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Does limestone show useful optically stimulated luminescence?

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Abstract: *Luminescence around 515 nm wavelength (2.41 eV) from limestone stimulated by pulsed light of 370 nm wavelength (3.36 eV) is found to decrease with increasing radiation dose.*

Introduction

Liritzis (1994) proposed a method for dating the construction of megalithic limestone buildings, based on the latent thermoluminescence of the surface of a limestone building block being bleached by exposure to light prior to incorporation in the building and then, in the inter-block surfaces from which light is excluded, growing again with the passage of time in a manner akin to the well known methods of dating sediment deposition using quartz or feldspar extracts, for example Wintle and Huntley (1980). The method has since given an age for the Temple of Apollo in Delphi consistent with the historical age (Liritzis *et al.*, 1997), and has been applied to determine the age of two Greek pyramids (Theocaris *et al.*, 1997). Liritzis and Bakopoulos (1997) observed the decrease in the thermoluminescence peak at 280ºC with exposure to sunlight for several samples of Greek limestone. However, a substantial residual signal was found after 100 hours of exposure. Just as the use of optically stimulated luminescence rather than thermoluminescence is advantageous with quartz or feldspar when dating sediments (e.g. Huntley *et al.*, 1985), the same advantage, namely the absence of residual signal from bleached material, could be hoped for if optically stimulated luminescence could be used with limestone. Wintle (1997), in a review of luminescence dating procedures, drew attention to the report by Ugumori and Ikeya (1980) of the optical stimulation of luminescence from $CaCO_3$ and noted that no further work on the topic had been reported. Ugumori and Ikeya (1980) observed luminescence (a broad band around 430 nm, 2.9 eV) stimulated by light from a N_2 laser (337 nm, 3.68 eV) from natural calcite, both crystalline and a piece of stalactite. The potential for archaeological dating was illustrated by an increase in luminescence intensity with increasing distance from the surface into the stalactite. Exposure to the laser light altered the thermoluminescence glow curve, reducing the peak at 347˚C, increasing the peaks at 287˚C and 237˚C, and creating a peak at 57˚C.

The work reported here was developed independently from the study of the bleaching and phototransfer properties of the 286˚C peak in the thermoluminescence glow curve from limestone (Bruce *et al.*, 1999). This is the dominant peak in the thermoluminescence glow curve from limestone and the peak used for dating megalithic buildings (Liritzis, 1994; Theocaris *et al.*, 1997). Bruce *et al.* (1999) found that the bleaching of the 286˚C peak by light in the wavelength range 350 – 600 nm was more rapid for shorter wavelengths of light, 350 – 400 nm being most effective and wavelengths longer than 500 nm having little effect. Accordingly for the present measurements, a Nichia light emitting diode (LED) with peak emission at 370 nm (3.36 eV) was used as stimulating light source.

Experimental details

The source of stimulating ultraviolet light was a Nichia LED type NSHU590E, which according to the manufacturer's data has a peak emission at 370 nm, a half-width of 12 nm, with the output intensity falling to about 1% at 360 and 410 nm, a power output of 750 µW, and an emission angle of 10º. Measurements with a spectrophotometer over the wavelength range 400-800 nm show a tiny emission relative to the ultraviolet output, which would however be quite significant at the level of photon counting, with a wide peak around 550 nm and a narrower peak around 750 nm. This unwanted emission in the visible region is greatly reduced by a Schott 7-60 optical filter (peak transmission at 370 nm, falling to 0.01% at 405 nm), which was mounted in front of the LED for all the measurements reported below, fig.1.

Green light emitted from the sample was selected by a combination of HA3, BG39 and GG495 optical filters (peak transmission 515 nm, half maximum at

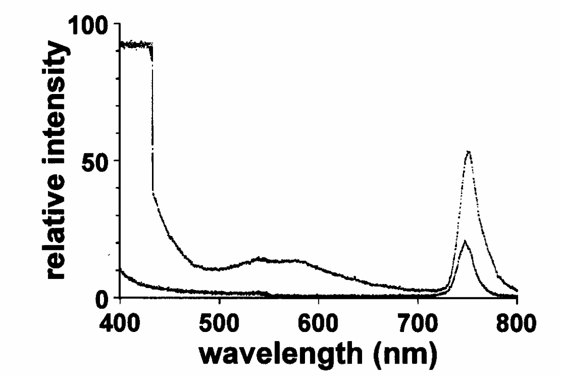

Figure 1.
The visible spectrum from a Nichia type NSHU590E LED compared with a spectrum of the light which has passed through a Schott 7-60 filter. The constant relative intensity of 93 from 400 to 430 nm in the unfiltered spectrum is due to high light intensity causing saturation of the detector.

495 and 600 nm, 0.01% at 480 and 780 nm) and detected by a 9635QA photomultiplier, the same arrangement as in the dating work by Liritzis (1994), Theocaris *et al.* (1997) and the bleaching study by Bruce *et al.* (1999).

The same French limestone, treated with dilute acetic acid to avoid spurious luminescence following Wintle (1975), as used by Bruce *et al.* (1999) was used for the present measurements. The grain size was ~ 100 µm.

The background counting rate with the LED on and a clean stainless steel disc in the sample position was ~$2.6x10^5$ s^{-1} which fell to less than half within 50 ms of the LED being switched off. This high background counting rate is attributed to fluorescence from the optical filters. No significantly higher counting rate was observed with natural limestone on the stainless steel disc, but on switching off the LED, it took about 250 ms for the light to fall to half of the maximum intensity. It was decided therefore to avoid the high background counting rate while the LED was on by using pulsed stimulation and to look for decaying luminescence after the end of the stimulating pulse, in the manner of the measurements on α-Al_2O_3:C by Bulur and Göksu (1997). The LED was pulsed on once for 1 s and photon counting for luminescence detection started at the end of the pulse for 250 successive intervals of 50 ms. Successive measurements were essentially identical, as shown below. The equipment was that used in this laboratory for thermoluminescence measurement (Galloway, 1990), with minor modification to the connections and controlling programme to pulse the LED rather than operate the heater.

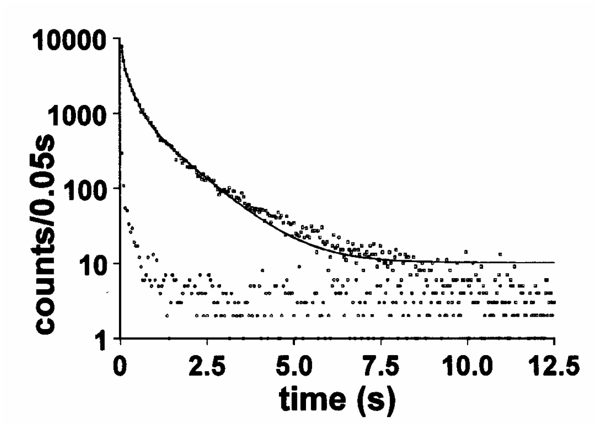

Figure 2.
Comparison of the time dependence of the light from a natural limestone sample with that from a stainless steel disc, following a pulse of ultraviolet from the LED of 1 s duration. The curve is a least squares fit to the data of a sum of three exponentials plus a constant with the parameters in table 1.

The measurements

With the pulsed system the signal from natural limestone stands out clearly from the measurement made with an empty disc, fig.2. The decay of luminescence after the end of the stimulating pulse follows Σ_i $A_i\exp(-t/\tau_i)$ (plus a small constant background) where τ_i are the lifetimes associated with the luminescence processes in the crystal and A_i are the amplitudes of the components, and the curve in fig. 2 shows a least squares fit of this expression to the data with lifetimes of 0.04, 0.25 and 1.06 s. Each component will increase exponentially during the stimulating pulse, reaching 95% of the maximum possible amplitude in 3 lifetimes of stimulation. Thus, shortening the stimulating pulse should emphasise the shorter lifetime components and lengthening the stimulating pulse should emphasise the longer lifetime components. This is found to be so, comparing stimulation by pulses of duration 0.1, 1.0 and 10 s in fig. 3, with the luminescence decaying more rapidly the shorter the pulse and the data being fitted by the parameters in table 1.

Stimulating pulse duration (s)	0.1	1.0	10
τ_1 (s) [relative amplitude]	0.04 [0.76]	0.04 [0.62]	0.05 [0.55]
τ_2 (s) [relative amplitude]	0.21 [0.21]	0.25 [0.29]	0.29 [0.33]
τ_3 (s) [relative amplitude]	0.93 [0.03]	1.06 [0.08]	1.36 [0.12]

Table 1.
Parameters resulting from least squares fitting of the data in fig. 3 for the decay of luminescence after the end of the stimulating pulse by $\Sigma_i A_i \exp(-t/\tau_i)$ (plus a small constant background), where τ_i are the lifetimes associated with the luminescence processes in the crystal and A_i are the amplitudes of the components. The relative amplitude is quoted below, $A_i/\Sigma_i A_i$. In each case there were only 3 statistically significant components.

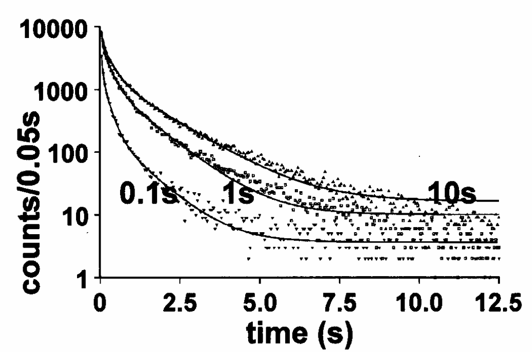

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Figure 3.
Comparison of the time dependence of the light from a natural limestone sample following pulses of ultraviolet from the LED of 0.1, 1.0 and 10 s duration. The curves are least squares fits to each data set of a sum of three exponentials plus a constant, with the parameters in table 1.

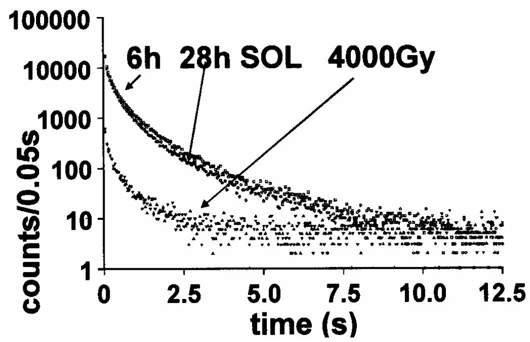

Figure 4.
Comparison of the time dependence of the light, following a 1 s duration ultraviolet pulse, from the limestone sample after 6 hours and 28 hours in a SOL-2 solar simulator and after a subsequent beta exposure of 4000Gy (for which the indistinguishable data from two successive measurements are shown).

The natural limestone sample used to produce fig. 2 was subsequently "bleached" in a SOL-2 solar simulator for 6 hours, the pulsed OSL measured, then bleached for a further 22 hours and the pulsed OSL measured, fig. 4. There is only a little difference between the results from 6 hours and 28 hours total bleaching, but the signal is increased compared with the signal from the natural limestone, fig. 2. The sample was then irradiated by beta particles to a dose of 4000 Gy and the pulsed OSL measured, giving a substantially smaller signal than after bleaching, fig. 4. Comparing the pulsed OSL signal from a limestone sample immediately it was removed from the SOL-2 after several months of exposure with the signal from the same sample after beta irradiation to a dose of 40 Gy, shows little change in signal immediately after the stimulating pulse, while beta irradiation to 800 Gy shows a clear reduction in signal, fig. 5.

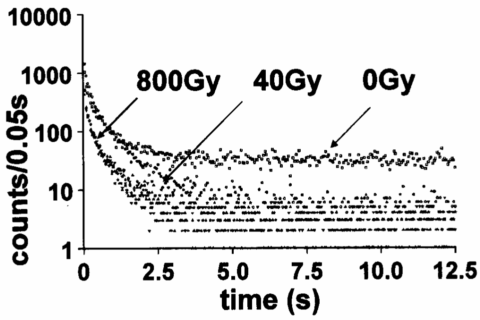

Figure 5.
The time dependence of light, following a 1 s duration ultraviolet pulse, from a limestone sample immediately after several months in the SOL-2 solar simulator, along with data for the same sample after receiving a beta dose of 40 Gy and 800 Gy (for which the indistinguishable data from 3 successive measurements are shown).

The data from the sample taken immediately from the SOL-2, fig. 5, have a higher constant background level than the other data, possibly due to phosphorescence induced by the light exposure in the SOL-2.

In general, measurements can be repeated without detectable loss of signal, as illustrated for the 4000Gy added dose data in fig. 4 and for the 800 Gy data in fig. 5.

Limestone which has been heated to 500°C before investigation behaves similarly, (maximum counting rate $4.8x10^5$ s^{-1}, after 60 Gy beta dose $4x10^5$ s^{-1} maximum, both with a similar decay to the bleached material).

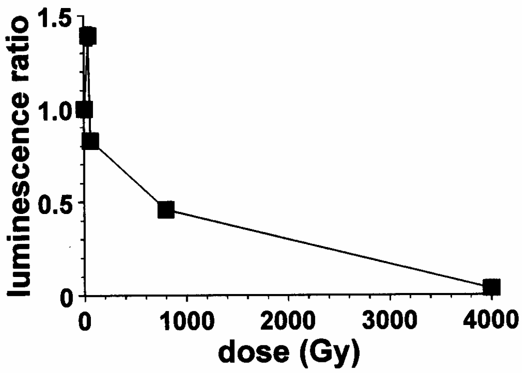

Figure 6.
The dependence on radiation dose of the luminescence detected during the 50 ms immediately following switch off of the stimulating light. The luminescence ratio plotted is the number of luminescence counts from a sample which has received a radiation dose to the number of luminescence counts from the same sample after bleaching for at least 24 hours in the SOL-2.

Discussion

Figs. 2, 4 and 5 show that limestone does not provide optically stimulated luminescence which increases with radiation dose, to permit dating in a manner similar to that employed with quartz or feldspar, at any rate not with the wavelength of stimulating light and the wavelength of detected luminescence used in this work. In contrast, the work by Ugumori and Ikeya (1980) indicated an increase in optically stimulated luminescence with radiation dose, but used a different stimulating wavelength (337 nm compared with 370 nm in the present work) and a different wavelength of luminescence (430 nm compared with 515 nm in the present work). Further, the Ugumori and Ikeya (1980) study related to the 347°C peak in the thermoluminescence glow curve, whereas the present study related to the 286°C peak.

The general trend in the measurements reported here is for the intensity of optically stimulated luminescence to fall with increasing radiation dose, shown quantitatively in fig. 6 for the luminescence detected in the 50 ms immediately following the switch off of the stimulating light, although there may be a small increase in luminescence up to about 50 Gy dose. This behaviour is reminiscent of the infrared radioluminescence of feldspar (Krbetschek *et al.*, 2000), which has been exploited for sediment dating. Whether the phenomenon shown by limestone in fig. 6 could be used for equivalent dose determination for the purpose of dating would require further investigation of the reproducibility of the data, the dependence of the luminescence signal on bleaching time and confirmation that the signal does relate to electrons trapped with long term stability appropriate to dating. A hint that the latter may be true is given by the luminescence from the natural limestone which, measured in the same way as the points in fig. 6, gives a luminescence ratio of 0.45 which would correspond to an equivalent dose of 800 Gy. However with regard to the problem which initiated this investigation, the dating of limestone buildings, the equivalent dose to be determined is typically less than 20 Gy (Theocaris *et al.*, 1997), which would require a much more detailed study of the phenomenon in fig. 6 for small radiation dose values.

Conclusion

Does limestone show useful optically stimulated luminescence? For the wavelengths of stimulation and detection studied, not immediately, but there is an indication of a way forward.

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Reviewer
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