# TL Behaviour of Some Limestone Rocks

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## Introduction

As part of a study of several limestone rocks from an archaeological site (Ganj Dareh, Iran) dating back 8-10 ka, we used an unorthodox method of preparing fine grains for TL analyses. The method was chosen to minimize the time required to produce a few hundred mg of sample. The purpose of this account is to describe our sample preparation, and the TL behaviour of different grain sizes for two of these rocks as observed through two spectral emission windows - the yellow-green ( ~550 nm), and the blue (< 500 nm).

The TL of calcite (our samples were largely pure calcite, as verified by X-ray diffraction and chemical analyses) has some attractive characteristics from the point of view of dating. In particular, there are usually two distinct peaks, both of which are normally free from detectable anomalous fading, and both of which are probably thermally stable at $\leq 15^{o}C$ for $\gtrsim 10^{6}$ years (e.g. Wintle 1978, Debenham 1983). However, difficulties have been encountered with stalagmitic and flowstone calcites because of non-uniformity of TL sensitivity and of radioactivity (e.g. Wintle 1978, Walton and Debenham 1982). Furthermore, calcite is especially susceptible to spurious TL attributed to mechanical and thermal disturbances during cutting and crushing. This spurious signal can overwhelm the high temperature peak and seriously affect the other. To avoid this spurious TL, workers have resorted to the slice technique, with its attendant disadvantages (e.g. Aitken and Wintle 1977), or the use of large ( ~100 μm) grains prepared by crushing in a vice (e.g. Wintle 1978). The use of fine grains (2-10μm, say) has been avoided because for them spurious TL apparently has been more difficult to control. Wintle (1974) did use 1-8μm grains for soft limestones with apparent success, but this has not been followed up.

Notwithstanding problems with inhomogeneity (which might be expected to be less for some types of massive limestone than for travertines), we think the use of fine grains of calcite offers some advantages over the use of coarse grains. In particular, it is relatively easy to prepare many uniform subsamples.

## Sample Preparation

All steps were performed in dull red or in amber light. Our samples were hard, most having a Mohs index of 3-4 1/2, and one (not discussed here) had an index of 5 1/2 (it also contained ~ 2-3% of $\alpha$-$SiO_2$). We used a water-cooled, high-speed, 10-inch carborundum blade to cut away the outer 2 mm of each rock. Each sample was hand-held against the cutting edge and a slight pressure was applied, just sufficient to overcome "chattering". Following this cutting, approximately 200 μm was removed from the surfaces by hand lapping with a wet 400-grade emery paper. Then each piece was placed in 1N HCl for 1-3 minutes and rinsed in distilled water.

Crushing was done in a way to minimize the number of impacts received by individual small grains, as follows: a cleaned piece of limestone was placed in a steel percussion mortar, a single sharp blow was given, and the resulting debris was dry sieved at 1 mm; only fragments > 1mm were returned to the mortar, and the crushing and sieving was thus repeated until a few grams of < 1 mm material were obtained. The < 1 mm grains produced in this way were wet sieved at 250 μm and 88 μm. The 88-250 μm grains then were soaked in 0.5% acetic acid for 1 minute (Wintle 1975) and washed in distilled water. The < 88 μm grains were sized at 11 μm by Stokes settling in water and at 2 μm by timed centrifugation. The resulting 2-11 μm grains were washed in 0.5% acetic acid for ~ 20 seconds and recovered by centrifugation, washed in water and then methanol.

For each sample, about 60 aluminum discs, each holding ~ 1 mg of 1-11 μm grains, were prepared from methanol suspensions, with ~ 5 minutes of ultra-sonic agitation just after pipetting. For each of three samples about 25 discs of 88-250 μm grains were prepared by first wiping each disc with a tissue "wetted" with a drop or two of silicone oil, weighing, sprinkling the grains from a small spatula, and weighing again. In this way ~ 5-10 mg of material were deposited fairly evenly onto each disc.

This method of sample preparation yielded very reproducible TL signals with low or insignificant levels of spurious TL in both the 2-11 μm and 88-250 μm size fractions. The essentially identical TL behaviour for the large and small grains confirmed that our preparation procedures did not significantly disturb the natural TL. In what follows, we describe the TL behaviour of only two samples, 060 and 061L, which were examined in most detail.

## TL Behaviour at Yellow-Green Wavelengths

Since some calcites have their most intense emission around 550 nm (e.g. Medlin 1968, Debenham et al. 1982), we chose an interference

filter with a transmission peak at 550 nm and a "window" of ~100 nm width (Spectracoat Monopass, No. 546 of set 246, Optics Technology Inc., Belmont, Calif.). This was used together with our usual infra-red rejection filter. All samples were glowed using the low-pressure flow of Ar and hot gas-purifier described elsewhere (Berger et al. 1982).

The additive-dose glow curves for the 2-11 μm grains of sample 061L are shown in Figure 1. Here it is seen that the dominant peak is

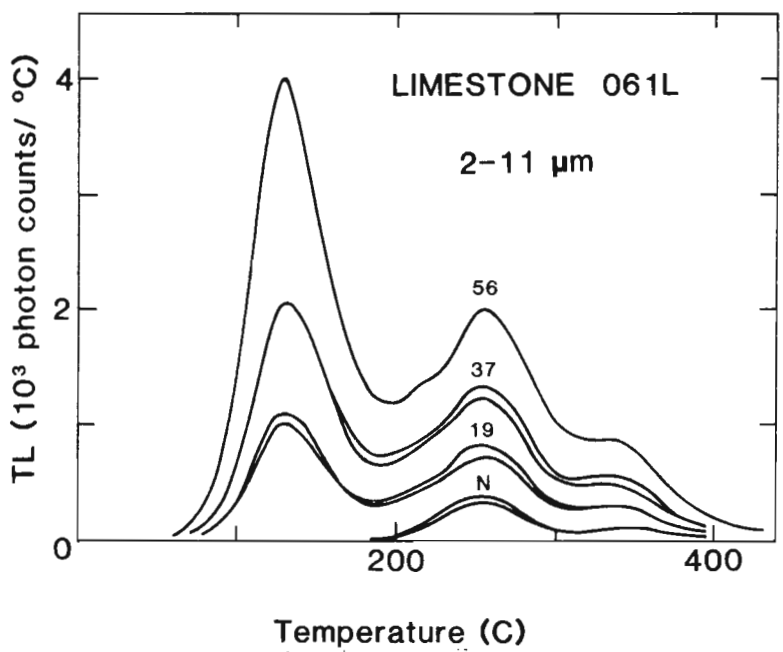


Fig. 1 Smoothed glow curves for the 2-11 μm fraction of sample 061L observed at the yellow-green ( ~ 550 nm) wavelengths (filter 546). There are 2 curves at each dose (in Grays) except for the unirradiated or natural (N) where there are 3. Reheats have been subtracted. The heating rate was 5°C/sec. See Wintle and Huntley (1980) for equipment descriptions.

at 260°C with a lower signal at higher temperatures. The ratio of natural TL peak heights is ~ 3.1 (260/330°C). Similar sets of glow curves were obtained for the 2-11 μm and 88-250μ fractions of sample 060, in which the ratio of peak heights was ~ 4:1.

We were surprised to observe prominent supralinearity in the growth of TL at both 260°C and 330°C for samples 060 and 061L. An example is shown in Figure 2 for 061L. This behaviour is reminiscent

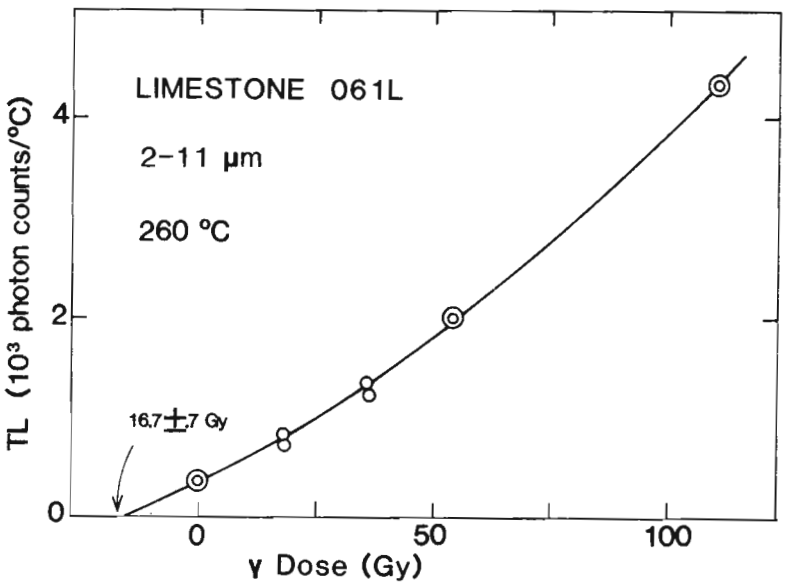


Fig. 2 Supralinear growth in TL at the 260°C peak of Figure 1.

of that observed by Debenham et al. (1982) for a Holocene travertine for which the natural TL emissions occurred above ~ 500 nm while the radiation induced TL had a broader emission, extending down to ~ 450 nm. This spectral distinction of the natural TL from the TL induced by ionizing radiation, coupled with their observation of supralinearity over the ~ 400-575 nm range (they used the Corning filter 4-96), suggested to us that the supralinearity we observed (e.g. Figure 2) might be eliminated if we were to block the > 500 nm emissions and examine the TL at the blue wavelengths. Unfortunately, second-glow growth curves at ~ 550 nm were uninformative because of poor reproducibility.

## TL Behaviour at Blue Wavelengths

We repeated some experiments on 060 and 061L using a Corning CS5-58 filter (transmission window ~ 375-475 nm) in place of the Spectracoat No. 546 filter. The effects were of two kinds. Firstly, there was a dramatic increase in the 330°C peak relative to the 260°C peak, such that the ratio of intensitites (260/330) was < 0.5. An example of the glow curves obtained for the 88-250 μm grains of sample 061L is shown in Figure 3. Secondly, the growth curve at each peak for sample 060 was linear, although for 061L the supralinearity remained.

It is heartening to see that the supralinear behaviour of calcite can be defeated in some cases; however, the differences between these two samples are not obvious, though 061L does contain a few per cent magnesium carbonate, while 060 does not.

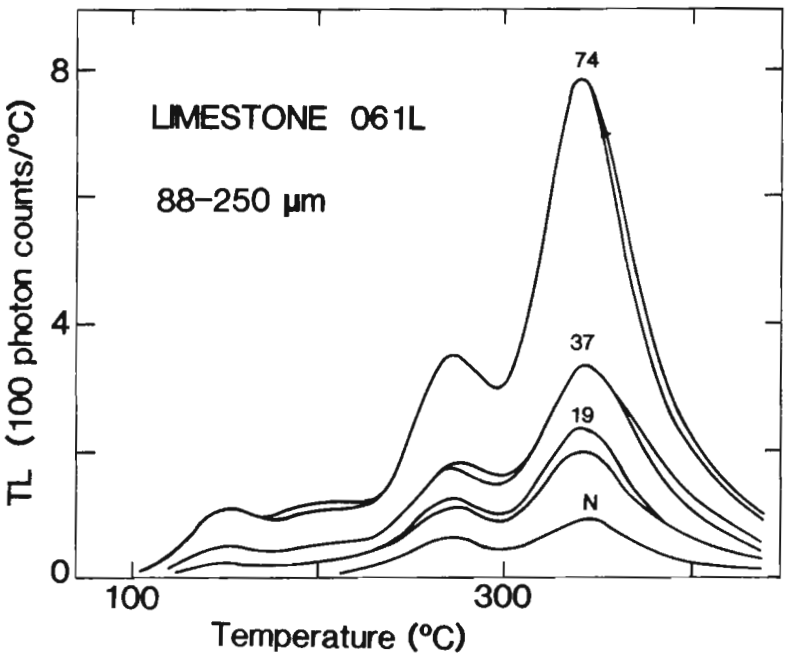


Fig. 3 Smoothed glow curves for the 88-250 µm fraction of sample 061L at the blue (< 500 nm) wavelengths. There are two curves at each dose. All data have been mass normalized.

## Implications

We speculate that if the cause of this supralinear behaviour can be determined and its effects controlled, then the fine grains of limestones should be useful for dating both cultural and geological heating events. For pre-Holocene ages it is not clear that supralinearity will be significant (e.g. Debenham et al. 1982). Even the sublinear behaviour of the high temperature peak from older calcite (Debenham 1983) is no obstacle to determination of EDs from first glow growth curves, because it is easy to prepare large numbers of uniform discs of fine grains in order to carefully define growth curves.

## Summary

We prepared 2-11 µm grains of calcite without disturbing their natural TL by using an inexpensive, high-speed, water-cooled carborundum blade such as is present in most geology departments, and by crushing the sample in a steel percussion mortar. The fine grains prepared in this way showed little spurious TL, given a low flow rate and low pressure (~ 0.3 l/min at ~ 150 µm) of purified argon.

Finally, two geologically old limestones, believed heated in the Holocene, exhibited supralinear TL growth curves. For one sample this supralinearity was eliminated by use of the < 500 nm emissions, rather than the dominant emission at ~ 550 nm.

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**Editorial Comment**

Although in the present work the motivation for using a blue filter was to avoid supralinearity, in the case of Debenham et al. (1982) the motivation was to avoid zero-age TL which in young samples was liable to give rise to too great a TL age. This is discussed further in a recent article by Debenham et al. (Archaeometry vol. 26, no. 2, pp 155-170) who also report the use of fine-grains from calcite for determination of alpha effectiveness.