown (Figs.12a, b, c).

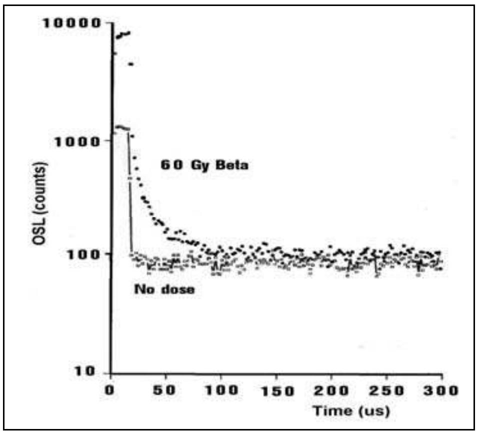

Fig.11 EGOS-7, granite. Stimulation by Pulsed blue LED, of daylight bleached microcline with no dose and with addition of 60 Gy,

Dose rates were measured by a Ge gamma-spectrometer, and in addition the betas with a plastic scintillator. The age estimation is given equal to 10.30 Gy / 0.00274 Gy/yr or 1760±220 BC (±6%)

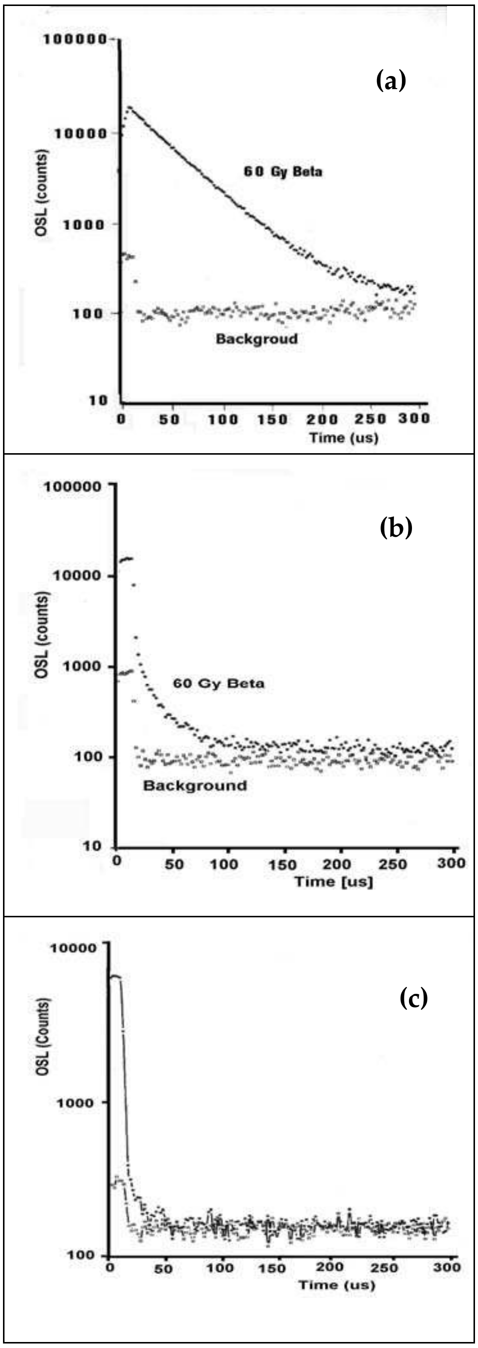

Fig.12 EGOS-7, granite. Stimulation by pulsed blue LED of, (a) daylight bleached quartz, with background and addition of 60 Gy, (b) daylight bleached orthoclase, with background and addition of 60 Gy, and (c) SOL bleached with background and addition of 40 Gy.

c) Anomalous fading results

Method		Sensitivity Change (%)	Signal Change Before and after the 20 days (%)	AF
OSL	Blue	25±1	19±1	N
	IR	47±0.4	17±0.3	N

Table 3: Anomalous fading (AF) results for sample EGOS-7 for OSL measurements.

Table 3 indicates that the sensitivity change percentage is higher than the signal change percentage which means that the phenomenon does not occur.

EGOS-7

TL measurements

*a) Bleaching.*This granite differs from the EGMYK as it consists of two main grain components according to color, black and white. The surface of the original portion not exposed to light was cleaned with 40% HCL to remove any organics and contaminated substrates. The grain powder removed with gentle brushing had diameter 2-10 μm. The brass discs accommodated a powder mass of 1.5 mg/cm^2.

Solar bleaching of TL with grains deposited onto brass discs in acetone phase and subsequent drying did indicate a rather fast bleaching. This was expected, as the main mineral component is quartz. The main TL peak is at 320^{0}C. Fig.13 shows the glow curves bleached after 6 hr, 16 hr and 28 hr exposure time. It is noted that within 6 hours the TL bleaches by about 56%, faster than the sandstone EGOS-6. The reduction of TL due to the solar bleaching is plotted in a normalized response for three different temperature regions, which is 280-350^{0}C, 360-400^{0}C and 410-450^{0}C (Fig.14). After 30 hrs the bleach approaches a plateau. The small TL between 100-220^{0}C, after exposure to sunlight, is electron phototransfer to lower depth traps due to solar UV (Liritzis et al., 1996)

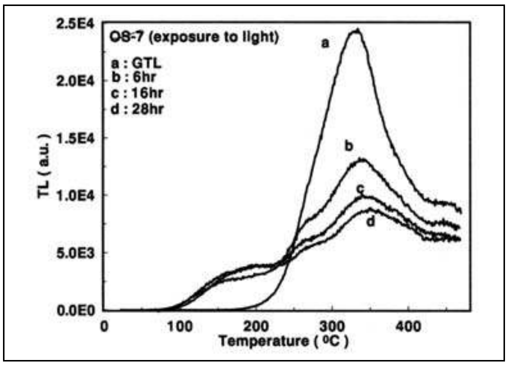

Fig.13 EGOS-7. Bleaching of TL after exposure to sunlight for a) geological TL, no exposure, b) 6 hrs, c) 16 hrs and d) 28 hrs.

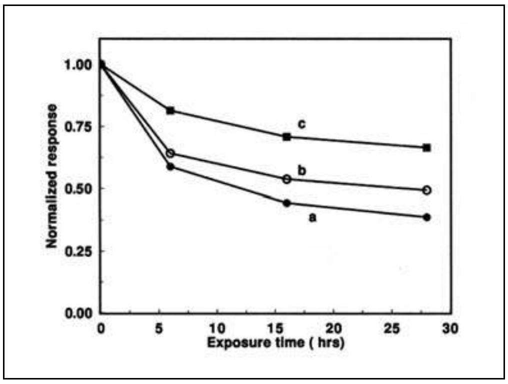

Fig.14 EGOS-7. The reduction of TL due to the solar bleaching is plotted in a normalized response for three different temperature regions, that is 280-350^{o}C, 360-400^{o}C and 410-450^{o}C after 30 hrs the bleach approaches a plateau.

b) Dose growth and sensitivity. The k-value of relative response of beta to alphas was found equal to 0.11±0.0065. It was estimated by additive dose procedure and the ratio of relative responses of betas to alphas.

Repeated readouts of the same aliquot with prior irradiation with a 1.2 Gy beta dose showed the influence of heating on the sensitivity, especially the variation of the sensitivity in the high temperature region of the glow-curve is not important. The apparent decrease is a consequence of the shape of the glow-curve.

Further test on the sensitivity variation included the following: TL induced by 1.2, 6, 12 and 24 Gy, and at the end again a 1.2 Gy dose of beta source for the same aliquot. Before the readout a pre-heat to 150^{0}C for 30 sec was applied. The difference between first and final administered dose of 1.2 Gy (i.e. five successive cycles, a total of six heating cycles) is small.

c) Anomalous fading results

Method	Sensitivity Change (%)	Signal Change Before and after the 20 days (%)	AF
TL	5±0.1	34±0.1	Y

Table 4: Anomalous fading (AF) results for sample EGOS-7 for TL measurements

Table 4 shows that the signal fades since there is a 30% difference in the signal change and in the sensitivity change.

EGBAS, Basalt

XRD

Dark grey color, crystalline with apparent crystals as large as 1-2 mm. The crystal hardness is 6-7 in Mohs' scale. XRD have shown about 80% feldspar (mainly anorthite and albite), 15% augite, and a little quantity of vesuvianite.

TL measurements

a) Bleaching

Initially an outer layer of a part of the sample not exposed to light was gently removed. Powder of grain size <40 microns was prepared and deposited on brass disks of 1 cm^2. As the disk-to-disk reproduce-bility was of the order of 20%, normalization was made with a monitor beta dose. Fig.15 shows the solar bleaching of TL as a function of bleaching time in a log scale. It is clearly noticed a very rapid loss of TL due to solar radiation, a drop of 60% within 24 hours. This fast bleaching rate is similar to quartz. The built up dose in the additive dose procedure exhibits a linear behavior.

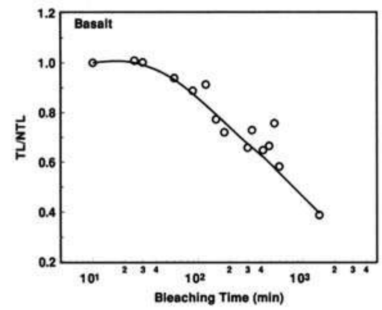

Fig.15 EGBAS, basalt. Solar bleaching of TL as a function of bleaching time in a log scale.

c) Anomalous fading results

In the case of sample EGBAS, (Table 5) the signal fades since there is a 20% difference between the signal change and the sensitivity change.

Method	Sensitivity Change (%)	Signal Change Before and after the 20 days (%)	AF
TL	13±0.1	34±0.1	Y

Table 5: Anomalous fading (AF) results for sample EGBAS for TL measurements

OSL measurements

a) Blue stimulation-bleaching-additive dose response

Bleaching of basalt has been confirmed by blue stimulation as follows. The luminescence of the bleaching by blue LEDs was measured over a period of 3 hours. Fig. 16a shows the first 250 sec, the straight line is the background, and the curve fit to the data is the sum of three exponentials. Fig. 16b shows the whole 3 hours of measurement. The curve fitted to the data is the sum of 4 exponentials, with lifetimes 1.1±0.1, 39±1, 438±18 and 4699±46s.

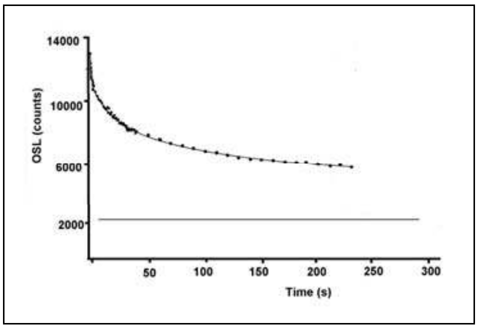

Fig.16a EGBAS, basalt. Bleaching by blue LEDs, for the first 250 sec. The straight line is the background, and the curve fit to the data is the sum of three exponentials.

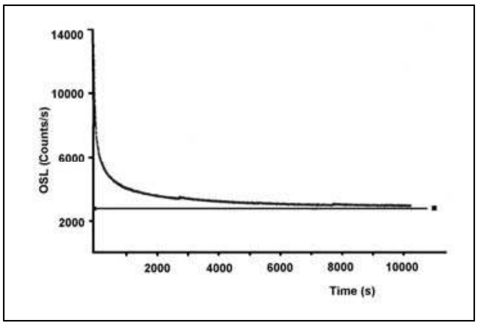

Fig.16b EGBAS, basalt. Bleaching by blue LEDs, for the whole 3 hours of measurement. The curve fitted to the data is the sum of 4 exponentials, with lifetimes 1.1±0.1, 39±1, 438±18 and 4699±46 sec.

Single aliquot additive dose measurements were made following the single aliquot additive dose procedure. For correction, measurements were made with a 300 sec preheating at 220^{0}C to see whether the preheat duration made a difference, compared to repeated cycles of 60 sec at 220^{0}C and 0.1 sec blue LED stimulation. Following the relationship for relative luminescence of 1-aln(n), for higher preheating time 300 sec at 220^{0}C the single aliquot additive dose measurements gave ED=4.7±0.5 Gy (Fig.17a), and a further exposure of this sample to 7 hours of SOL left no residual signal (ED=0.2±0.8 Gy)(Fig.17b). While for the shorter preheating the ED=4±0.4 (average of 3.8±0.4, 3.9±0.4, 4.4±0.5)(Fig.17c), and a subsequent SOL bleaching for 5 hours indicated ED=0.1±0.6 or zero. This average ED seems to be within the errors similar to previous ED, but with a tendency of being higher the higher preheating duration.

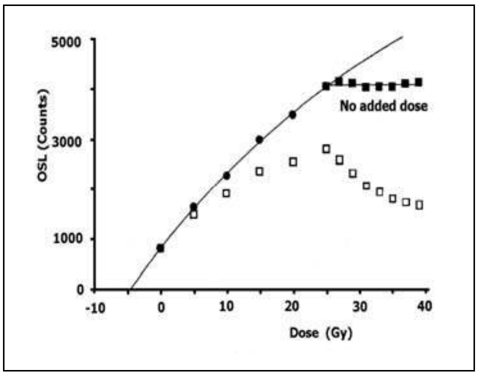

Fig.17a EGBAS, basalt. Following the relationship for relative luminescence of 1-aln(n), for higher preheating time 300 s at 220^{o}C the single aliquot additive dose measurements gave ED=4.7±0.5 Gy.

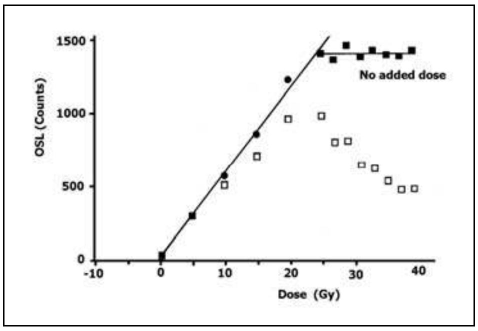

Fig.17b Single aliquot additive dose determination of ED. Exposure of EGBAS to 7 hours of SOL left no residual signal (ED=0.2±0.8 Gy).

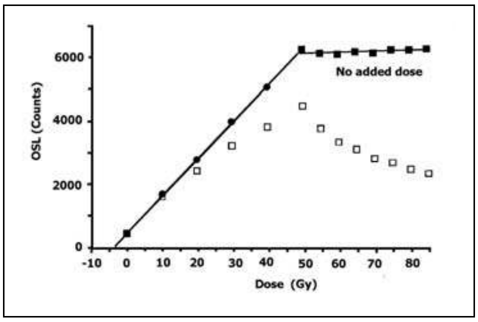

Fig.17c Single aliquot additive dose of EGBAS, by blue LEDs for ED determination, for the shorter preheating (ED=4±0.4 as the average of average of 3.8±0.4, 3.9±0.4, 4.4±0.5).

It was noticed that there is a significant difference between natural and laboratory dosed material, in a sequence of preheat and read cycles. This was deduced during the process for correction of single aliquot additive dose measurements, where repeated cycles of 60 sec at 220^{0}C plus 0.1 sec blue LED stimulation were made. Fig.17d is for material with the natural dose, compared with exposure to light only, and Fig.17e is for material with natural dose + 50 Gy, and Fig.17f is SOL for 6.5 hours and dosed with 50 Gy.

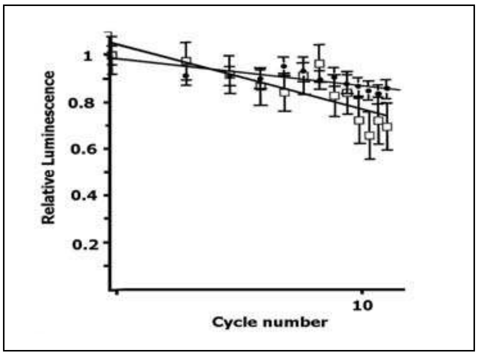

Fig.17d EGBAS, basalt. Decay curves for repeated preheat (60 sec at 220°C) and read (0.1 sec by blue LEDs) cycles, for material with the natural dose, compared with exposure to light only (with lower slope).

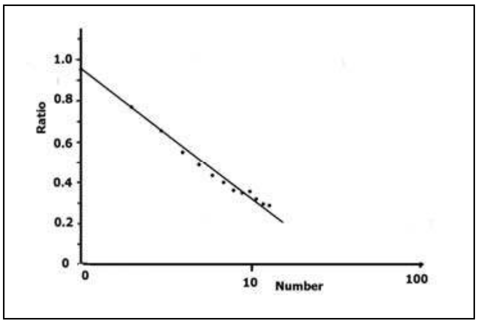

Fig.17e EGBAS, basalt. Decay curves for repeated preheat (60 sec at 220°C) and read (0.1 sec by blue LEDs) cycles, for material with the natural+50 Gy dose.

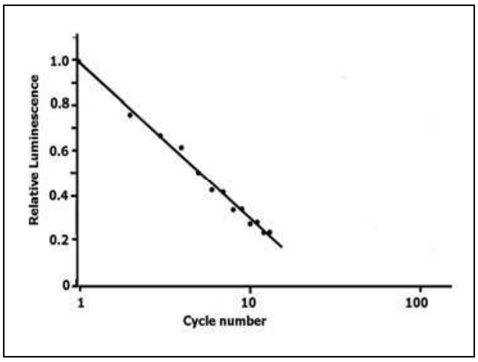

Fig.17f EGBAS, basalt. Decay curves for repeated preheat (300 sec at 220°C) and read (0.1 sec by blue LEDs) cycles, for material with SOL bleached for 6.5 hours, added 50 Gy dose.

Using the relationship: relative luminescence = 1 – aln(n), the factor (a) is 0.13±0.03 for the natural (Fig.17d), and 0.28±0.01 for the dosed material (Figs.17e, f), that is a significant difference.

Using pulsed blue LEDs the feldspar presence and quartz absence were both recognized. The time resolved spectrum is similar to that of EGOS-7 granite. The lifetime is very short on this scale, as for feldspar (plagioclase) and there is no sign of the quartz lifetime, which is much longer (see, Fig.12a-c).

IR stimulation- Bleaching- Additive dose response

Bleaching with IR proved that the IR signal was closer to the background than for the investigation of bleaching by blue LEDs (due to the smaller size of sample), so the bleaching was only measured for 800 sec (Fig.18). The curve is the sum of 2 exponentials with lifetimes of 20±2 and 208±22 sec.

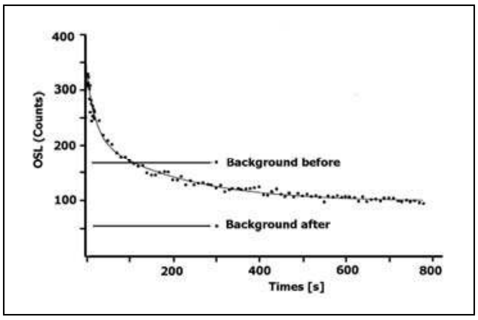

Fig.18 EGBAS, basalt. Natural bleaching by IR LEDs. Note the background before and after the reading. The curve is the sum of two exponentials (lifetimes 20±2 and 208±22 sec)

The correction procedure of the preheated and read single aliquot was fitted better by a power law than by 1-aln(n), similarly to the EGOS-7 material stimulated by IR. The measurements for the correction law were made for preheating with 300 sec at 220^{0}C and IR stimulation for 1 sec for each cycle. A previously used sample was SOL bleached for 5.5 hours and dosed to 50 Gy, to conserve the 'natural' material. The power law correction used and the corrected data was fitted by a saturating exponential. The ED was 4.1±0.5 Gy, and the residual dose after SOL exposure for 5.5 hours was 2.8±0.7 Gy (see Fig.19a,b for logarithmic and power law respectively).

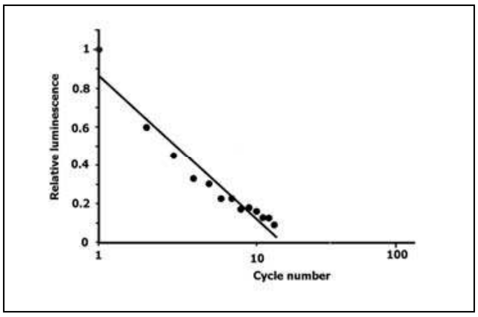

Fig.19a EGBAS, basalt. Decay OSL after exposure to SOL for 5.5 hrs, and take readings of 1 sec by IR with preheating at each cycle of 300 sec at 220^{o}C. The fitting follows exponential law.

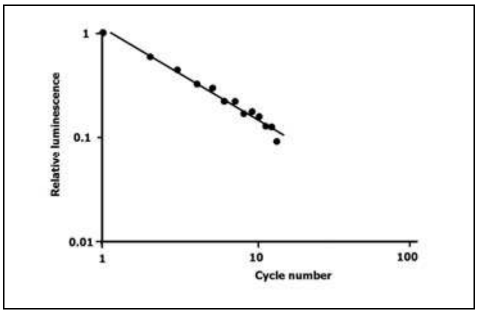

Fig.19b EGBAS, basalt. Decay OSL after exposure to SOL for 5.5 hrs, and take readings of 1 sec by IR with preheating at each cycle of 300 sec at 220^{o}C. The fitting follows power law.

The residual dose left after SOL bleaching was also noticed in another stimulation by IR after a 7 hours SOL bleaching (ED=2±0.2 Gy).

The power law correction was used and the corrected data was fitted to a saturating exponential giving an ED=3.6±0.5 Gy (average of 4±0.6 and 3.2±0.2 Gy) (Fig.20).

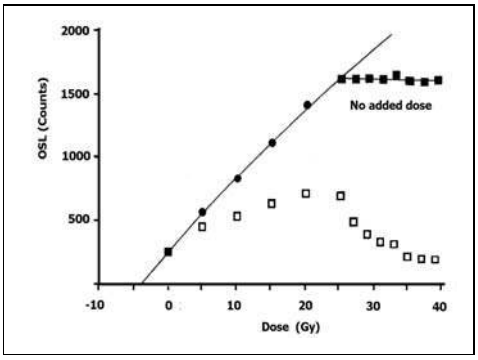

Fig.20 EGBAS, basalt. Single aliquot added dose by IR, corrected ED=4.7 Gy applying power law.

For ED determinations it should be born in mind the residual dose after bleaching, at least in SOL, and must be subtracted.

b) Anomalous fading (AF) results

Method		Sensitivity Change (%)	Signal Change Before and after the 20 days (%)	AF
OSL	Blue	47±0.2	17±0.2	N
	IR	37±0.9	18±0.9	N

Table 6: Anomalous fading (AF) results for sample EGBAS for OSL measurements

In Table 6 we can see that the sensitivity change percentage is higher than the signal change percentage which means that both signals, Blue and IR, do not fade.

Calcite

The following measurements concern the TL of archaeological limestone. The OSL of calcites is still under investigation.

XRD

EGKH: Limestone, whitish, 3-4 hardness in Mohs' scale with larger than ITH-4 crystals. Does not exhibit veins but a surface crust is present in one of the surfaces (not the dated one). XRD have shown 93-95% $CaCO_3$ and 5-7% gypsum ($CaSO_4.2H_2O$). The latter is due to the formation of secondary soluble products from the weathering and erosion of calcite.

ITH-4: Robust limestone of whitish appearance and small size crystals. Apparent veins of grey and white color are observed. Hardness is 4 in Mohs' scale. It consists of 96-98% $CaCO_3$, and a little amount of albite.

EGKH, calcite

Powder of 2-10 um was prepared from gentle remove of under 500 um surface layer (Liritzis et al, 1997b) the powder was deposited onto brass disks with 1.5mg/cm^2. Several disk aliquots were exposed to sunlight for up to 50 hours. Fig.21 shows the residual TL glow curves from the solar bleaching of TL. The ED was measured from subtraction of the bleached glow curves from the natural TL for the TL peak of 280^{0}C. The best dose plateau - longer and less scattered- was for exposure time about 10 hours, equal to 5.15±0.24 Gy (Liritzis et al., 1997b). From dose rate values, made by gamma spectrometer for the calcite alpha and beta dose rate plus the environmental gamma and beta from covering sand and the cosmic, an age estimate is 5.15 Gy / 1.01 Gy/Kyr or 5100±650 years BP.

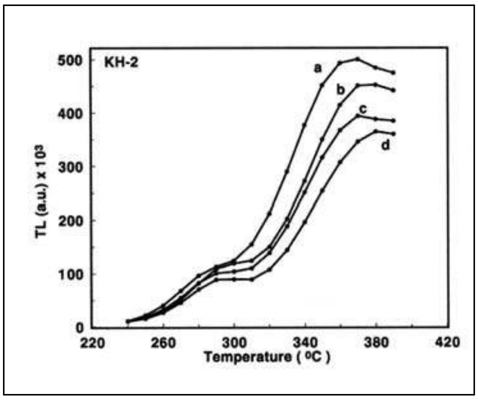

Fig.21 TL glow curves of EGKH, limestone. Solar bleaching as a function of exposure time, a) geological TL, b) 16 hrs, c) 25 hrs, d) 50 hrs.

ITH-4, calcite

The calcite is bleached under solar exposure. For the evaluation of the ED the glow curve from 200 to 430^{0}C was used. Temperature intervals of 10^{0}C each across the glow curves were used. The EDs were obtained with the additive dose procedure, from four natural TL glow curves and were plotted as a function of the glow curve temperature. The best and longer dose plateau is obtained for bleaching of 1-2 days in the temperature region 280-330^{0}C (Fig.22). The same result is reached for the dose plateau from alpha particles. The k-value was 0.132±0.02. The estimated age was 2.33 Gy / 0.75 Gy/Ky or 3100±500 years BP, or within the expected archaeological age estimation of this polygon wall i.e. archaic period, 6th-7th c. BC. For the evaluation of the ED for beta radiation, for ITH-4 and EGKH, the glow-curves were separated in intervals of 10^{0}C. Then, a calibration factor (CF) for each interval was obtained according to equation: CF = $(TL_{NTL+\beta} - TL_{bGTL}) / \beta_{dose}$, where $TL_{NTL+\beta}$ is the natural TL plus added beta doses, TL_{bGTL} the bleached (remaining) geological TL exposed in sunlight for various times. Then, the ED_{β} = NTL / CF, is plotted against temperature intervals, for each bleaching time. The ED is again the value with the longer plateau. Recent development has shown that calcite monuments can be dated baed on OSL of trace quartz inclusions embedded in the extracted powder (Liritzis et al, 2008).

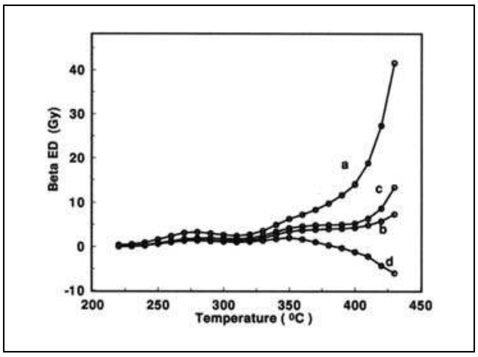

Fig.22 ITH-4, Determination of longer plateau. The best plateau is obtained for bleaching of 1-2 days in the temperature region 350-420^{o}C. Curves correspond to a) no bleaching, b) 20 hrs bleaching, c) 2 days, and d) 6 hrs bleaching.

c) Anomalus fading results

In the case of sample ITH-4, Table 7 shows that there is no change in the signal before and after the 20 days.

Method	Sensitivity Change (%)	Signal Change Before and after the 20 days (%)	AF
TL	14±0.3	14±0.3	Y

Table 7: Anomalous fading (AF) results for sample ITH-4 for TL measurements

DISCUSSION-CONCLUSION

The OSL and TL measurements made on particular rock types, that is, granites, sandstone and basalt, which comprise mainly of quartz and feldspar, have proved the potential use of these materials for dating in archaeology (provided that ancient monuments were made of these). This result is based on the well-known quartz and feldspar solar bleaching of sedimentary deposits (Liritzis, 2000, Roberts, 1997).

The most rapid bleaching of the OSET is observed for sandstone, followed by granite, while for the TSET the faster bleaching is for granite followed by sandstone and basalt. The granite with quartz, feldspar and biotite (EGMYK) bleaches slower than granite with its two-grain phases, mainly feldspar with little quartz and biotite (EGOS-7).

The criteria applied for dating purposes, that is, the solar bleaching and the radiation dose growth (either in additive or regeneration mode), are both well satisfied with thermal and optical stimulated luminescence, for three rock types, while the calcites studied follow the known behavior of TL bleaching verifying earlier studies (Liritzis, 2000; Liritzis and Bakopoulos, 1997; Liritzis et al, 1996, 2001).

The solar simulator (SOL) induces luminescence for long durations evidenced from OSL measurements, and the higher preheat seems to affect the ED, though at present not distinguishable from use of shorter preheat, within the errors. Thus, the potential dating of ancient monuments made by carved granites, sandstones or basalts, by TL and OSL methods, is possible.

The solar set zero-clock of TL in granites, sandstones and basalts, certainly in limestone, offers new applications to the method (coined optical thermoluminescence) of dating ancient megalithic buildings and artifacts, made of these materials (Liritzis et al, 2008).

Between the TL and OSL, the latter applied on a single aliquot minerals, except of calcites, offers additional advantages over TL regarding, rapidity, accuracy and effectiveness.

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