METEORITES AND THERMOLUMINESCENCE

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The TL techniques that have been developed successfully for archaeological and dosimetric applications cannot be unambiguously applied to meteorites because of the possibility that most or all of the meteorite TL is in dynamic equilibrium — its rate of thermal decay balancing its rate of build-up. In this situation, space irradiation temperature and, thereby, orbital information for the most recent eras (10^5-10^6 years), can be determined. In only a few instances (e.g. meteorites with very low exposure ages) will the possibility exist that equilibrium may not have been reached, but even here it has to be shown that the exposure event had removed previously existing TL before normal TL dating techniques can be employed.

There is some evidence to suggest that the TL sensitivity builds up with time. This raises the possibility of dating major shock and/or reheating events, if it can be shown that such events destroyed the TL sensitivity.

INTRODUCTION

The phenomenon of thermoluminescence has been applied with considerable success in the fields of archaeological dating and radiation dosimetry, and is now in routine use for these purposes (Aitken, 1974; Cameron *et al.*, 1968). The potential usefulness of the technique in meteorite research was recognized as early as the late 1950's by Houtermans and his colleagues (Houtermans *et al.*, 1957; Grögler *et al.*, 1958). Despite the fact that the natural thermoluminescence intensity in meteorites is greater than that in most archaeological specimens (indicating a property which might be usefully exploited) the overall lack of direction of the research has led Cassidy (1977) to remark that thermoluminescence studies of meteorites "have yet to reach maturity." In this paper we review the application of the phenomenon to meteorite research, and — in an attempt to locate the directions of enquiry most useful to pursue — try to identify the reasons for its sustained adolescence.

THE TL PHENOMENON

When ionizing radiation is absorbed by an insulating medium, some of the energy which is dissipated throughout the material excites electrons from

the Valence Band to the Conduction Band across the forbidden gap. The delocalized electrons are now free to move through the crystal until they either recombine with free holes in the Valence Band or until they become "trapped" at a region of crystalline imperfection (*e.g.*, an impurity atom, a lattice vacancy or a dislocation). The probability of release of an electron from a trap is temperature-dependent, so that heating the sample excites the electrons back into the Conduction Band. Thermoluminescence (TL) occurs when a free electron returns to the Valence Band via a luminescence centre, with the emission of a photon of visible wavelength. (For general reference, see Curie, 1963; Garlick, 1949; Randall and Wilkins, 1945.) Although the exact nature of the traps and luminescence centres is known only for a few simple systems, the essential features of thermoluminescence are that it is increased by ionizing radiations and is decreased in a temperature-dependent fashion.

Thermoluminescence results are usually represented as plots of light output against temperature ("glow curves"). The number and temperature of the peaks reflect the number of trap-types and their energy depth below the Conduction Band. For meteorites, the glow curve shape is governed primarily by the mineral responsible for the thermoluminescence (Figure 1). Information about the luminescence centres involved in the TL process is provided by a study of the wavelength spectra of the emitted light, but only a few observations of this type have been made for meteorites (for example, Sun and Gonzales, 1966; Lalou *et al.*, 1970).

APPLICATION TO METEORITE RESEARCH

Dating – Secular Build-up

The archaeological dating and radiation dosimetry applications utilize TL in the same way. The natural glow curve from the sample is first recorded: the sample is then subjected to known doses of artificial irradiation and the artificial glow curves are recorded. From a calibration curve of TL glow intensity against dose of artificial radiation, an estimate of the dose received by the sample in its natural state can be made. To calculate the age of a specimen, the natural dose is divided by the estimated natural dose rate. (For a more detailed discussion, see Aitken, 1973 and Cameron *et al.*, 1968).

Inherent in the use of TL to calculate natural dose levels in this way is the assumption that the TL intensity is directly proportional to the dose received. Before applying the technique to meteorite research it is essential to examine any factors which may invalidate this assumption.

The first point to consider is whether or not there has been any significant thermal drainage of the TL during the period for which the sample is irradiated. The rate of filling traps during irradiation at dose rate r and temperature T_{irr} is
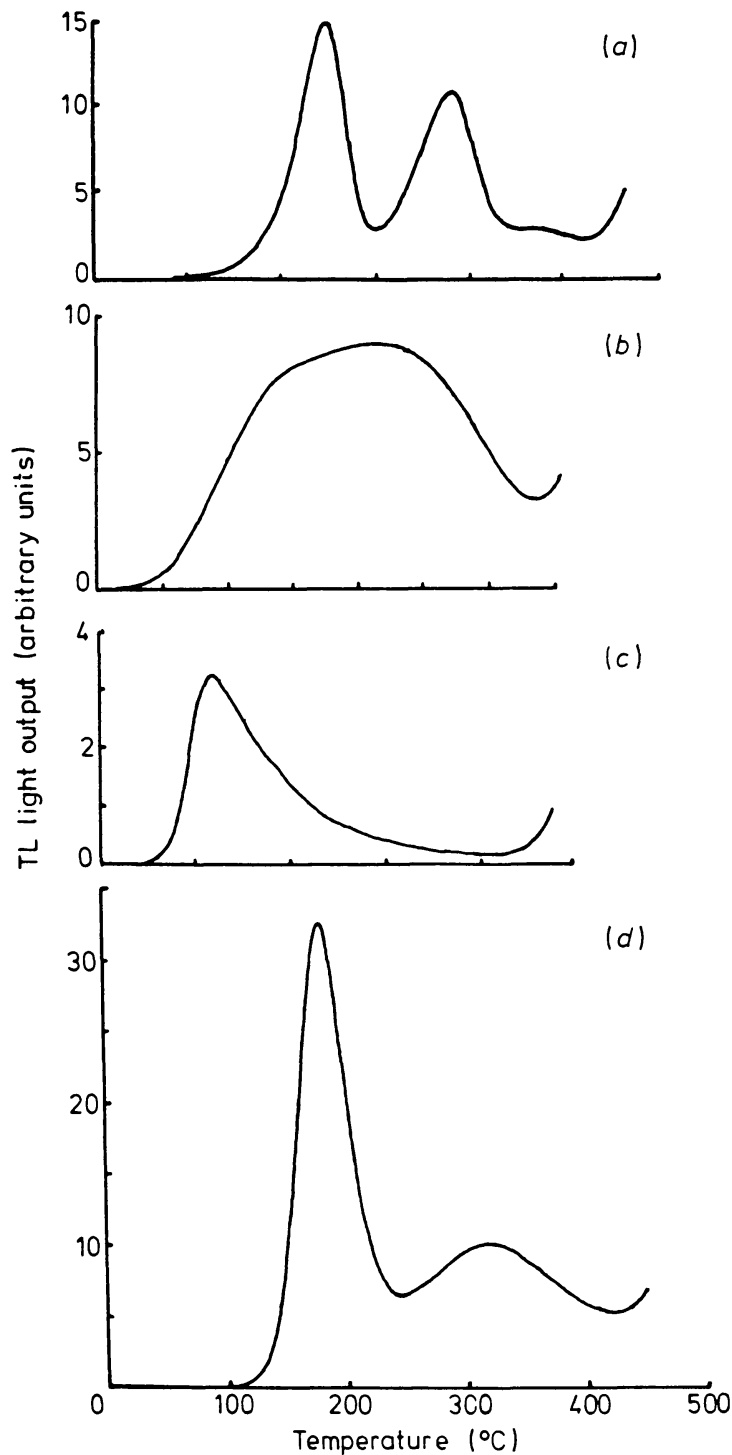
Fig. 1   Glow curves for meteorites of four different classes. (a) The Khor Temiki
aubrite in which the phosphor is enstatite and possibly plagioclase. E
chondrites have the same curve, although less intense. (b) An unidentified
phase associated with gehlenite in the Allende Ca-Al — rich aggregates. (c) The
Kapoeta howardite, after artificial irradiation, in which the phosphor is
plagioclase. In the natural state the TL is extremely weak. (d) The Durala L6
chondrite in which the phosphor is also plagioclase. The reason for the marked
difference in TL between Durala and Kapoeta is noteworthy, and due to no
obvious difference in major elements.

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$$\frac{dn}{dt} = \frac{0.693}{R_{\frac{1}{2}}} (N-n)r - s\,n\,\exp\left(\frac{-E}{kT_{irr}}\right) \tag{1}$$

where n = number of filled traps; N = number of available traps; s = a frequency factor; E = trap depth; $R_{\frac{1}{2}}$ = the dose required to fill half the remaining traps at any stage of the irradiation; and k = Boltzmann's constant.

The first term on the righthand side of this equation governs the rate at which the radiation fills the traps whilst the second term governs the rate at which the traps are thermally emptied assuming first-order kinetics. Non-first-order kinetics would change the equations, but the arguments remain the same. The higher temperature peaks within a glow curve are less likely to be affected by thermal drainage than the lower temperature peaks because of their greater thermal stability. A plot of natural TL/artificial TL against glow curve temperature reflects this behaviour and indicates the glow curve temperatures for which thermal drainage has been insignificant. From Figure 2(a) it is evident that for glow curve temperatures greater than T_S, there has been negligible thermal drainage during the irradiation period, *i.e.*,

$$s\,n\,\exp\left(\frac{-E}{kT_{irr}}\right) \simeq 0$$

and thus

$$\frac{dn}{dt} = \frac{0.693}{R_{\frac{1}{2}}} (N-n)\,r \tag{2}$$

Only glow curve temperatures greater than T_S are used for archaeological dating and dosimetry.

It is evident that in order for the glow intensity (from the region above T_S) to be proportional to the dose (and, therefore, to time) it is necessary that the TL is far below its saturation level [Figure 2(b)]. (Saturation corresponds to all traps full.) This certainly appears to be the case for doses up to ~ 5 krad, equivalent to the archaeological specimens with an age of $\sim 10^4$ years, because this has been tested using specimens of known age. For meteorites, saturation levels appear to be reached with doses of $\sim 10^6$ rad; so, assuming an average dose rate of 1 rad year^{-1} over the meteorite's exposure lifetime, it can be seen that TL cannot be used to calculate exposure ages greater than $\sim 10^6$ years. Valladas and Lalou (1973) have reported saturation in the very high temperature portion of the St. Severin glow curve. The method used by Sears and Mills (1974), by which they claim that almost half of the meteorites they examined were saturated when they entered the atmosphere, is wrong because it fails to take into account the lower thermal stability of the low temperature TL peaks.
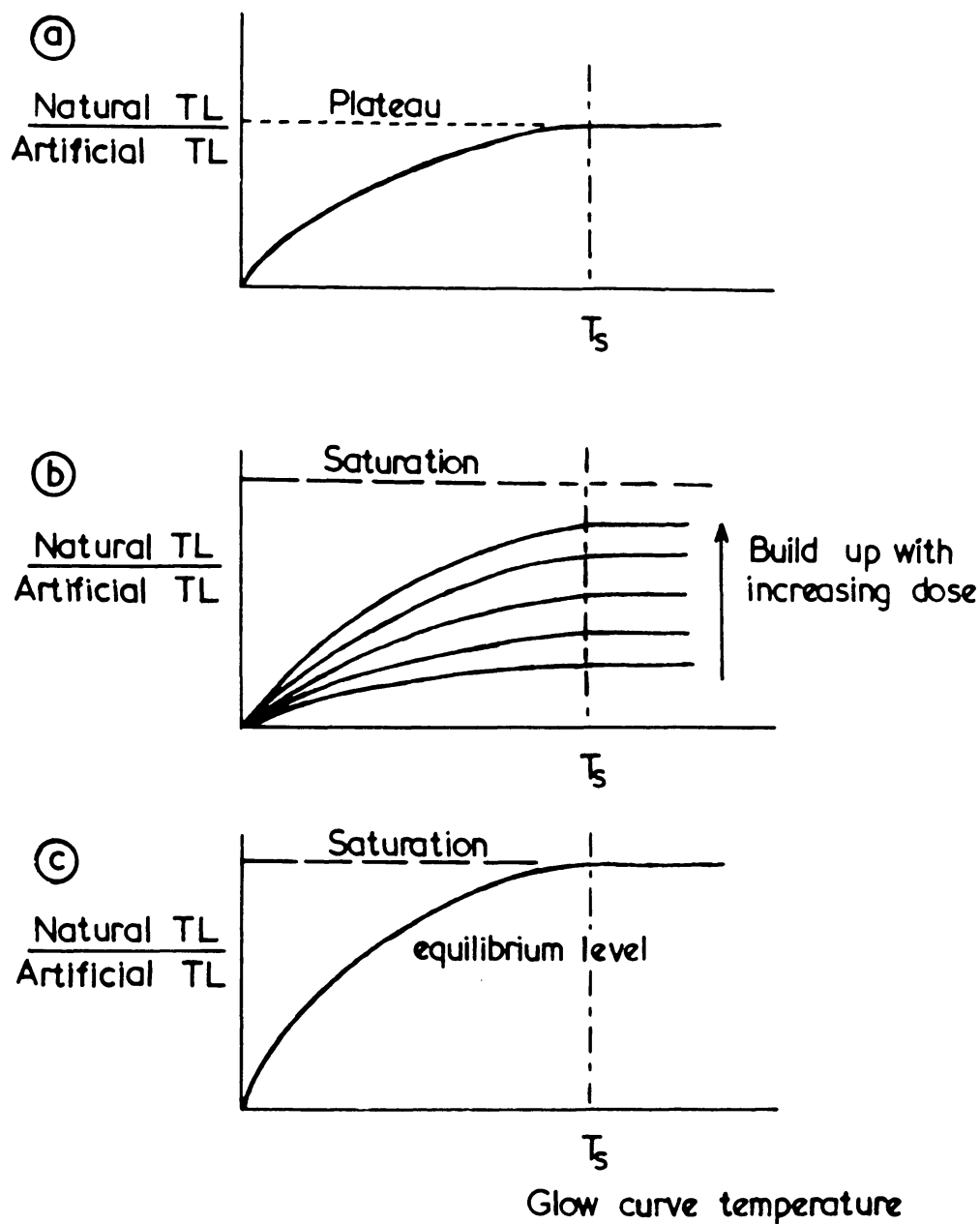
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Fig. 2 (a) Plateau test: Natural TL/artificial TL against glow curve temperature. If the trapped electrons are thermally stable at the temperature of irradiation, then a plateau (*i.e.* constant ratio) is obtained. Any traps giving TL above the temperature T_S are seen to be thermally stable at the natural irradiation temperature; whilst those below T_S exhibit some thermal drainage. (b) Secular build up: Here the level of the plateau above T_S increases with dose up to the saturation level (correxponding to all traps full). (c) Equilibrium: If, for the glow curve regions below T_S, the rate of trap filling equals the rate of trap emptying, an equilibrium level will be established. The level of TL no longer increases with the time even though it is below the saturation level.

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Before TL can be used to determine exposure ages, two extra provisos must be considered. Firstly, the event which the exposure ages are measuring must have set the TL clock to zero; *i.e.*, it must have completely drained the traps (otherwise only a lower limit to the exposure age will be calculated). It is not clear at this stage whether the shock and/or reheating conditions associated with the event are sufficient to do this. Heating to 550 °C will drain the TL and dynamic pressures of 300-500 kbar seem to be required to cause drainage by shock (Liener and Geiss, 1968). Such severe conditions may also give rise to diffusive loss of ^{4}He and ^{39}Ar from the meteorites, and this does not appear to have been the case; although drainage of the TL is likely to be more responsive to high temperatures than gas diffusion.

Secondly, drainage of the TL by other (unknown) processes must not be significant during irradiation. The kinetics of thermal drainage from traps are usually adequately described by the equations of Randall and Wilkins (1945), but recently Wintle (1973) has observed fading of TL from feldspar which does not accord with the Randall and Wilkins model. Similarly, Garlick and Robinson (1972) and Durrani *et al.* (1977) have noted anomalous drainage of TL from some lunar samples. Anomalous fading does not appear to have presented serious problems to the archaeological dating of pottery. However, in the case of meteorite dating, which involves periods of well over 10^4 years, it may well become important.

Attempts have been made to determine ages of three meteorites by direct application of archaeological techniques (Allende, Barwell and Brownfield: Christodoulides *et al.*, 1970; Durrani and Christodoulides, 1969). The authors obtain ages of the order of 10^7 years which they interpret as an upper limit — because not all sources of ionizing radiation were considered — to the exposure ages. If the TL in these meteorites was at equilibrium, these ages would reflect the time taken to reach equilibrium from zero.

Thermal Fading — Equilibrium

In the use of TL to calculate ages, it is necessary that the portion of the glow-curve below temperature T_S (cf. Figure 2) is not used. Nevertheless this portion of the glow curve can provide data of some value. By choosing the low temperature region of the glow curve — for which drainage of the TL was fast enough to be significant even during the meteorite's short life-span on earth — Sears and Mills (1974) used the TL in this region to estimate the terrestrial ages of several chondrites. The use of TL in this fashion has recently been extended by McKeever and Sears (1978) and refined by Melcher (1978). Sears and Mills (1974) also observed that the TL in this region faded faster for breccias than for other, non-brecciated, ordinary chondrites. Similarly, Liener and Geiss (1968) noticed that brecciated and unequilibrated meteorites also had a lower TL in the low temperature region of the glow curve than non-brecciated samples (Figure 4). At the moment

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there is too little evidence to indicate whether the cause of these differences is compositional or structural, or whether it is due to differences in thermal and radiation histories.

Over longer periods of time, thermal fading may become significant over higher temperature regions of the glow curve. If the meteorite is of sufficient age, a point will eventually be reached at which the rate of trap filling equals the rate of trap emptying. Under these equilibrium conditions the TL no longer increases with dose (and, therefore, with time) and yet is still below the saturation level. The level of the equilibrium TL, in relation to the saturation level, is governed by the trapping parameters of the particular trap under study (trap depth E; frequency factor s) and the temperature T_{irr} and rate r at which the sample is being irradiated. Equilibrium conditions now provide the possibility of determining the irradiation temperature. From equation (1), setting $dn/dt = 0$, after Christodoulides *et al.* (1971) we have

$$T_{irr} = \frac{E/k}{\ln\left[\dfrac{sR_{1/2}}{0.693\left(\dfrac{N}{n_{eq}} - 1\right)}\right]} \qquad (2)$$

The importance of determining T_{irr} lies in its strong dependence upon the orbit described by the meteroid during the last few thousand years. Using this technique McKeever and Durrani (1977) have argued that Estacado was on an orbit not too dissimilar to Lost City's. Melcher and Walker (1977) have also attempted to obtain orbital information from TL. They examined the plateau (*cf.* Figure 2) of 30 meteorites and found that two of them (Farmville and Ensisheim) exhibited greater thermal fading throughout the glow curve than the others. This was interpreted as evidence for a very recent passage to within 0.35-0.4 AU of the sun.

Before applying the TL method, it is important to decide whether the TL within the meteorite is in equilibrium or in secular build-up, *i.e.*, still increasing with time. In the parent body at a distance of typically 2.5 AU (or greater) from the sun, the conditions of temperature and dose rate are such that over the long periods of time for which the meteoroid is in this orbit, the TL must be saturated. If the event which perturbed the meteoroid from its original orbit into an earth-crossing orbit also fragmented the meteoroid, then the exposure age will be comparable to the lifetime within the new orbit. Under the new conditions of temperature and dose rate now experienced by the meteoroid, the rate of trap filling can be calculated to be approximately equal to the rate of trap emptying. Hence, if the meteoroid is in the new orbit for a sufficiently long period of time, dynamic equilibrium will be reached. The time required to reach equilibrium will be between 10^5-10^6 years depending, primarily, upon how much (if any) of the TL was removed by the

event which perturbured and fragmented the meteoroid. Exposure age and orbital lifetime calculations indicate that the meteoroids are in an earth-crossing orbit for 10^5-10^7 years, so it can be seen that in all probability the TL within the meteoroid will be in equilibrium. In only a few cases is this probably untrue; namely, for those meteorites of extremely low exposure age. The TL from low ^{26}Al meteorites, with exposure ages of 10^4-10^5 years, may not have reached equilibrium. Instead the TL may still be changing with time. Furthermore, if the fragmentation event completely drained all existing TL so that the TL clock started afresh, then it is possible to determine the exposure age by employing archaeological dating techniques.

Effect of Dose Rate

The temperature of a meteoroid during irradiation plays an important rôle in determining the level of natural TL within a sample, but the dose rate also appears to be an important factor. The dose rate from ionizing radiations from internal sources will be uniform when variations of the order of a centimetre or more are considered. However, ionizing radiations caused by cosmic ray bombardment show considerable variation throughout the meteorite body. Measurements on isotopes (Wright *et al.*, 1973), calculations (Reedy and Arnold, 1972) and laboratory simulations (Lalou *et al.*, 1970) illustrate this well. Variations in the natural TL reflect this phenomenon and they have been observed in many meteorites. An example is shown in Figure 3. Although such studies are aimed essentially at determining production rates for TL by cosmic ray bombardment, an interesting bonus is the calculation of the pre-atmospheric mass and shape (Sears, 1975). The observed variations in the natural TL also illustrate the need to consider shielding corrections in studies of this nature.

Use of TL Sensitivity

Another, and rather intriguing, possibility for TL application to meteorite research was investigated by Houtermans and Liener (1966) and Leiner and Geiss (1968). If a significant number of the traps within the meteorite are produced by radiation damage, then the TL can be used to indicate the time during which trap production (as distinct from trap population) has occurred. Vaz and Sears (1977) have described a number of instances in which artificial TL varies systematically with depth within a meteorite, and this they interpret as an indication that some of the traps are produced by cosmic ray bombardment (or, more accurately, that cosmic ray bombardment can induce increases in TL sensitivity). Liener and Geiss (1968) have also presented data which may be interpreted this way — their figure II.4 is reproduced here as Figure 4. This represents the data from several meteorites which had been grouped together in certain intervals of K-Ar age.
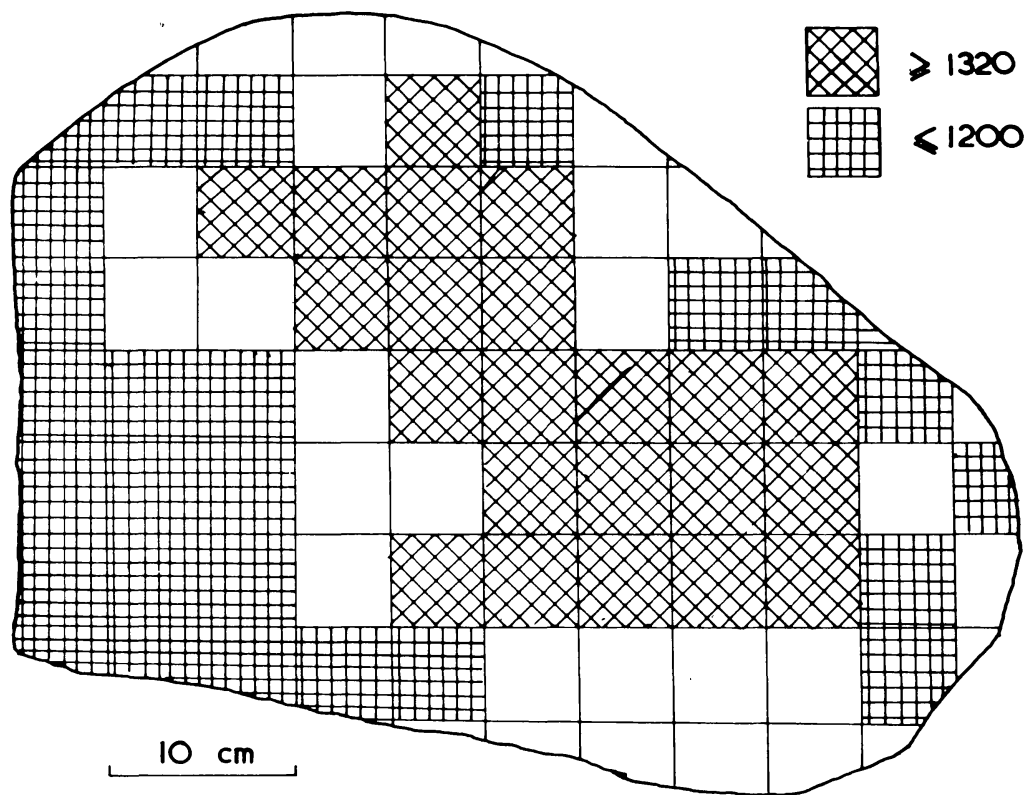
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Fig. 3   A plot of natural TL intensity over a slice cut from the Estacado H6 chondrite. The shaded regions refer to TL intensities, measured in arbitrary units, given in the key. The unshaded regions have TL intermediate between these values.

The samples had been given the same dose of β-radiation so the TL level reflects the samples' sensitivity. The authors found that the correlation between artificial TL and K-Ar age is "definitely established" and cite Komovsky (1961) as having come to the same conclusion. Such a correlation suggests either that the TL sensitivity of the meteorite is increasing with time, due to radiation damage of the sample, or that the process which caused Ar loss also lowered TL sensitivity. Heymann (1967) has shown that the meteorites with K-Ar ages of 500 million years have all been severely shocked and/or reheated, and, although good quantitative data are lacking, it seems clear that both shock and reheating will lower TL sensitivity (Liener and Geiss, 1968). [This may also explain the lack of correlation between TL sensitivity and exposure age (Houtermans and Liener, 1966; Liener and Geiss, 1968). The exposure events, which were too weak to cause any measurable shock symptoms of Ar loss, may also have been too weak to cause loss of TL sensitivity.]
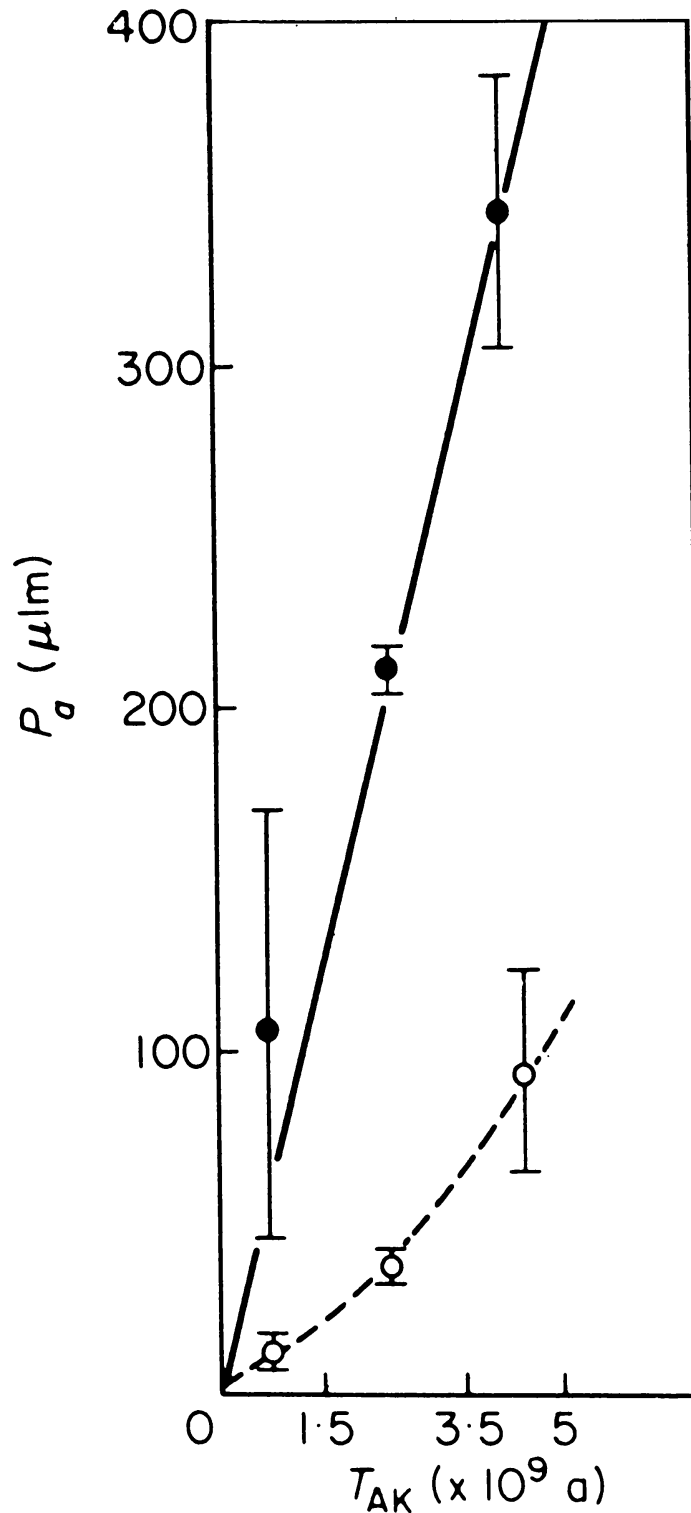
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Fig. 4 A plot of TL intensity against K-Ar age (from Liener and Geiss, 1968). The TL intensity is that observed after artificially irradiating the drained samples to 50 krad using β particles (*i.e.* it is a measure of the sample's TL sensitivity to radiation). The error bars refer to one standard deviation and the samples have been clumped together in K-Ar age intervals of less than 1.5, 1.6-3.5 and 3.6-4.9 aeons. Brecciated and unequilibrated chondrites (open symbols) have lower TL than the other, but all meteorites show a correlation between TL sensitivity and K-Ar age.

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Either or both of these alternatives may be responsible for the observed correlation between TL sensitivity and K-Ar age and, although the true picture will only fully emerge after further experimentation, it does appear that we may have a method of age determination which is independent of established chronology techniques. To a first approximation, it seems to be dating the same events which caused major ^{4}He and ^{39}Ar loss, but specifically it describes an event which reduces TL sensitivity.

CONCLUSIONS

Research on meteorite TL has so far tended to concentrate mostly on the population of traps. This is the quantity most easily measured. However, interpretation is complicated by uncertainty over which situation applies: secular build up, equilibrium or saturation. From a consideration of orbital lifetimes, and the temperature and rate of irradiation of the meteoroids, it seems unlikely that the TL will still be changing with time and, hence, equilibrium should prevail. If this is the case, the most important results to emerge from such studies are estimates of the meteoroid's temperature in space and the implications of these estimates for orbital studies.

For some meteorites the TL may not have reached equilibrium. Such is the case for meteorites with low ^{26}Al concentrations, for which the exposure ages could be determined by normal archaeological techniques, since they are very low. However, it has to be shown that the previously existing TL was destroyed by the exposure event. This can be tested by seeking a correlation between natural TL and exposure age for low ^{26}Al meteorites.

The alternative approach, that of studying TL sensitivity to artificial radiation (rather than studying the TL naturally present), does not have these limitations and holds much promise. Ultimately one may obtain a method of dating the last major shock and/or reheating event, the magnitude of which can be assessed by laboratory calibration.

It is also apparent from our discussion that there are many aspects of meteorite TL for which we simply do not have enough data: brecciation and TL; shock/reheating and TL; characterisation of the traps and trap parameters. The initiation of TL to manhood seems to have been delayed more by the lack of willing foster parents than by the incentive of a good career.

ACKNOWLEDGMENTS

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