Earth and Planetary Science Letters, 22 (1974) 391–396

THERMOLUMINESCENCE STUDIES OF THE ALLENDE METEORITE

D.W. SEARS and A.A. MILLS

Departments of Astronomy and Geology, University of Leicester, Leicester (Great Britain)

Received March 28, 1974
Revised version received May 17, 1974

The Allende meteorite has been examined with a view to applying thermoluminescence (TL) to the study of a meteorite's passage through the atmosphere. At least three kinds of TL-bearing minerals are present. A strong peak at 140°C is due to forsterite, and one at 200°C is probably caused by cordierite. By far the most intense TL comes from an alteration product associated with gehlenite.

In the 4-cm diameter meteorite examined the 200°C TL varied in intensity across the stone, showing it to be produced by fragmentation. Temperature gradients induced by atmospheric heating can also be derived, and indicate the orientation of the meteorite. Together with fusion crust measurements these results enable the final phase of the meteorite's passage through the atmosphere to be delineated.

1. Introduction

The Allende meteorite fell on 8th February 1969, the explosion leaving thousands of stones strewn over an area exceeding 300 km^2. It is a Type III carbonaceous chondrite. The morphology and fusion crust of many specimens has been reported by Clarke et al. [1]. The size and the great general interest in Allende led us to attempt a study of the atmospheric passage of this meteorite. The specimen used here (NMNH 3636) was a completely encrusted 67-g stone, roughly 4 cm in diameter.

In this report we describe thermoluminescence (TL) measurements. TL is the luminescence produced on releasing electrons from traps (lattice defects, etc.) by thermal excitation. They drop to the valence band via a luminescent centre and in doing so emit light.

Durrani and Christodoulides [2] explored the use of TL for determining the exposure age of Allende, whilst Keil and Fuchs [3] have described an electroluminescent mineral, hibonite. One may expect many luminescent species to be present because Allende is an extremely heterogeneous meteorite containing many Ca–Al-rich aggregates. The mineralogy of Allende has been described by Clarke et al. [1] and the Ca–Al-rich aggregates discussed by Marvin et al. [4].

2. Method

We removed a 4 mm thick central section from the stone using a Metals Research Ltd. Microtome II diamond saw. From this we cut eight bars (*a–h*, see Fig. 1.), and from these obtained 106 4 × 4 × 1 mm slices. The slices were powdered and passed through a 50-μm sieve. A glow curve (light emitted vs. temperature) was recorded for each slice, using both powder in its natural state and powder that had been drained of its TL by heating to 500°C and given a standard dose of about 50 krad from a ^{60}Co γ-ray source. The light emitted was measured by an EMI 9635B photomultiplier tube at a heating rate of 5 ± 0.05°/sec. A chance HA3 heat filter was inserted between a 6-mm aperture and the photomultiplier tube. A standard lamp was used to check constancy of sensitivity and a device based on integrating spheres was used to prove linearity of response of the photomultiplier to light.

Examination of electroluminescence was performed using both a luminescence microscope of our own construction [5] in which the luminescence is excited by 6 keV electrons, and a Cambridge Microscan 5 electron-probe operated at 20 kV accelerating voltage. Some minerals appeared to have different colours in the two instruments, presumably because additional or dif-

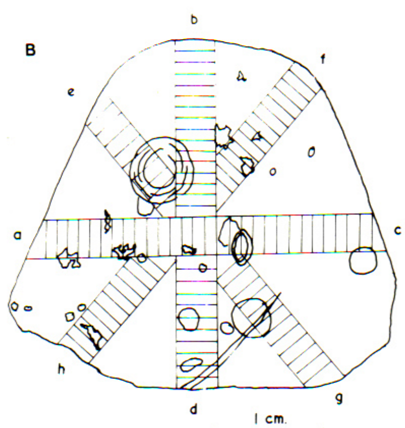

Fig. 1. Photograph (A) and sketch (B) of the slice of Allende used for thermoluminescence measurements. The locations of the 106 slices are marked on the sketch.

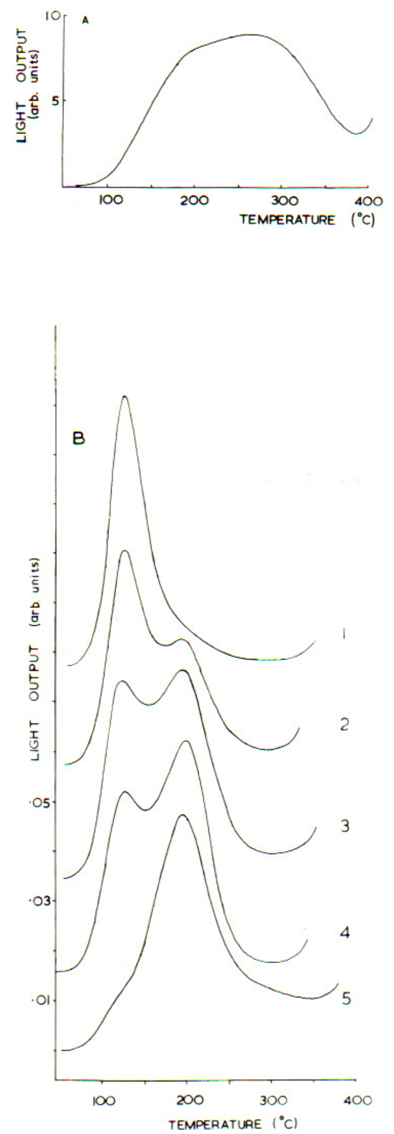

Fig. 2. The three types of artificial glow curve found in the Allende meteorite: (A) types 1 and 5, with intermediate groups resulting from various combinations; (B) type 6 glow curves.

ferent peaks were being excited. The colours mentioned here refer to those seen with the electroluminescence microscope.

3. Results

3.1. Types of glow curve

Three basic kinds of glow curve were obtained from the 106 specimens. These are shown in Fig. 2. Type 1, in which a peak at 140°C dominates the glow curve (this was only present in specimens that had been irradiated); type 5, in which a peak at 200°C dominates; and finally type 6 in which an extremely broad band of luminosity occurs with a peak at about 270°C. All combinations of types 1 and 5 were possible; these combinations are called 2, 3, and 4, where 3 has peaks at 140° and 200°C of similar intensity. These peaks are known to be due to different minerals since their intensities vary independently over extremely short distances. For types 1, 5 and 6 the relative intensities are 0.05, 0.05 and 10 respectively. For comparison, ordinary chondrites are about 30 and enstatite achondrites (the most luminous meteorites) are about 100 on the same arbitrary scale.

TABLE 1
Quantitative electron microprobe analyses of the main thermoluminescent minerals in the Allende meteorite*

	A	B	C	D
CaO	0.5	10.6 (3.1–20.9)	39.2	30.0
SiO_2	38.5	39.7 (36.4–42.1)	22.7	37.2
Al_2O_3	0.5	22.3 (10.8–33.8)	33.2	30.2
FeO	0.5	6.4 (1.5– 7.6)	0.2	1.7
MgO	57.4	20.5 (7.0–32.3)	2.4	1.8
TiO_2	0.1	n.d.	n.d.	n.d.
Total	97.5	99.5	97.7	100.9
Number of points	3	6	6	3

* Oxides calculated by stoichiometry; n.d. = not detectable.
A: Forsterite giving the 140°C thermoluminescent peak.
B: Blue electroluminescent grains in white aggregates, probably cordierite, responsible for the 200°C peak.
C: Gehlenite.
D: Luminescent bands, associated with gehlenite, responsible for the strong thermoluminescence between 200 and 400°C.
Analyses for A, C and D are accurate to about 10% of the value for the element.

3.2. Distribution of glow curve types

By examining the distribution of glow curve types over the specimen it is possible to relate certain types with structures, and thereby suggest the minerals responsible for the glow curves. Type 6 is associated with Ca—Al-rich white aggregates and type 1 with chondrules. The chondrules in Allende are mainly forsteritic olivine.

3.3. The luminescent minerals in Allende

The residual powders and a slice from a region giving type 6 glow curves were investigated by X-ray diffraction, electroluminescence and electron-microprobe analyses. X-ray diffraction showed the type 1 material to be rich in forsteritic olivine. The electroluminescence of this type was red, and in polished section forsterite was found to give a red electroluminescence.

The type 5 powder showed blue electroluminescence. In polished sections the blue grains most frequently appeared as micron or submicron grains in white aggregates. They were difficult to electron-probe, because when the beam size was small enough to cover only the grain its luminescence could not be seen. An average of 6 analyses of blue grains in white aggregates (Table 1) suggests that cordierite ($Mg_2Al_4Si_5O_{18}$) is responsible. Our calcium value is probably almost entirely due to the beam extending beyond the grain and on to the Ca-rich matrix of the aggregate. Keil and Fuchs [3] have shown that hibonite can have these luminescence properties, but it then contains appreciable titanium.

The most intense luminescence in the slice from the type 6 region came from an orange-pink electroluminescent material. Closer inspection showed the the electroluminescence was associated with alteration bands, usually of a brownish tinge. The host mineral is gehlenite ($Ca_2Al_2SiO_7$) but the luminescent band had an appreciably different composition (Table 1).

3.4. Distribution of TL intensity

Since the 140°C peak was absent in the natural specimen it is of no use in determining either TL shape contours or atmospheric heating effects. For these the 200°C peak must be employed. Being an extremely heterogeneous meteorite the amount of the originating mineral in any one particular slice is highly variable. To some extent this will be allowed for by expressing the natural TL relative to the TL of the same specimen when drained and given a standard dose of radiation.

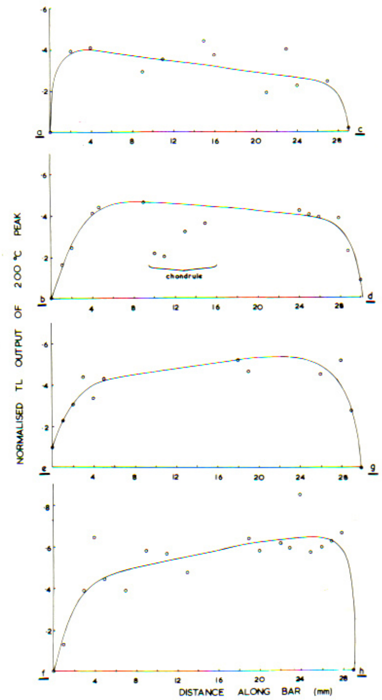

Fig. 3. Distribution of thermoluminescence intensity along bars *ac, db, ef* and *hf*. The area of the natural curves has been normalised to the area under the curves produced by drained powder that has been given 50 krad of γ-radiation from a ^{60}Co source.

Fig. 3 presents plots of normalised TL output vs. distance along bars *ac, bd, ef* and *gh*. The area of the 140°C peak had to be subtracted from the area of the artificial glow curves and this may introduce some error. Glow curves of types 1 and 6 have been omitted from Fig. 3 since the 200°C peak cannot be measured in these. As expected from a meteorite of the heterogeneity of Allende the scatter is considerable. However, it is possible to discern some trends, and these are presented on the original section across the stone in Fig. 4. It can be seen that there appears to be a variation in the intensity of the 200°C peak across the meteorite. This is ascribed to cosmic ray bombardment in space whilst part of a larger body.

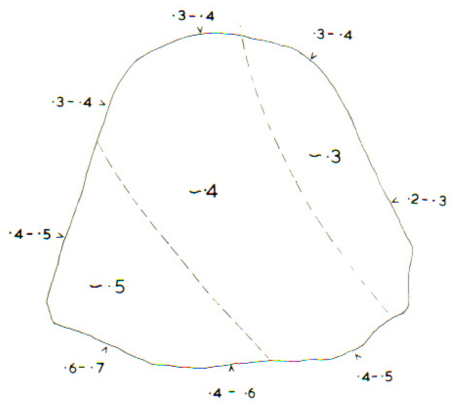

Fig. 4. Variation of the intensity of the 200°C peak over the slice.

3.5. Temperature gradients

At the eight points at which a bar intercepts the fusion crust it should be possible to determine a temperature gradient using the method of Vaz [6]. Four of our bars show reasonable gradients (Fig. 5), heterogeneity obscuring the gradient in the other four locations. The reduction in TL due to atmospheric heating may be expressed in terms of temperature by a calibration curve. This is obtained by annealing some natural powder at various temperatures prior to determining the glow curves. The percentage drop in the TL is then expressed as a function of the annealing temperature to obtain the calibration curve. The period of annealing was found to be of minor importance, similar results being found for 1 and 10 sec. It is thus possible to assign approximate temperatures to the observed gradients. From Fig. 5 it is apparent that face *d* has a steeper gradient due to atmospheric heating than the others, especially *b*. From this we conclude *d* to be the front and *b* the rear of the stone when the meteorite was near the end of its luminous flight. The temperature gradient may also be determined from the dimensions of certain zones in the fusion crust [7]. The values so obtained have the same relative values; face *d* has a temperature gradient of 5°C/μm (for an ablation rate of 0.39 cm/sec) and face *b* a value of 4.1°C/μm (for an ablation rate of 0.31 cm/sec). These values are much greater than the values indicated by the TL measurement since they apply to much hotter regions, namely to a boundary about 200 μm from the surface, and the temperature drops off approximately exponentially with distance.

4. Discussion and conclusions

As one would expect from the complexity and var-

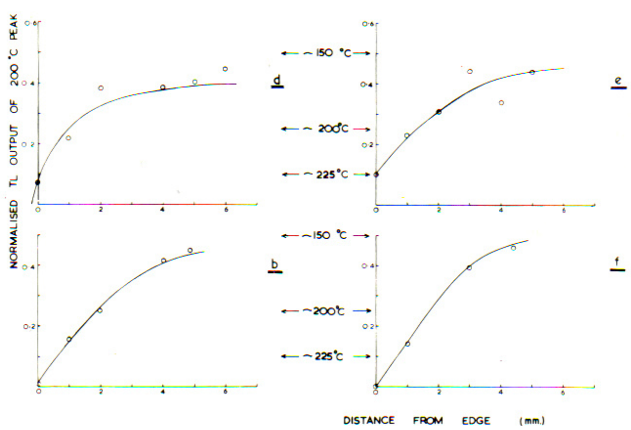

Fig. 5. Drop in thermoluminescence at the edge of the slice, due to atmospheric heating.

ied nature of the mineralogy of Allende, the luminescent properties are very complicated. The TL indicates that at least three kinds of material are responsible, while electroluminescence appears in at least three colours. When structures and associations are taken into account the number of types of electroluminescence rises to at least six.

We believe that the 140°C peak is due to forsterite. The peak at 200°C is very probably caused by cordierite, whilst the most intense luminosity, occupying a range of temperatures between 200 and 500°C, is due to an alteration product of gehlenite. Gehlenite occurs in the aggregates and in a few chondrules. The nature of the alteration is unclear. The luminous material can occur in lines across the gehlenite, as if caused by shock, and around the edges in a way suggestive of reaction with the matrix. Structural changes are probably responsible for the TL in this material since the composition gives no clear indication of a chemical cause. In Ca-bearing minerals it is usually considered that Mn substitution for Ca produces the luminescence [8].

Heterogeneity makes it difficult to determine shape-contours and atmospheric heating gradients for Allende. It has been shown that the 200°C peak tends to more intense on one side of the specimen, which is consistent with the meteoroid fragmenting in the atmosphere rather than the stone being part of a shower before entry. The temperature gradients determined by TL are lower than the values indicated by the fusion crust method since they are a measure of the gradient further into the meteorite. However, the results suggest that *d* is the front and *b* the rear of the stone. The morphology of the specimen, although not conclusive, is consistent with this (Fig. 1).

The effective heating time [7] can be deduced from the fusion crust, and is about 1 sec. The temperature gradients determined by TL indicate oriented flight. One may, therefore, conclude that the fragmentation which produced the stone occurred at least 1 sec before the end of luminous flight, and that for part of this period the stone was oriented.

Acknowledgements

We are grateful to Dr. R.S. Clarke (National Museum of Natural History, Smithsonian Institution) for the donation of the specimen and to Professor Symons and the staff of the Chemistry Department, University of Leicester, for permission to use and help with the ^{60}Co bomb. We also thank Dr. R. Hutchison (British Museum, Natural History) for useful discussions.

References

1 R.S. Clarke, E. Jarosewich, B. Mason, J. Nelen, M. Gomez and J.R. Hyde, The Allende, Mexico, meteorite shower, Smithsonian Contrib. Earth Sci. 5 (1970).

2 S.A. Durrani and C. Christodoulides, Allende meteorite: age determination by thermoluminescence, Nature 223 (1969) 1219.

3 K.Keil and L.H. Fuchs, Hibonite [$Ca_2(Al, Ti)_{24}O_{38}$] from the Leoville and Allende chondritic meteorites, Earth Planet. Sci. Lett. 12 (1971) 184.

4 M.B. Marvin, J.A. Wood and J.S. Dickey, Ca–Al-rich phases in the Allende meteorite, Earth Planet. Sci. Lett. 7 (1970) 346.

5 J.E. Geake, G. Walker and A.A. Mills, Luminescence excitation by protons and electrons, applied to lunar samples, in: H.C. Urey and S.K. Runcorn, eds., The Moon (IAU, 1972).

6 J.E. Vaz, The Lost City meteorite: determination of temperature gradient induced by atmospheric friction using thermoluminescence, Meteoritics 6 (1971) 207.

7 D.W. Sears and A.A. Mills, Temperature gradients and atmospheric ablation rates for the Barwell meteorite, Nature Phys. Sci. 242 (1973) 25.

8 W.L. Medlin, The nature of traps and emission centres in thermoluminescent rock materials, in: D.J. McDougall, ed., Thermoluminescence of Geological Materials (1968) 193.