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Thermoluminescence studies of some natural and synthetic opals

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Abstract

The thermoluminescence (TL) of 30 natural and synthetic opals from a wide range of sources has been investigated as a method of determining opal origin. Natural opal gave TL responses around 230°, 300° and 360°C, the intensity of each being sample-dependent. Studies on the TL of silica gel suggest that the water in opal is responsible for the 230°C peak and for further TL sometimes seen on reheating the same sample. The 360°C peak was seen only with opals originating from Australian sedimentary opal fields. Investigations of the effect of gamma radiation and light on producing TL in opal are reported and the use of fluorescent-light-induced TL is suggested as a means of distinguishing between synthetic and natural opal. Gamma radiation had no positive effect on opal TL.

Introduction

Opal is a hydrated form of silica with a water content ranging from 4 to 10 percent. It is commonly known for the bright speckles or play of colors that some samples show as they are rotated in light, though these 'precious' opals are a minority. Most opal is of the 'common' or 'potch' variety which can have a wide range of uniform colors.

Studies on the internal structure of opal (Jones *et al.*, 1964; Sanders, 1975) have shown the silica to be in the form of spheres of between 50 and 400 nm in diameter. In precious opal the spheres are stacked in systematic arrays, resulting in a regular array of voids between the spheres. This acts as a three-dimensional grating and, depending on the size of the silica spheres, can diffract different beams of color from the visible spectrum. Silica and water can also fill the voids (Langer and Flörke, 1974), or the spheres can vary in size, both resulting in the diffuse scattering of light as in potch opal.

Recently, several methods have been described for synthesizing opal (Darragh and Perdrix, 1975), and synthetic opal manufactured by Pierre Gilson, Saint Sulpice, Switzerland, has become commercially available. In the methods reported, a silica substrate is first prepared from either sodium silicate or tetraethyl orthosilicate (TEOS) solutions and then heated to between 500 and 800°C. This causes the material to shrink and become stronger and harder.

In this paper we report an investigation of the light emission during the heating of opal, with a view to distinguishing the different origins of opal samples. Light emission on heating of a natural material can arise from annealing of radiation-induced defects [thermoluminescence (TL)], or from chemical and structural change due to the heating (Townsend and Kelly, 1973). The effect on opal TL of exposure to various types of radiation has also been examined as a means of clarifying opal origin and to investigate the source of opal TL.

Sample preparation

The TL samples were prepared by depositing finely-ground opal uniformly onto an aluminum disc. Samples of approximately 20 mg were drilled from each opal sample by means of a diamond burr. The powder was further ground with an agate mortar and pestle to ensure a particle size in the order of 1–10 μm. It was then transferred to a test-tube containing acetone to a depth of 6 cm and shaken until the grains were in suspension. The test tube was allowed to stand for 2 min, after which time only grains smaller than 8 μm were left in suspension (Zimmerman, 1971). The remaining suspended particles were allowed to settle on to 10 mm diameter, 0.3 mm thick aluminum discs. After 20 min the excess acetone was removed and the discs left to dry in air at room temperature. All operations were performed under fluorescent lighting.

Initially a number of samples were prepared by the

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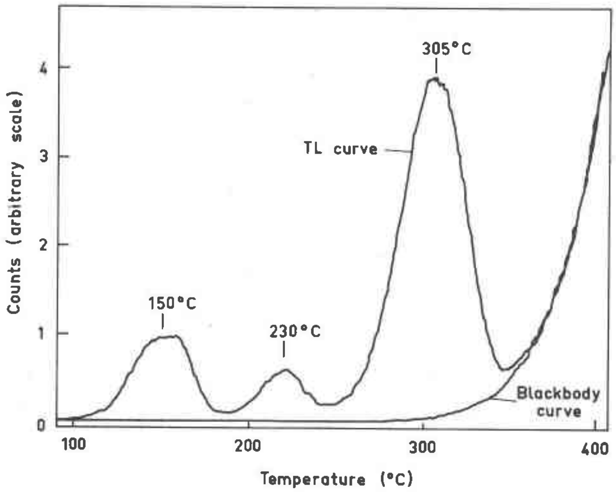

Fig. 1. The thermoluminescence (TL) curve of the CaF_2 standard shown with a normal black-body curve obtained upon reheating.

technique of Mejdahl (1968), in which the deposited powder is attached to the disc with a silicone resin glue, Dow Corning Type (DC 805). This glue, which is widely used in radiation dosimeters, gave no TL response when placed alone on an aluminum disc. However, with opal samples the use of glue led to enhancement by factors of up to five in the intensity of observed TL peaks. Because of this effect, the glue method was not used.

Thermoluminescence apparatus

The thermoluminescence apparatus consists of a glow oven for heating the sample, a photomultiplier tube for detecting the emitted light, and the necessary control and recording electronics. The glow oven used was similar to that described by Zimmerman (1971). The oven was flushed continuously during use with oxygen-free nitrogen at a flow rate of 5 l/min to prevent spurious background luminescence induced by oxygen or water vapor (Aitken *et al.*, 1968). The sample disc was placed on a Nichrome heating strip connected via a thermocouple to a temperature controller, which permitted the pre-heating of the Nichrome strip to a preset temperature, followed by heating to a chosen final temperature at a constant heating rate. By displaying the thermocouple output on an *X*,*T* plotter, the rate of temperature increase was shown to be constant with time. A heating rate of 14°C/sec was used. The temperature scale was calibrated by measuring the TL curve of ^{60}Co-irradiated natural fluorite phosphor (MBLE[1], type S) and comparing our spectra, shown in Figure 1, with those given by Aitken (1968) for a similar treatment of the same material.

The light emitted was detected by an EMI-9824B photomultiplier fitted with an infrared filter. Pulses from the photomultiplier tube were amplified and shaped via standard nuclear modules and stored in a multichannel analyzer operated in the multiscaler mode.

Experimental results

Natural opal

TL curves were measured for samples obtained from a suite of opals covering a wide range of opal type, location, and color, the details of which are given in Table 1. For each sample the TL curves from at least two different discs were measured, and in some cases several samples were obtained from the same opal. TL responses from such replicates were found to be similar. All the TL curves showed some combination of three responses in the region of 230, 300, and 360°C, but with markedly varying intensity. Details of the TL curves obtained from all the samples are summarized in Table 2, using the following three classifications for the response above 250°C. Type I TL curves are characterized by an intense response, centered at 360°C. Curves with the highest temperature response at ~ 300°C are subdivided into Types II and III, with Type III being much weaker than Type II. The 300°C response could also be present in Type I curves, but the strong 360°C response masks out this region of the curve. These curve types are illustrated in Figure 2. Note that the log scale used to show the small peaks around 230°C underemphasizes the large responses above 300°C, which become peaks after subtraction of the black-body radiation.

After the sample had cooled to room temperature from the initial TL measurement, a reheat curve was immediately obtained by repeating the same heating cycle. Most samples showed further luminescent peaks and the reheat curves are also classified into three types. Type A, shown in Figure 1, is the TL curve due to black-body radiation obtained for a disc with no sample. Type B refers to a curve of Type A shape but which has a higher count rate in the high-temperature region, and Type C refers to those reheat curves which have a low-temperature peak. Types B and C are shown in Figure 2. Heating for periods of up to 30 min at 400°C was required to change a sample with a Type B or C reheat curve to give a Type A curve.

[1]MBLE, 80 Rue des Deux Gênes, Brussels 7, Belgium.

Table 1. Details of opal samples

Sample No.	Location	Deposit type	Opal type	Colour	Source
An1	Andamooka, SA	Sedimentary	Matrix*	White	Aust. Museum (No. 50122)
An2	"	"	Potch	Amber	" (-)
An3	"	"	Potch	Brown-red	" (-)
Lr1	Lightning Ridge, NSW	"	Potch	Blue	" (No. 50123)
Lr2	"	"	Precious	Purple	J. Taylor, Lapidary Studio, St Leonards
Lr3	"	"	Precious (Translucent)	Pale yellow green	"
Lr4	"	"	Precious	Green	"
Lr5	"	"	Potch	White	"
Cp1	Coober Pedy, SA	"	Potch	White	P. Darragh, CSIRO Div. of Mineralogy
Cp2	"	"	Precious (Opaque)	White	J. Taylor
Cp3	"	"	Precious	White	Aust. Museum (-)
Wc1	White Cliffs, NSW	"	Potch	White	P. Darragh
Wc2	"	"	Precious (Opaque)	White	Aust. Museum (D12455)
Wc3	"	"	Precious (Translucent)	Blue-purple	" "
Cd1	Cowarna Downs, WA	"	Precious (Opaque)	White	P. Darragh
Wa1	Western Australia	"	Precious (Opaque)	White	"
Ms1	Mainside	Sedimentary (Boulder)	Potch	Purple	"
Wt1	Winton	"	Precious	Blue	"
Wt2	Winton	"	Potch	Specked	"
Bd1	Queensland	"	Potch	Blue	"
Hn1	Hungary	Volcanic	Potch (Opaque)	White	"
Br1	Brazil	"	Precious (Translucent)	Milky-purple	"
Ri1	100 miles NW Redlands USA	"	Potch (Opaque)	Light-blue	"
Ml1	Mullumbimby, NSW	"	Potch (Opaque)	White	"
Gd1	Jedong, Java	"	Potch (Opaque)	White	"
Bu1	Butchers Ridge, Vic	"	Potch	Pale Yellow	"
Rb1	Rocky Bridge Creek, NSW		Potch (Opaque)	Blue	"

* Matrix is opal intermixed with fine sand.

The grouping of the opal samples by host rock shows that only opals originating from certain sedimentary fields exhibit a Type I response. These include the major fields of Andamooka, Lightning Ridge, and Coober Pedy, where opal occurs as thick seams in bleached sandy claystone deposited during the Cretaceous period and deeply weathered during the Tertiary (Hiern, 1965). In the TL curves of both precious and common opal from these deposits, the presence of Type I response is independent of either color or variety.

No Type I responses were obtained with opals from either volcanic host rocks or from the dark iron-stained Tertiary sedimentary sandstones of Queensland ('boulder opal'). In both host types opal fills narrow cracks or cavities and does not form the massive deposits found in the major sedimentary fields.

The effect on opal TL of various types of radiation was studied with eight samples whose TL had been previously measured. Exposure of the samples to light from a yellow-filtered tungsten lamp for 64 hours resulted in similar broad TL responses in the region 200 to 300°C, as shown in Figure 3. The same samples were then exposed for 16 hours to the light from a fluorescent tube. The TL curves of all samples have a broad response from 180 to 330°C with a peak intensity at 190°C, as illustrated in Figure 3. A dose of 19 mrad of ^{60}Co γ-rays produced very little response in the TL curve, with a small broad response centered at ~ 230°C. One sample, Cp1, further irradiated with a 1850 rad dose, showed the same TL curve, suggesting that the small response could be due to light effects during handling of the sample. Three freshly-prepared samples Br1, Nm1, and Ms1 were also exposed to this large γ dose without any discernible variations in their TL curves.

Synthetic materials

TL curves were obtained for three Gilson synthetic opals, two substrates, and wet (pink) and dry (blue) silica gel. The samples and their responses are detailed in Table 3. The synthetic opals gave similar TL curves with a small peak at 230°C and a weak Type II response at ~ 300°C. The TL and reheat curves for the white synthetic opal (A) and the two substrates are shown in Figure 4. The absence of a Type I response enables these synthetic opals to be distin-

Table 2. Classification of TL responses from natural opals using curve types shown in Fig. 2

Sample No.	Opal type	High temperature peak	Reheat curve	Intensity* 230°C peak	Comments
		A. Major Sedimentary Opal Sources			
An1	Matrix	I	B		Irradiation studied
An2	Potch	I	B	†	Irradiation studied
An3	Potch	I	B		
Lr1	Potch	I	B		
Lr2	Precious	I	B		Irradiation studied
Lr3	Precious	I	B		
Lr4	Precious	I	B		
Lr5	Potch	I (w)**	B	Weak	
Cp1	Potch	I (w)	B	Weak	
Cp2	Precious	I	B		Irradiation studied
Cp3	Precious	I	B		
Wc1	Potch	I (w)	C (w)	Strong	
Wc2	Precious	I	B		
Wc3	Precious	I	B		
Cd1	Precious	I	C (s)	Strong	
Wa1	Precious	I	B		
		B. Sedimentary (Boulder) Opal Sources			
Ms1	Potch	III	C	Strong	Irradiation studied
Wt1	Precious	III	B (w)	Weak	
Wt2	Potch	III	B	Weak	
Bd1	Potch	III	B (w)	Weak	
		C. Volcanic Rock Opals			
Hn1	Potch	III	B		
Br1	Precious	II	B		Irradiation studied
Rl1	Potch	II	B		Irradiation studied
Ml1	Potch	II	B		
Gd1	Potch	III	B (w)	Weak†	Irradiation studied
Bu1	Potch	III	C	Strong	
Rb1	Potch	III	B		

* All samples gave a 230°C temperature peak and only peaks of exceptional intensity are noted.

** w = weaker, s = stronger than usual.

† Sample gave a further low temperature peak at 190°C.

guished from the visually-similar precious sedimentary opals. The TL curves of the two substrates and the silica gel samples had a 230°C peak but no high-temperature responses. Unusually large responses in the reheat curves were seen for both the sodium silicate substrate and the pink silica gel (Figs. 4 and 5 respectively).

The substrates and synthetic opals were exposed to the various radiations described previously. All six of the samples gave TL curves showing a strong peak at 180°C after exposure to fluorescent lighting for 16 hours. The black synthetic opal also gave a plateau in the 250–300°C region, whereas the other samples had little response. The TL curve for the white synthetic opal (A) is compared in Figure 6 with the TL curve for a similarly-treated natural opal (Cp1). Values for the ratio of the intensity of the TL peak at 180°C to the intensity at 240°C of all samples exposed to fluorescent lighting are given in Table 4. For natural opals values fall between 1 and 1.5, whereas the synthetic opals and substrates yielded values greater than 4. Consequently this ratio is a possible method for distinguishing synthetic opals from natural opals of any origin.

The TL of the white synthetic opal, sample A, was measured again after exposure to the yellow-filtered light for 16 hours. Only a weak TL was induced in the sample, similar to that obtained with the natural opals after similar treatment. A previously unheated sample of the white opal was also given a 1850 rad dose of ^{60}Co γ-radiation, which led to no discernible changes in its TL curve.

The synthetic opal exhibited considerable regenerated TL response when left for several hours in the dark after a TL run. The curve obtained was Type III with a large low-temperature peak. Comparable regeneration was also observed with the two substrates.

Discussion

The major TL responses of opal are broad peaks at 230° and 300° and a peak at 360°C in some opals from sedimentary rocks. A peak near 180°C was found to be induced by fluorescent light.

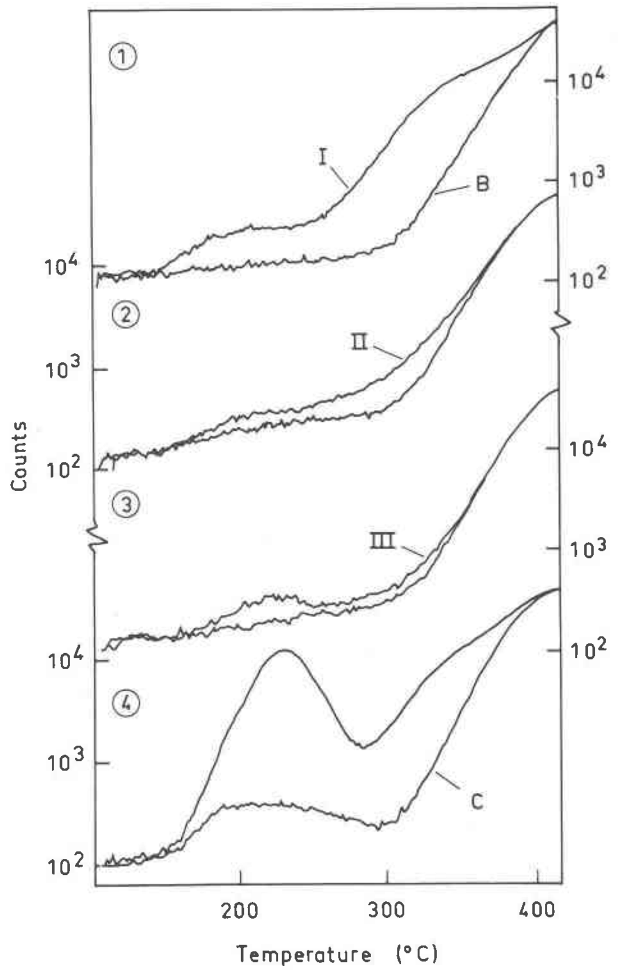

Fig. 2. The three types, I, II, and III, of high-temperature TL peaks and two types of reheat (RH) curves, B and C, are illustrated with curves obtained from sample Lr2(1), Br1(2), Nm1(3), and Cd1(4).

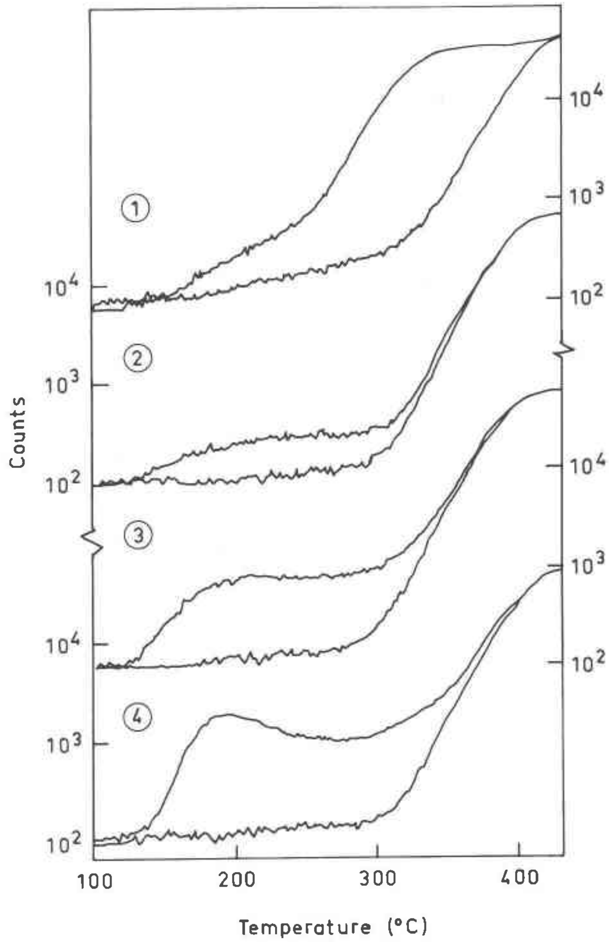

Fig. 3. TL and reheat (RH) curves obtained from the Lr1 sample after (1) sample preparation, (2) ^{60}Co γ-irradiation, (3) subdued incandescent light, and (4) fluorescent light irradiation.

The intensity of the 230°C and reheat curves are unrelated to opal source, but measurements on the two silica-gel samples suggest that they may result from the presence of water. The TL curve of the blue low-water-content silica gel had a strong 230°C peak, whereas the wet pink gel gave a strong reheat response. This suggests that loosely bound or free water which can be readily lost is not involved in a TL response, but more firmly bound water can give rise to TL. A similar result was obtained in a study on the effect of water on the TL of 50–920 μm diameter silica beads (Douglas and McDougall, 1970). The loss of free water gave no TL peaks, but a peak at ~ 420°C was attributed to the loss of water bound to the silica surface. The reheat TL in the opal samples may result from some of the more firmly bound water remaining after the first heating, and on being removed on reheating yielding further TL.

Table 3. Classification of TL responses from synthetic opal

Material	High temp. peak	Reheat curve	230°C peak
White synthetic (A)	II	A	medium
White synthetic (B)	II	B	"
Black synthetic (C)	II	A	"
TEOS substrate	Nil	B	"
Sodium silicate substrate	Nil	C (w)	"
Pink silica gel	Nil	B (s)	"
Blue silica gel	III	B (w)	strong

The total water content of an opal consists of both molecular water and various forms of hydroxyl species (Langer and Flörke, 1974). The rate of water loss from an opal will depend on the varying amounts of the different species present and on the ease of diffusion of the water through the structure. For precious opal from the Australian sedimentary field the rate of water loss is slow, with loss of water occurring up to 500°C, whereas some common opals lose all their water rapidly (by 250°C) (Segnit *et al.*, 1965; Bayliss and Males, 1965).

Little is known about the form of the water in the opals studied here. Two of the samples, Ms1 and Br1, which gave both a strong 230°C peak and a large reheat response, have high water contents of up to 8

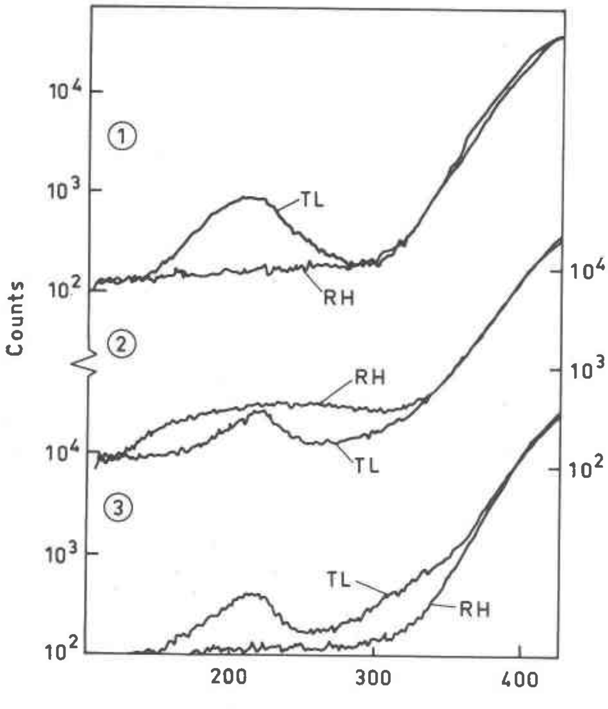

Fig. 4. TL and reheat (RH) curves from the TEOS (1) and sodium silicate (2) based substrates and the Gilson synthetic opal (3).

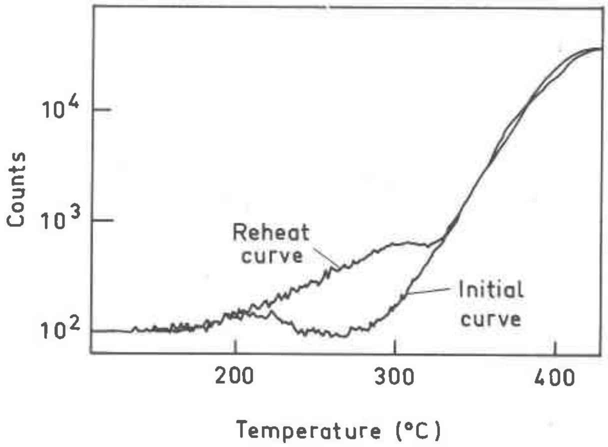

Fig. 5. TL and reheat (RH) curves obtained from the pink silica gel sample, showing the large TL response generated in the 320°C region after initial heating.

percent (P. Darragh, personal communication), though porosity may be more significant than total water content in determining the TL response. Two of the opals studied, Wt2 and Wa1, showed a rapid increase in their play of color on wetting, indicating a very porous structure. They gave average 230°C and no reheat peaks, in accord with the suggested explanation of the reheat peaks occurring when water remains after the initial heating. However, an understanding of the exact role water plays in TL response requires detailed study of opals with well-characterized internal water.

The sources of the Type I and fluorescent-light-induced TL peaks are not known. The negligible effects of both small and large doses of ^{60}Co radiation on annealed and unannealed samples of the opals indicate that γ-radiation-induced defects are unlikely to be the cause of the Type I TL peaks. A similar treatment of quartz gives two very intense peaks in the 325–375°C region (Aitken and Fleming, 1972); this would indicate an absence of crystalline structure, in agreement with X-ray diffraction studies of these opals (Sanders, 1975). Although a large num-

Table 4. Ratio of TL responses at 180°C and 240°C of opal preheated and irradiated under fluorescent lighting

Natural opal		Synthetic materials	
An1	1.5	White opal, A	5.8
An2	1.5	White opal, B	4.2
Lr1	1.1	Black opal, C	4.2
Cp2	1.5	TEOS substrate	4.0
Cd1	1.0	Sodium silicate substrate	4.0
Br1	1.3		
R11	1.1		
Gd1	1.5		

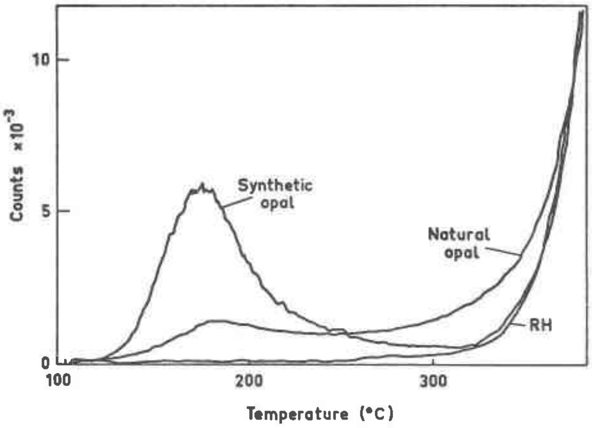

Fig. 6. A comparison of the TL curves from the A Gilson synthetic opal (1) and of the natural Cp2 opal (2) after similar time exposure to fluorescent lighting.

ber of metallic impurities such as Na, Ca, Al, Mg, Fe, and Ti occur in opals from the sedimentary fields (Bayliss and Males, 1965), the lack of crystalline structure in the opal and of radiation response makes it unlikely that defect centers are responsible for the Type I TL peaks. Similarly, it is unlikely that inclusions such as calcium sulphate can be involved in the opal TL, since calcium sulphate thermoluminesces only after γ-irradiation (Mejdahl, 1972).

Conclusions

The TL glow curves of opal contain several peaks, of which one at 230°C may be related to the presence of water in the opal and another at 360°C is seen only with opals from certain Australian sedimentary fields. Opal color and type do not affect these observations. Exposure of the previously-heated opal samples to fluorescent lighting induces a further TL peak near 180°C, while γ-irradiation of heated and unheated samples had no effects. Similar examination of several synthetic opals showed no 360°C peak in the initial TL curve, and no γ-irradiation effects but a much stronger 180°C peak after the exposure to fluorescent lighting. These features may serve as methods of distinguishing synthetic from natural opal, though a wider range of samples would need to be examined before this could be conclusively proposed.

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