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THERMOLUMINESCENCE INVESTIGATIONS OF NATURAL CALCITE CRYSTALS OF DIFFERING GENESIS

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ABSTRACT

Natural calcite crystals containing Mn^{2+}, were collected from three different genetic assemblages — hydrothermal, sedimentary and metamorphic — and examined for their thermoluminescence characteristics and possible correlation with geological environments of formation. Features appearing in their natural and artificially induced TL glow curves seem to indicate roughly the relative temperatures of formations. The TL sensitivity of the sample of hydrothermal origin is the highest among the three samples studied, although it has the lowest concentration of the TL emitting centres, viz. the manganese impurity.

INTRODUCTION

Of all the rock forming minerals exhibiting good thermoluminescence (TL) sensitivity, calcite has been studied in detail by earlier workers to determine the basic TL mechanisms involved [1(a)]. The build-up of TL due to natural uranium and thorium alpha activity has also been studied in great detail, with a view to using it as the basis for a method of age determination [1(b)]. This paper describes the results obtained in an attempt to correlate the TL characteristics with the known genesis of natural calcite crystals.

EXPERIMENTAL

Details of the three samples studied are given in Table 1. The sample were surface-cleaned, powdered and the fractions collected between 80 and 140 mesh size sieves were used for the TL measurements. The instruments used to record the TL glow curves and the TL emission spectra are the same as described by Nambi et al.[2]

TL glow curves were recorded above room temperature at about 550 °C and at a linear heating rate to about 70 °C and the light intensities were measured with an EMI 9514S photomultiplier. Usually 5 mg of the irradiated samples was spread uni-

TABLE II

DETAILS OF THE NATURAL CALCITE SAMPLES STUDIED FOR THEIR THERMOLUMINESCENCE

Sample code	*Description of sample with its place of origin*	*Gross alpha activity (Cts. h^{-1})*	*Mn conc. (p.p.m.)*
I	Light yellow crystals from hydrothermal vein deposits near Mt. Abu, Western India	0.20	27
S	Yellow crystals generated in sedimentary limestone deposits in Purna Chaibasa area, Bihar	0.66	2900
M	Pink crystals of metamorphic origin occurring at Borda Kumari, near Nagpur, Maharashtra	0.16	1200

formly over a tiny Kanthal heater strip to which a thermocouple was spot-welded for measuring instantaneous temperatures and activating the programming of the heater current. Nitrogen gas was passed through the sample compartment to eliminate the occurrence of spurious TL.

The TL emission spectra were recorded using a 0.25 m Jarrel Ash Grating Monochromator and an EMI 9558 QB photomultiplier. To record the TL emission spectrum at a particular temperature about 15 mg of the irradiated powder was spread uniformly over the heater and the sample was maintained isothermally at that temperature while the monochromator was scanned repeatedly between 200 and 800 nm using a motor drive at a rate of 100 nm min^{-1}.

Gamma irradiation was usually carried out inside ^{60}Co gamma cells where the dose rate at the sample was 5620 R min^{-1}. Alpha irradiations were carried out using a 300 Ci plated ^{241}Am source on 5 mg of finely powdered sample evenly spread over a circular area of 1 cm diameter.

The samples, after artificial irradiation, were stored in a refrigerator until their TL were read out to minimise the decay of the earlier part of the TL glow curve. Also, irradiated samples were handled in light-tight containers and under low ambient illumination in the laboratory to avoid any unwanted exposure to UV rays.

TL runs were made in two steps: first, the TL was recorded upto 250 °C, the sample was cooled to room temperature, then reheated upto about 500 °C and the TL recorded. While virgin samples gave TL peaks only at temperatures above 250 °C (i.e. only during the second run yielding NTL, the natural thermoluminescence) the samples after artificial irradiation in the laboratory gave ATL peaks at temperatures below 250 °C also. The calibration of NTL outputs in terms of equivalent artificial gamma doses was carried out by comparison of outputs obtained in the second runs after artificial gamma irradiation to various doses.

The TL glow peak temperatures obtained in the present study have been compared with the already published figures in the literature and are given in Table 2. The NTL and ATL glow curves for the three samples are presented in Figs. 1 and 2. There is, in general, agreement in the peak temperatures, but an extra peak at 285 °C is seen only in the case of sample I which is of hydrothermal origin. All three samples exhibit the same TL emission spectra, peaking broadly at 600 nm, as shown in Fig. 3. The TL age index, (NTL in equivalent gamma dose)/gross alpha activity, is evaluated as discussed by Nambi and Mitra[6], and is given in Table 3.

TABLE 2

CALCITE TL GLOW PEAK TEMPERATURE

Material	*Ref.*	*TL glow peak temperatures (°C)*					
Calcite	1(a,b)	80	150	230		330	
$CaCO_3$(ppt.)	1(a,b)	80		230		330	
$CaCO_3$(ppt.)	3	100	150	250			
Calcite	4	110		230		325	
Calcite	5	100		220		320	350
Calcite	Present work	100		215	285	330	

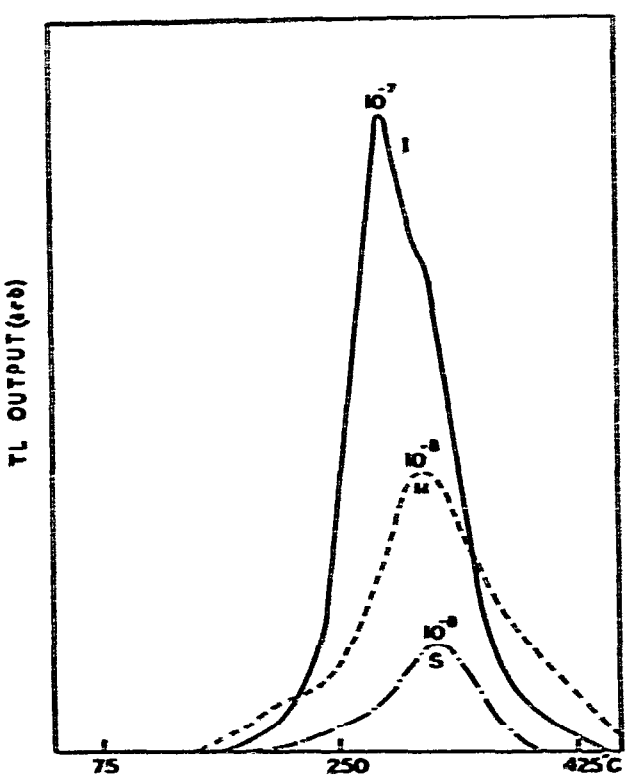

Fig. 1. NTL glow curves of natural calcites.

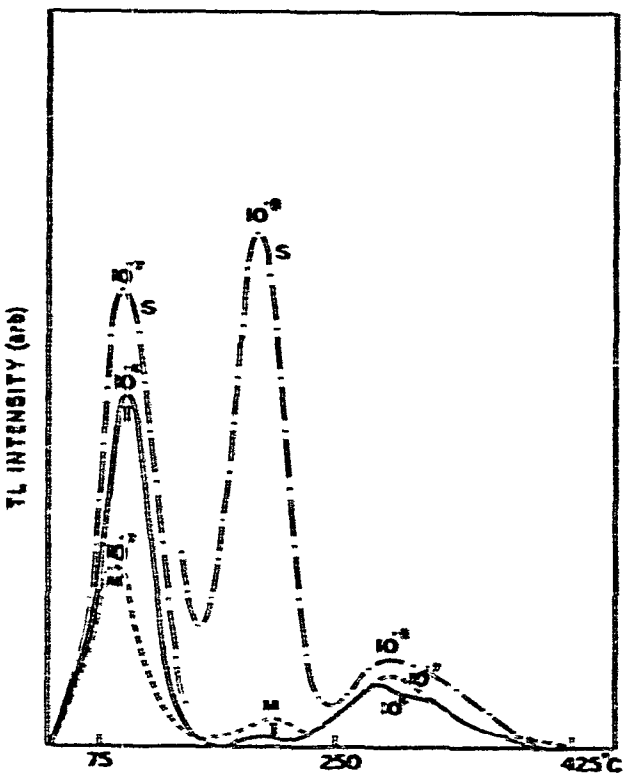

Fig. 2. TL glow curves of natural calcites after gamma irradiation (12000 R).

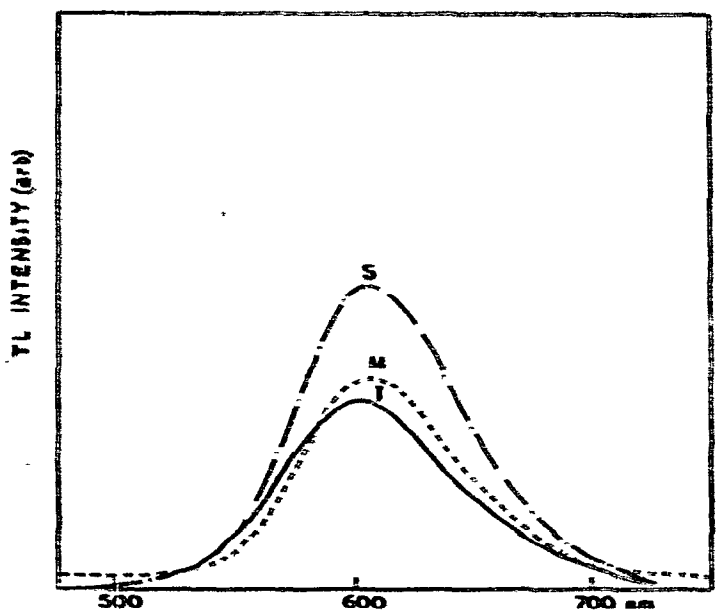

Fig. 3. Typical TL emission spectra of calcite samples.

TABLE 3

NTL AND TL AGE INDEX FOR VARIOUS NATURAL CALCITES

Sample code	*Gross alpha activity (Cts. h^{-1})*	*NTL as % of TL saturation possible*	*NTL in Co-60 gamma equivalent exposure (R)*	*TL age index Col.4/Col.2*
I	0.20	68	2.7×10^{2}	1.35×10^{8}
S	0.66	27	9.0×10^{1}	1.36×10^{5}
M	0.16	40	10^{5}	6.25×10^{5}

DISCUSSIONS AND CONCLUSIONS

(i) Of the three samples studied for their natural TL, sample M exhibited a relatively more prominent output at temperatures below 250 °C in addition to the usual NTL peak around 330 °C. In terms of thermal decay, this may be indicative of a geothermal history of a lower average temperature compared to other samples. On the same basis, sample I can be said to have a geothermal history with the highest average temperature.

(ii) The ATL glow curves (Fig. 2) point out that the ratio of 330/110 °C peaks is the highest for sample M and lowest for sample S. Thermal sensitisation studies on $CaCO_3$ in this laboratory[3] have indicated that high temperature peaks appear more pronounced in samples annealed at high temperatures prior to exposure. It may then be said that perhaps sample M belongs to the highest temperature of formation among the three samples and sample S to the lowest. Such a conclusion stands vindicated from the geological descriptions given in Table 1.

(iii) It is well known that in the TL of $CaCO_3$ where manganese content is high, the low temperature peak is intense relative to the other peaks present[7]. Perhaps this is why sample S, with the highest Mn content among the three samples, has yielded the lowest value for the ratio of 330/110 °C peaks.

(iv) The TL emission spectra presented in Fig. 3 match well with those already available in literature and no doubt refer to Mn^{2+} characteristic emission in the $CaCO_3$ lattice. While sample I has the least Mn content among the three samples studied, it is interesting to note from Fig. 2 that sample I exhibits the maximum TL sensitivity. Mn concentrations in the range of 1000–3000 p.p.m. as found in the other samples, M and S, are not expected to introduce quenching factors of an order of magnitude large enough to explain the reduced TL sensitivities of these as compared with sample I. Perhaps the type of genesis (hydrothermal in the case of sample I) has a prominent role in the resulting increased TL sensitivity, most probably by way of introducing suitable lattice defects or to a lesser extent, by a selective inclusion of yet another TL sensitive impurity like Mg.

Mg in the carbonate lattice brings about also a shift in the peak position. Mg in Ca-sites strengthens the crystal field and thus decreases the energy of the $^4G(T_{1g})$ state of Mn^{2+} which is the emitting centre [3].

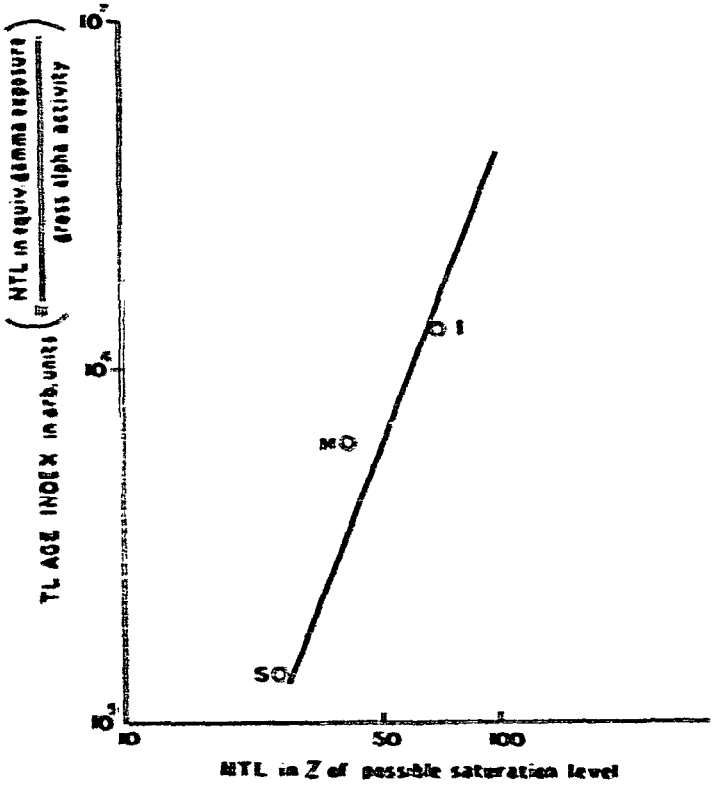

Fig. 4. TL age index as a function of extent of filling up in the NTL of natural calcites.

(v) The limitations of any TL age estimate on geologically very old samples have been fully discussed with regard to dolomitic limestones in Nambi and Mitra[6]. The same considerations have been found to be applicable to these calcites too and hence only the TL age index, = (NTL in equivalent gamma dose)/gross alpha activity, is given in Table 3, which could be used to calculate the relative ages of these samples. As in the case of dolomitic limestones, here also there seems to be a progressive increase in the extent of filling up of TL traps constituting NTL (in terms of fraction of possible saturation TL level in each sample) with age of the sample (Fig. 4), when not fully reconstituted by metamorphism.

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