Chapter 11

Induced Thermoluminescence and Cathodoluminescence Studies of Meteorites

Relevance to Structure and Active Sites in Feldspar

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The thermoluminescence (TL) sensitivity of meteorites is primarily related to the amount of feldspar present, and since feldspar is formed by devitrification during metamorphism and destroyed during shock these processes may be monitored by its measurement. For instance, the ordinary chondrite class shows a 10^5-fold variation in TL sensitivity as devitrification during metamorphism causes the crystallization of feldspar (the TL phosphor) in the primary igneous glass (which has little or no TL); this is particularly true at the lowest levels of metamorphism. The cathodoluminescence (CL) properties of polished sections of ordinary chondrites also vary systematically with metamorphism and enable petrographic studies of the processes presumably controlling the TL variations to be made. Such studies demonstrate (1) the importance of feldspar in determining the bulk TL properties of meteorites, and (2) that the active sites vary as metamorphism causes compositional, as well as structural, changes in the feldspar. Annealing experiments on meteorites and terrestrial feldspars, and studies of separated components from meteorites, suggest that the high and low temperature forms of feldspar have distinctive TL peak temperatures and widths and thus provide a new means of exploring equilibration temperatures and cooling rates. Induced TL properties have therefore enabled new insights into low-grade metamorphism and devitrification, shock, brecciation and the postulated Martian origin of certain meteorites and their components.

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Probably the first modern reference to meteorite thermoluminescence is that of Herschel (1), although it is possible that the luminescence observed by Howard after passing an electric charge "from 34 square feet of glass" across the Siena meteorite could, in part, have been TL (2). Herschel reported naked eye observations of the TL produced by dust from the Middlesbrough meteorite as it was sprinkled on a hotplate, and he suggested, correctly, that the luminescent component was feldspar.

During this century there has been considerable interest in the application of thermoluminescence studies to the recent history of meteorites. Natural TL provides a means of exploring radiation history and thermal environment in a manner which is complementary to isotopic methods, and the measurement of natural TL is now routine for the numerous meteorites being returned each year from the Antarctic (3,4). However, induced TL measurements have also proved of considerable interest, because the measurements have implications for the earliest history of meteorites. Essentially, the induced TL properties of meteorites are determined, with a few notable exceptions, by the amount and the nature of the feldspar in them, and feldspar is very sensitive to the major processes experienced by meteorites. In the present paper, we describe our recent work on the induced TL properties of meteorites and briefly discuss how these data relate to early meteorite history. We emphasize the relationship between the TL data and mineral properties. We also present here detailed descriptions of the cathodoluminescence properties of primitive meteorites, as these provide new insights into mineralogical controls on TL properties.

Thermoluminescence Sensitivity Variations in Ordinary Chondrites

The largest class of meteorites are the ordinary chondrites; aggregates of olivine, pyroxene, feldspar, Fe,Ni alloys, FeS and over 100 minor and trace minerals. Structurally, they are noteworthy for containing 50-75 volume % of "chondrules", silicate beads, ~100 micron to a few millimeters or so in diameter. Chondrules consist of olivine or pyroxene grains, with a variety of textures, imbedded in a "mesostasis" of glass or feldspar. The origin of the chondrules has long perplexed meteorite researchers, most modern workers preferring a theory in which pre-existing dust was flash melted and allowed to cool rapidly. The aggregates of dust, metal, sulfide and chondrules are presumed to have formed in the early solar system as part of the process which formed the planets, and there is some evidence that grains of pre-solar origin may also be present in certain meteorites. Once formed, these aggregates accumulated into the parent bodies of the present meteorites, and on these bodies a number of secondary processes occurred, such as metamorphism, shock, brecciation and aqueous alteration. Fortunately, not all ordinary chondrites suffered all these processes to equal degree, and a fruitful line of enquiry has been to sort the meteorites according to the degree of alteration. This has not only enabled particularly significant individual meteorites to be identified, but is also leading to an improved understanding of the various processes. For metamorphism, Van Schmus and Wood have developed the highly successful petrologic types 1-6 (5). Time has led to a better understanding of some of the geological parameters used in the scheme, and it now appears that the least metamorphosed ordinary chondrites are type 3 and the most heavily metamorphosed are type 6; there are also one or two partially melted individuals sometimes described as type 7.

The level of thermoluminescence that can be induced in an ordinary chondrite (i.e. the "TL sensitivity") shows a 10^5-fold range, which is related to petrologic type (Figure 1). The type 3 chondrites alone show a 10^3-fold range, and several of the petrologic parameters that enable types 1-6 to be defined vary with TL sensitivity within the type 3 ordinary chondrites (6), suggesting that metamorphism is responsible for the range in TL sensitivity. On the basis of the TL data, it would seem that the type 3 chondrites, although clumped together by Van Schmus and Wood and others, exhibit a range of metamorphism comparable to, or perhaps greater than, the other types put together. Since the type 3 ordinary chondrites are especially significant, as they best represent the least altered solar system material available in our laboratories, subdivision of type 3 into types 3.0-3.9 has proved worthwhile. The scheme is now widely used and has enabled several new insights into the metamorphic process and the nature of unaltered solid solar system material.

Van Schmus and Wood used the relative abundance of glass and feldspar as an important criterion in establishing the petrologic types (5). In type 3 chondrites, there appears to be no feldspar, but instead there exists a glass of, approximately, feldspathic composition. In type 4 chondrites, this glass becomes translucent, and in type 5 chondrites grains of feldspar <50 microns in size have crystallized in the glass. In type 6 chondrites, the grains have grown to >50 micron. Mineral separations by French researchers have confirmed Herschel's suggestion that the phosphor in ordinary chondrites, at least in the type 5 or 6 (sometimes called the 'equilibrated' ordinary chondrites), is feldspar (7). It was therefore suggested that the range of TL sensitivity observed in the ordinary chondrites reflects the amount of feldspar in the meteorite and that the reason for the relationship between TL sensitivity and metamorphism was that unmetamorphosed meteorites contain glass which crystallizes during metamorphism to produce feldspar (6). This being so, TL sensitivity is capable of determining the relative abundance of feldspar when it is present in the meteorite in trace amounts, far

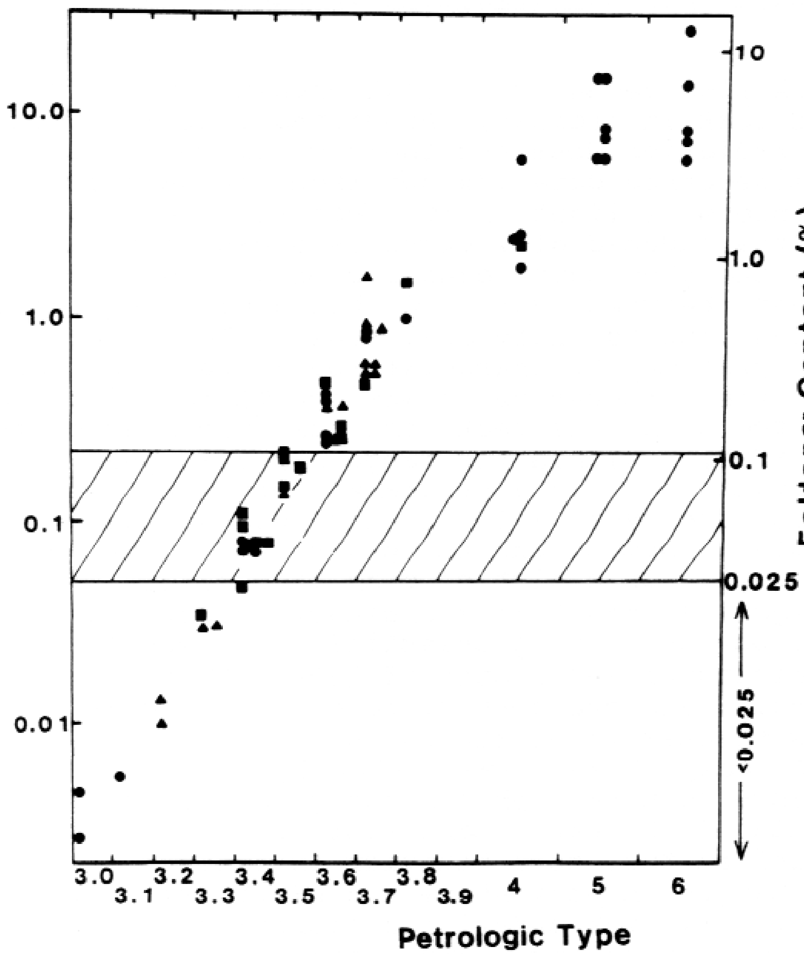


Figure 1. Plot of thermoluminescence sensitivity against petrologic type (5,6), which reflects the degree of metamorphic alteration : 3, least metamorphosed; 6, most metamorphosed. The feldspar scale is calculated on the assumption that the TL sensitivity is directly proportional to feldspar abundance and type 5,6 chondrites typically contain about 8% of this mineral. The cross-hatched region refers to TL sensitivity levels at which the feldspar is thought to be in the low-temperature ordered form (see Figure 13). The symbols refer to the three data sources (6,8,14). (Reprinted by permission from Ref. 31. Copyright 1986 American Geophysical Union.)

below the detection limits of X-ray diffraction and even electron microscopy. The "detection limit" for the feldspar is determined by the presence of other phosphors and is approximately 0.025wt%.

Metamorphism-Related Variations in Thermoluminescence Peak Shape

Early work also revealed a relationship between the shape of the TL peak in ordinary chondrites that was induced by a standard radiation dose and their metamorphic history (8). Thermoluminescence data are obtained in the form of "glow curves", plots of light emitted against temperature. The shape of the induced glow curve is shown in Figure 2. Typically the glow curve consists of a single broad band of luminescence between 100-250°C; the band is a composite of several overlapping individual peaks. The apparent composite peak may be characterized in terms of peak temperature (the temperature of maximum TL emission), and the width of the composite peak (the full-width at half-maximum, FWHM). Within the range 3.2-3.9, peak temperature and peak width vary in a systematic way with petrologic type. (For the types 3.0-3.1, the peak shapes vary widely from sample to sample and the peaks tend to be very broad and hummocky). On a plot of peak temperature versus peak width (Figure 3) the type 3 ordinary chondrites produce two clusters, one consisting essentially of type 3.2-3.5 with peak temperatures and widths of 120-160°C and 80-130°C, respectively, and one consisting of essentially of types 3.5-3.9 with peak temperatures and widths of 160-220°C and 140-180°C, respectively (9). Clearly, there is information of relevance to metamorphic history contained in the shape of the induced TL peak. Laboratory experiments, described below, confirm that this behavior is typical of feldspar and the changes in peak shape and width are controlled by thermal history; the underlying mechanism is associated, in a complex way, with structural changes in the feldspar lattice.

The Characterization and the CL and TL Properties of Feldspars and Feldspathic Materials

In natural systems such as ordinary chondrites, with their bewildering array of minerals and mineral chemistries, reasonable interpretation of the meteorite TL trends need further investigation which is best achieved using a variety of approaches. We have tested the idea that crystallization of the glass was the major process affecting TL sensitivity and that the peak width and temperature changes were related to disordering by three sets of measurements. (1) We examined the cathodoluminescence of a suite of type 3 ordinary chondrites of various petrologic types, and performed complementary analytical studies with the electron microprobe, to characterize in

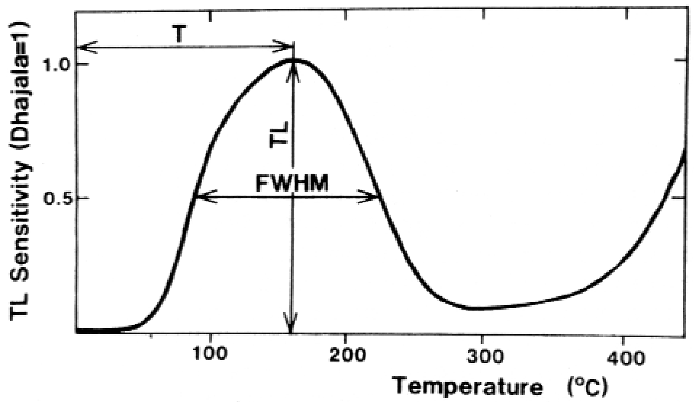


Figure 2. Typical glow curve for an ordinary chondrite meteorite (in this case Dhajala) showing how peak temperature (T), peak width (FWHM) and TL sensitivity (TL) are measured. TL sensitivity is the level of TL emitted at the peak divided by the same quantity for an arbitrarily chosen meteorite, Dhajala (14). (Reprinted by permission from ref. 14. Copyright 1983 American Geophysical Union.)

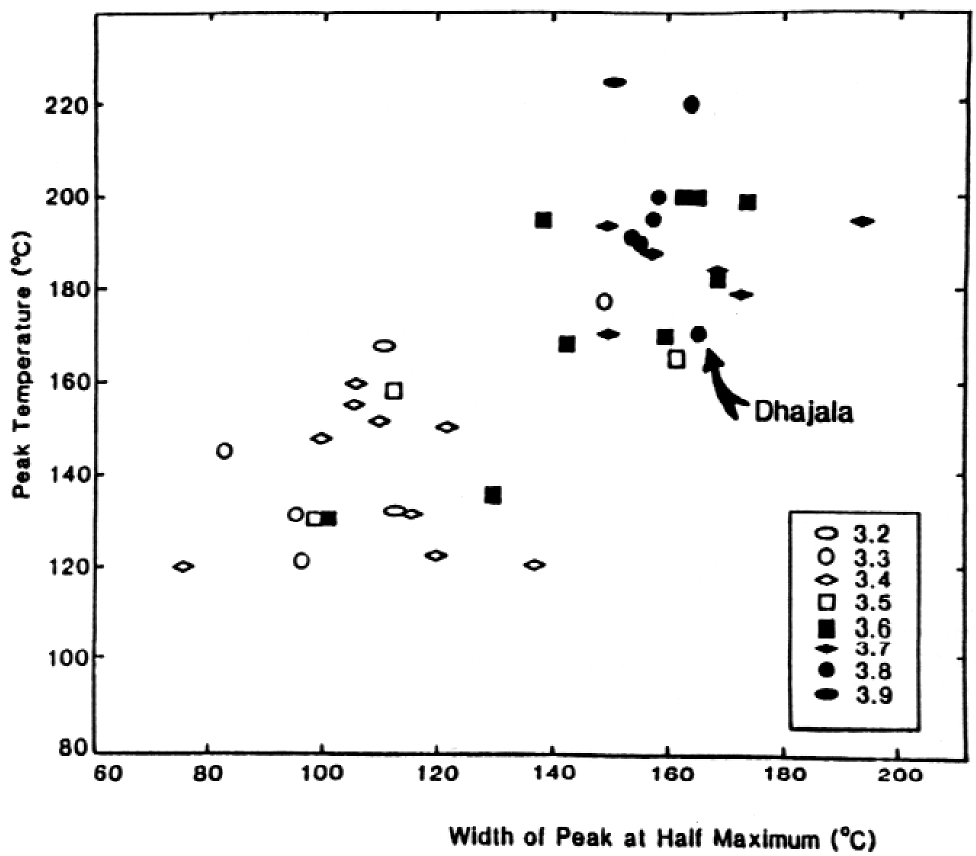


Figure 3. Peak temperature against peak width for type 3.2–3.9 ordinary chondrites. The petrologic types are indicated by the symbols. (Reprinted with permission from ref. 9. Copyright 1985 Pergamon.)

detail the CL and compositional properties of the luminescent material (most of which is feldspathic) and their relationship to metamorphism. (2) We attempted to reproduce the increase in TL sensitivity by treating low type meteorites in a way that would cause crystallization of the glass. Both studies confirmed the original theory for the TL sensitivity-metamorphism relationship, but both studies also revealed new and significant details. (3) We have also performed laboratory annealing experiments on meteorites and terrestrial feldspars and found that we could reproduce the meteorite TL peak temperature and width trends. X-ray diffraction measurements of the annealed terrestrial feldspar showed that the trends are probably related to disordering but that the details are not well understood.

Cathodoluminescence Studies of Type 3 Ordinary Chondrites

Our photomosaics of the cathodoluminescence of a suite of type 3 ordinary chondrites are presented as Figs. 4-7. To obtain these photomosaics, a Nuclide Corporation "Luminoscope" was attached to a standard petrographic microscope and a defocussed electron beam (typically 1 cm x 0.7 cm), operated at 14±1 keV and 7±1 μA, was directed onto a polished section of the meteorite using hand magnets. Photographs were taken at 50x using a 35mm camera with Kodak VR400 film and exposure times of 1.0-2.5 minutes. The commercial C-40 process was used for development. Each photomosaic consists of 30-40 photographs.

In terms of their CL, as well as many other properties, Semarkona is unique, and Bishunpur and Krymka are unusual and share several of Semarkona's properties (Figure 4). On the basis of these CL properties, Krymka has been reassigned type 3.1 from our previous TL-based assignment of type 3.0. These three low-type ordinary chondrites (type 3.0-3.1) contain a great diversity in: (1) CL color, (2) kinds of components displaying CL, and (3) the textures of the CL-bearing components. Chainpur and Allan Hills A77214, both type 3.4, have relatively few CL-bearing components, but the most noteworthy are the mesostases of the chondrules (Figure 5a,b). The fine-grained smoke-like matrix that produced red CL in Semarkona, and little CL in Bishunpur and Krymka, shows virtually none in the two type 3.4 chondrites. With petrologic types >3.4 the proportion of chondrules showing CL increases, and at even higher types the matrix begins to show blue CL, but the intensity, color and texture of the CL of the matrix suggests that it may simply be chondrule fragments (Figure 6). Ngawi is a spectacular example of a breccia, a rock composed of fragments of previously existing rock, in which there are fragments of type 3.1 material in a host which is a mixture of types, but predominantly type 3.6 (Figure 5c).

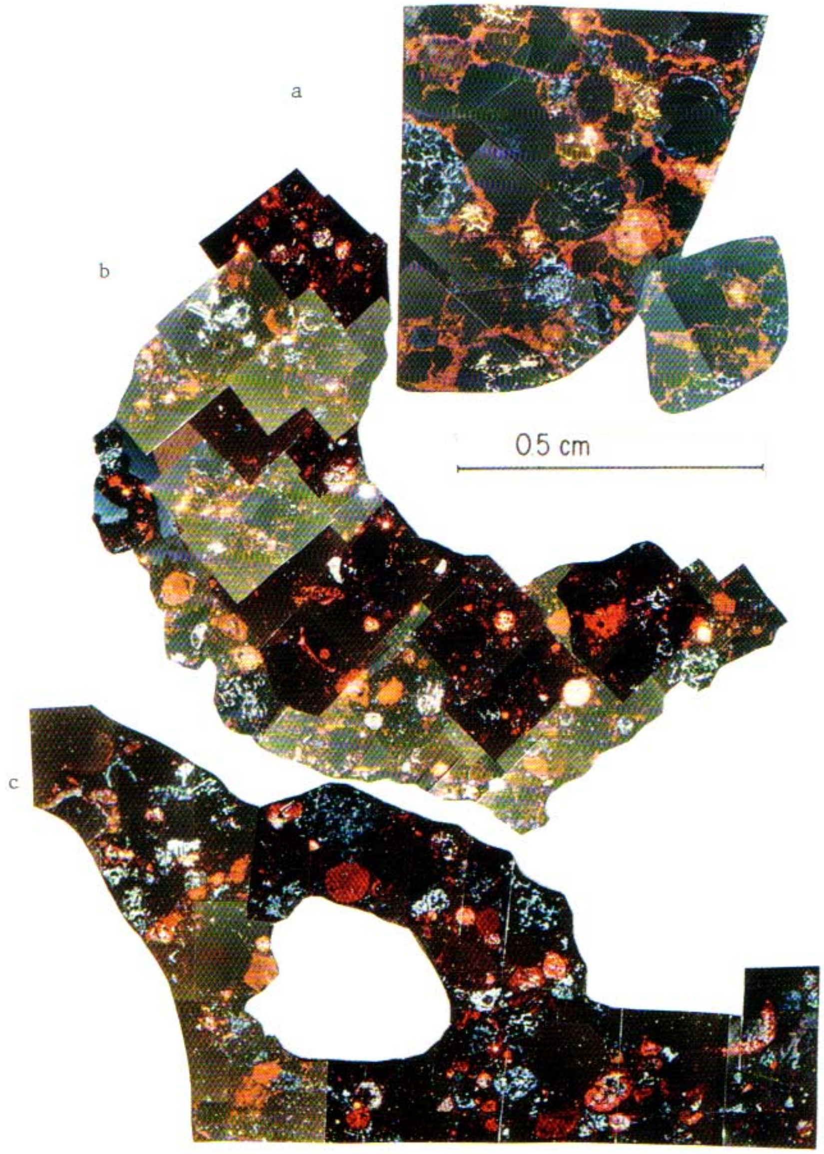


Figure 4. Photomosaics of the cathodoluminescence of three low petrologic type meteorites; (a) Semarkona (type 3.0, top), (b) Bishunpur (type 3.1, middle), and (c) Krymka (type 3.1, bottom). The scale bar shown refers to Semarkona, the scale bar for the others is the same as in Figure 5. In general, red luminescence is produced by Fe-free olivine and pyroxene, and blue and yellow CL is produced by chondrule mesostases of plagioclase composition.

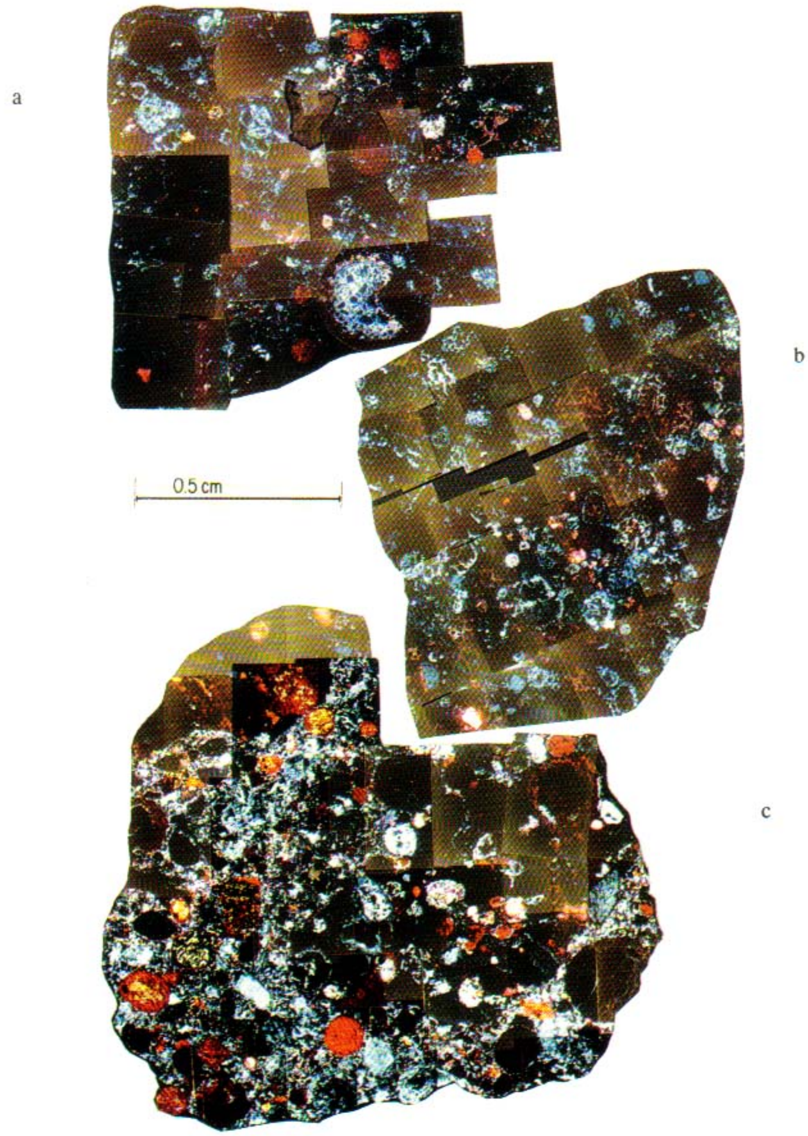


Figure 5. Photomosaics of the cathodoluminescence of three intermediate petrologic type meteorites; (a) Chainpur (type 3.4, top), (b) Allan Hills A77214 (type 3.4, middle), and (c) Ngawi (host predominantly type 3.6 containing clasts of type 3.1, bottom). With increasing petrologic type, the diversity of CL properties within a meteorite decreases, red luminescent material becomes scarce and blue material becomes more abundant.

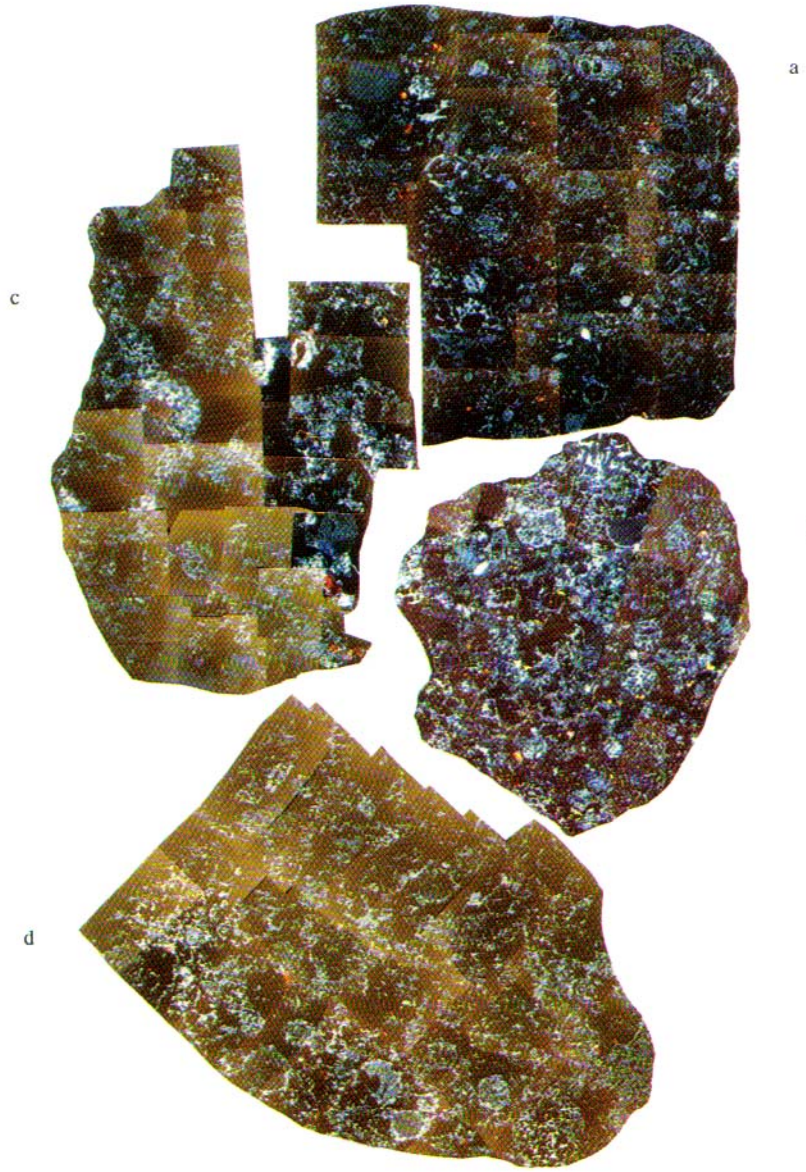
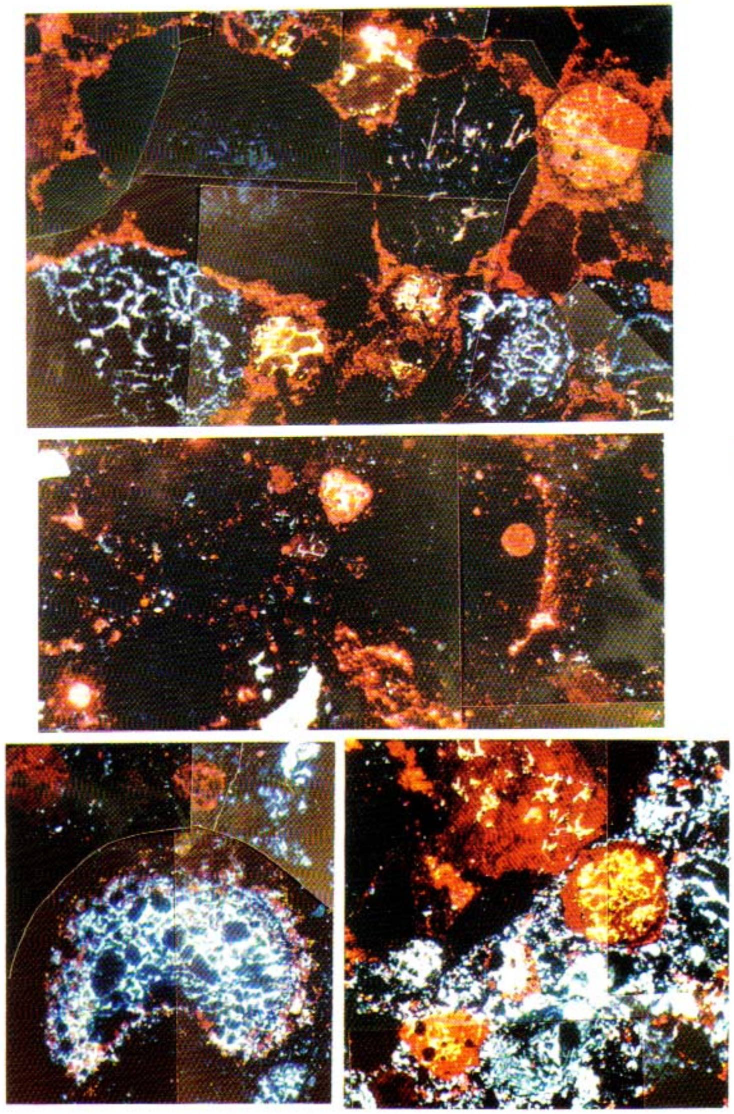


Figure 6. Photomosaics of the cathodoluminescence of four meteorites of types 3.7-5; (a) Hedjaz (type 3.7, top right), (b) Dhajala (type 3.8, center right), (c) Bremervorde (type 4, center left), and (d) Barwell (type 5, bottom). Scale bar, as in Figure 5. These relatively high petrologic type chondrites show a uniform blue feldspar CL, with only an occasional phosphate grain with red CL.



a

b

c

d

Figure 7. Details from four photomosaics of the cathodoluminescence of type 3 ordinary chondrites. (a) Detail from Semarkona (top, horizontal field of view 5.0 mm). (b) Detail from Bishunpur (middle, horizontal field of view 3.5 mm). (c) Detail from Chainpur (bottom left, horizontal field of view 2.0 mm). (d) Detail from Ngawi showing the boundary between type 3.1 clast material in the top left half of the field, and the host matrix of type 3.6 material (bottom right, horizontal field of view 2.3 mm).

We have analyzed the cathodoluminescent phases in four of these meteorites in detail (10-12), and found that a major source of CL is the chondrule mesostasis and it is those mesostases which most readily crystallize that first display CL as the level of metamorphism experienced by the meteorite increases. Some of the analytical data obtained with the electron microprobe are shown in Figure 8, a plot of CaO against Na_2O. The regression line through the luminescent chondrule mesostases has a slope with a CaO/Na_2O ratio corresponding to the feldspar, plagioclase (a solid solution of albite, $NaAlSi_3O_8$, and anorthite, $CaAl_2Si_2O_8$). Chondrules whose mesostases are either not luminescent, or only weakly luminescent, have compositions which are rich in quartz (SiO_2). The other CL-producing phases in Semarkona and the other low types are not yet well studied, but are usually Fe-free olivines and pyroxenes. With these important exceptions, the CL in ordinary chondrites is almost entirely produced by feldspar, whose composition homogenizes with increasing metamorphism. Some of the trace minerals in ordinary chondrites, like calcium phosphates and rare Ca-Al rich minerals, show CL in the higher types, but do not contribute significantly to the bulk TL properties of the meteorites.

A surprise difference between the chondrule mesostases of Semarkona and Krymka was that while the luminescent chondrule mesostases in Krymka luminesce blue, in Semarkona, chondrule mesostases display yellow CL when the mesostasis is calcic in composition and blue CL when they are sodic (Figure 8). Calcic compositions differ from sodic compositions in that they crystallize more readily, and, in terrestrial weathering studies, react more readily with water than sodic feldspars. It is probable that the yellow CL may be signalling aqueous alteration or the presence of a metastable phase easily destroyed by metamorphism.

The detailed CL trends displayed by the type 3 ordinary chondrites are therefore a unique means of determining not only the mineralogical factors affecting TL sensitivity, but they also provide a new means of examining the compositional (by complementary electron microprobe analysis) and structural (i.e. petrographic) changes associated with metamorphism-induced changes in CL properties. In the next few sections we summarize the CL properties of the ordinary chondrites.

Semarkona (3.0) (Figure 4a, detail Figure 7a). The ubiquitous fine-grained, opaque matrix in Semarkona, which appears interstitial to all the major components, produces a distinctive uniform red CL. There appears no perceptible difference in CL between the matrix material that rims chondrules and that which lies between chondrules, although some workers have argued that there is a compositional difference. There are also a small proportion of the chondrules which contain euhedral grains with red CL, and some chondrules appear a uniform dull

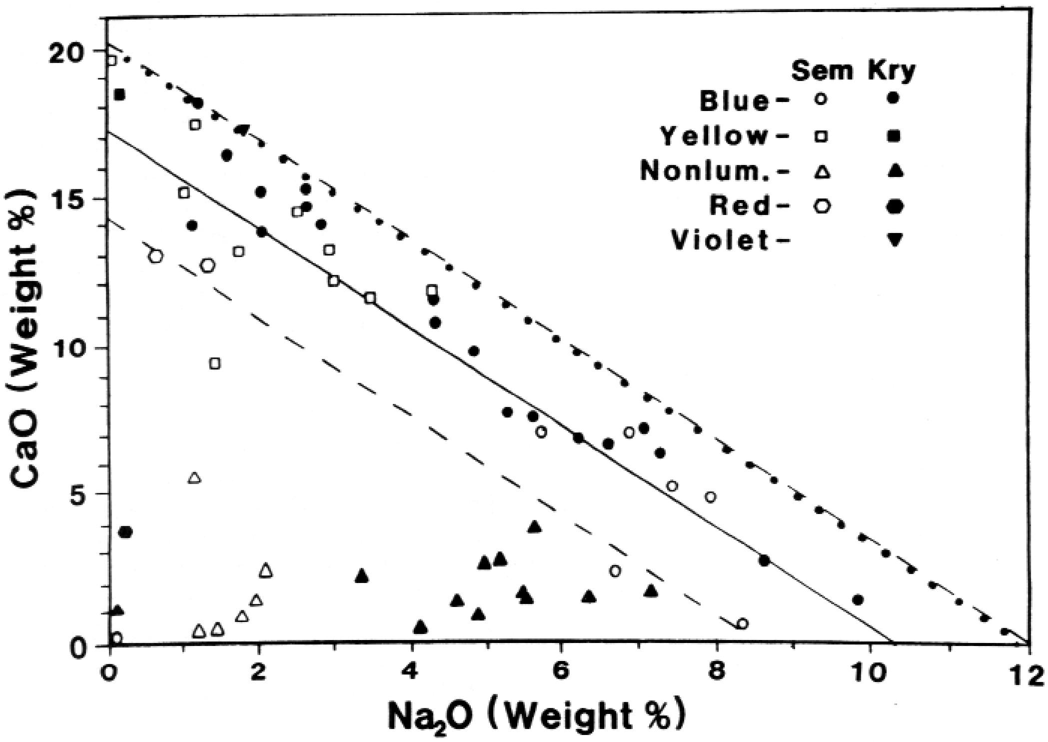


Figure 8. Plot of CaO against Na_2O for the chondrule mesostases in Semarkona and Krymka. The diagonal line is a regression line through the data for mesostases which luminesce and the broken lines refer to 2 σ uncertainties on the intercepts of this line. The dotted line refers to the theoretical line for plagioclase. (Reprinted by permission from Ref. 11. Copyright 1987 Lunar and Planetary Institute.)

red. In the case of the chondrule grains, and probably also the matrix, the red CL is being produced by low-Fe olivine.

The glassy mesostases of the chondrules may show either yellow or blue CL, or be non-luminescent. In many instances, usually larger chondrules, there are large uniform areas of yellow luminescing mesostasis enclosing non-luminescent euhedral grains, while in other instances the yellow material and the enclosed grains have a very fine texture. There are many spectacular instances of yellow mesostasis enclosing euhedral grains with red CL, the proportion of red grains to yellow mesostasis varying considerably from chondrule to chondrule. Some of the blue luminescing chondrule mesostases in Semarkona are bright enough to grade into white on the photomosaics, while several particularly large chondrules have centers which luminesce dull-blue, and there are several irregular-shaped fine-grained objects that luminesce blue. Additionally, some chondrules have strings of fine-grained material on their circumference.

<u>Bishunpur (3.1) (Figure 4b, detail Figure 7b)</u>. The interstitial material that most resembles the fine-grained material in Semarkona, has quite different CL properties in Bishunpur; it is largely non-luminescent, but where it appears to show some luminescence, the grains are coarse and irregularly scattered throughout the matrix and display red CL. Although it is difficult to be sure, it seems that the very fine-grained non-luminescent interstitial matrix is the primary dust (termed "Huss matrix" by some workers), while the coarse-grained material is composed of chondrule fragments. The chondrules sometimes contain red euhedral grains, in some cases with blue luminescent mesostases. Chondrule mesostases are either non-luminescent or show blue CL, and often the intensity is so high, relative to the red luminescence, that they quickly grade into over-exposed white features. Chondrules with yellow mesostases are rare. A few blue/blue-white chondrules are irregular and fine-grained.

Overall, the CL properties of Bishunpur are very distinct from Semarkona, the luminescence being lower in intensity, less diverse in color and the grains coarser and less well developed.

<u>Krymka (3.1) (Figure 4c)</u>. Like Bishunpur, the material analogous to the fine-grained matrix in Semarkona does not luminesce, except for occasional isolated grains. Chondrule mesostases are either non-luminescent or show blue/blue-white CL, but occasional fine-grained objects are also present. The grains within the chondrules are generally non-luminescent, but in a few instances luminesce red, and there is one instance in our section of lathes of red euhedral grains imbedded in a red mesostasis with the composition of Fe-free, calcic pyroxene. A few chondrules contain fine-grained material, surrounding material with red luminescence.

<u>Chainpur (3.4) (Figure 5a, detail Figure 7c)</u>. Like Bishunpur and Krymka, Chainpur has much less luminescent material than Semarkona, but there are some noteworthy exceptions to this generalization. The matrix material is virtually all non-luminescent, although there are regions where relatively coarse and irregularly dispersed blue grains occur. However, the chondrule mesostasis is either non-luminescent or shows bright luminescence (grading into overexposed blue/white), and

in this form the appearance can be quite spectacular. A few chondrules contain grains which show red CL, some are very low in intensity, and there are a few isolated grains with red CL which may be chondrule fragments. One large chondrule with a bright blue luminescing mesostasis has a string of fine red grains encircling it (Figure 7c). There is also a large region of chondrule mesostasis which appears purple to the naked eye. There are also many fine-grained irregular shaped objects with blue luminescence, and several isolated grains with blue interiors and red exteriors; presumably the isolated olivine grains described by Steele (13).

Allan Hills A77214 (3.4) (Figure 5b). Chondrule mesostases in Allan Hills A77214 (ALHA 77214) show either blue/blue-white or dull-red to purple CL, and in several cases it is only the mesostasis near the outer perimeter of the chondrule that luminesces. The electron microprobe data show that these regions are also higher in Na than the more central mesostasis regions (12). As in Chainpur, the matrix shows very little cathodoluminescence, only a few areas of coarse grains with blue CL are randomly scattered throughout.

Ngawi (clasts of type 3.1 in a brecciated host of mean type 3.6) (Figure 5c, detail Figure 7d). Ngawi shows a spectacular range of CL colors and textures, consisting primarily of a brecciated "host" of high type 3 material and clasts of low type 3 material. The host does not resemble any particular type 3 ordinary chondrite in its CL properties, but appears to consist of fragments resembling type 3.6 to type 4 material enclosing chondrules with a variety of CL properties, similar to those in Semarkona, Bishunpur and Krymka; yellow mesostases enclosing red euhedral grains, bright to dull red chondrules, non-luminescent chondrules. There are two clasts in our section, both resemble Bishunpur and Krymka in their CL properties; the interface between the type 3.1 clast material and type 3.7 host material is shown in Figure 7d. The clasts both contain spectacular chondrules with a variety of CL textures and colors, and virtually a non-luminescent matrix. One of the clasts contains matrix with occasional dull red grains, similar to that in Bishunpur.

Hedjaz (3.7) and Dhajala (3.8) (Figs. 6a and 6b). In many chondrules, the mesostasis is an intense blue (grading into white), while in approximately half of the chondrules the mesostasis is a dull-blue grading into purple. In both cases the mesostasis often exists as large uniform fields. In Hedjaz and Dhajala, the interchondrule material is also producing blue CL, but the intensity is consistently lower than that of the bulk of the chondrules, so that the chondrules and their interior textures stand out clearly. In Hedjaz, much of the matrix contains occasional grains of very dull red material, reminiscent of the matrix of Bishunpur and Krymka but much less abundant.

Bremervorde (4) and Barwell (5) (Figs. 6c and 6d). Bremervorde is a breccia of type 3.8 and type 4 (14); our section is entirely type 4 material. Chondrule mesostases luminesce brightly, often highlighting chondrule textures. The non-chondrule silicate portions of the meteorites appear to consist of fragmental material similar to the chondrules in its CL colors and intensities; clearly any interstitial material present is quite different to the matrix in the previous meteorites. Thus the CL of Bremervorde and Barwell is almost entirely blue, due to feldspar, with only occasional isolated grains of phosphate minerals with red CL dispersed throughout the sections.

Increasing levels of metamorphism therefore destroy the red luminescence typical of olivine and pyroxene in types 3.0-3.1 by causing Fe levels to homogenize and Fe-free olivines and pyroxenes to disappear. Similarly, metamorphism causes chondrule glass to devitrify, sometimes also converting the quartz-rich mesostases to feldspar-rich mesostases in the process. The usual CL color for feldspar in ordinary chondrites is blue (probably due to Mn^{2+} activation), but a highly unstable phase (with bulk feldspar composition but of unknown identity) in Semarkona has yellow CL and a weakly luminescing material of feldspar composition in Allan Hills A77214 has dull-red purple CL (possibly Fe^{3+} activated feldspar). The CL data for this metamorphic suite of ordinary chondrites therefore not only provides further insight into the processes accompanying metamorphism, they provide fresh data on active sites in feldspar. These points are discussed at length by DeHart, Lofgren and Sears (Geochim. Cosmochim. Acta, in press).

Laboratory Studies of the Induced Thermoluminescence Properties of Ordinary Chondrites and Feldspar

Our attempts to explore the role of devitrification, in determining the TL sensitivity of ordinary chondrites, are partially summarized by Figure 9, a series of glow curves for the Sharps type 3.4 chondrite. Samples were annealed at 755-855°C with various quantities of water and sodium disilicate, agents which facilitate the formation of feldspar from glass in conventional phase diagram studies (15), in sealed gold vials at a pressure of 1000 atmospheres. In the Sharps case, the TL sensitivity increased by a factor of 3. A subsequent, detailed series of annealings for four type 3 ordinary chondrites produced more spectacular increases in TL sensitivity. The Semarkona meteorite underwent a 40-fold increase in TL sensitivity after annealing at 900°C for 168 h (Figure 10). The data confirm the idea that the increase in the TL sensitivity of ordinary chondrites as a result of increasing metamorphism is caused by the formation of feldspar via the crystallization of primary glass.

We also observed, during the annealing experiments on Semarkona and Allan Hills A77214, that annealing under relatively mild conditions did not cause an increase in TL sensitivity, but rather caused a significant (factor of 10 or so) decrease in TL sensitivity. Either activators were being affected, or the phosphor was being physically destroyed by reaction with the water in the capsules. Simultaneously with the production of these data, Hutchison et al. reported the observation of calcite and hydrated

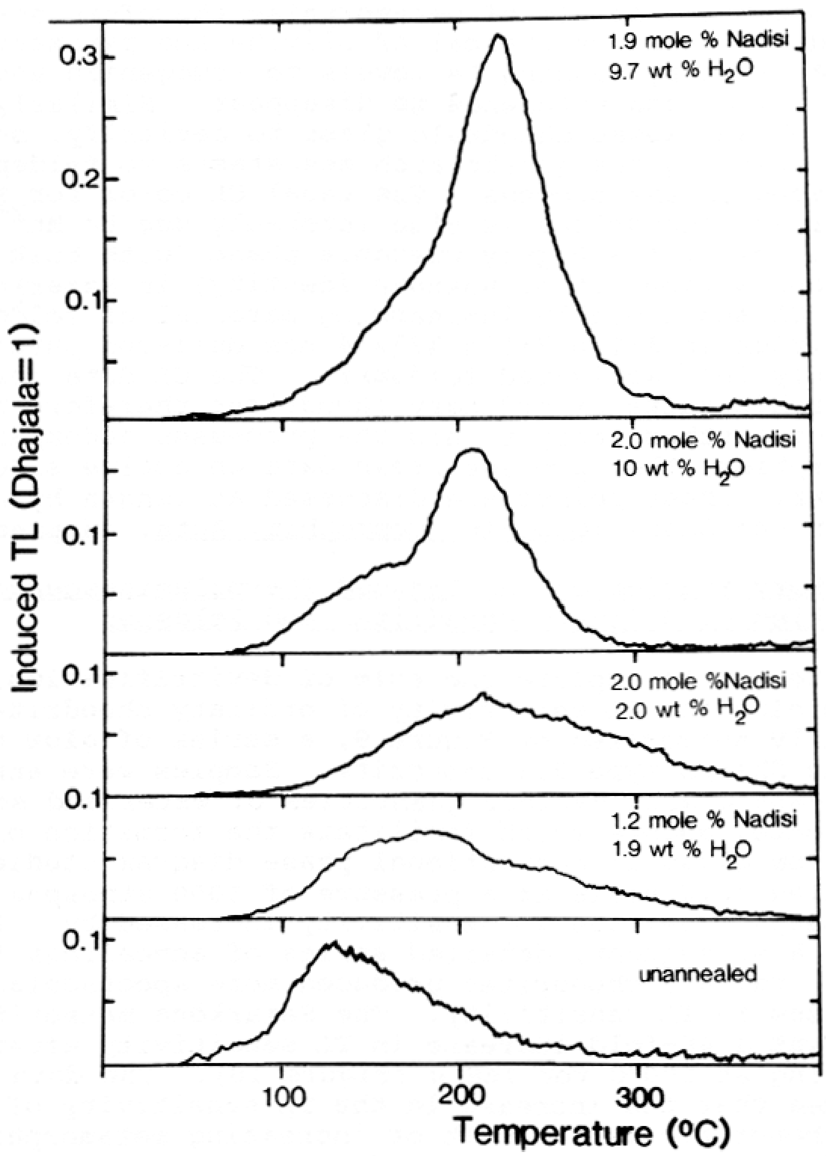


Figure 9. Glow curves for the Sharps meteorite (type 3.4) before and after annealing at 755-855°C and 0.77-1 kbar for 168-174 h in the presence of water and sodium disilicate. (Reprinted by permission from Ref. 31. Copyright 1986 American Geophysical Union.)

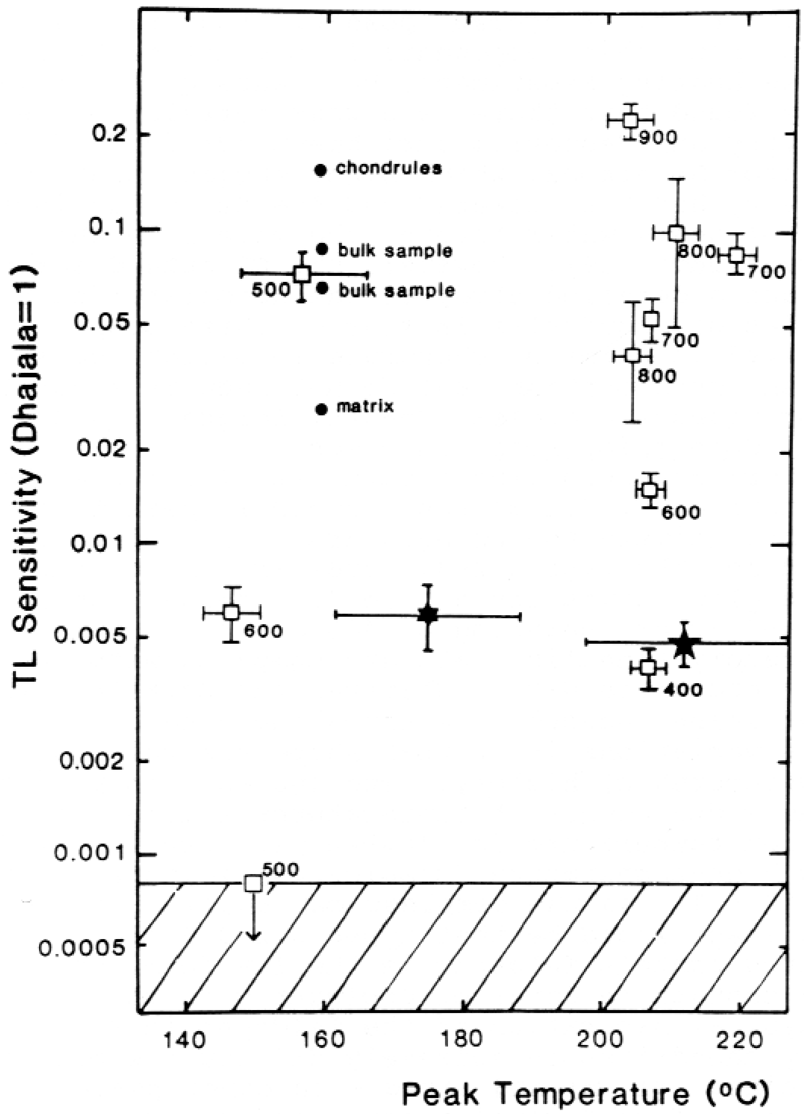


Figure 10. Samples of the Semarkona meteorite annealed at 1 kbar at the temperatures indicated (°C) for 168 hours, in the presence of water and sodium disilicate. The stars refer to data for samples of the unannealed material, which is very heterogeneous, and the dots refer to four samples produced by subdividing the sample responsible for the anomalous 500°C data. The cross-hatched field refers to 11 samples whose TL sensitivity was below detection limits. (Reprinted by permission from Ref. 32. Copyright 1988 Pergamon Press.)

silicates in Semarkona and suggested that the meteorite had been aqueously altered (16). They suggested that the water was extraterrestrial because Semarkona releases water with considerable deuterium enrichments upon step-wise heating (17,18). It is, of course, possible that the water was produced from other components in the meteorite during the step-wise heating experiment, but Sears et al. have recently found that there is a weak correlation between TL sensitivity and deuterium enrichment for individual chondrules from Semarkona, which might suggest that the TL sensitivity had been lowered and the deuterium increased by passage of heavy water through the meteorite while still on its parent body (19). However, the CL data described above, and a detailed study of the associated compositional properties of chondrules in four of these samples, are best interpreted in terms of chondrule formation mechanisms and subsequent metamorphism, and do not require a substantial role for aqueous proceses (DeHart, Lofgren and Sears, Geochim. Cosmochim. Acta, in press).

Laboratory annealing treatments also cause the temperature and width of the induced TL peak to increase, and quantitatively the changes are very similar to those observed for the type 3.2-3.9 ordinary chondrites. Figure 11 shows glow curves for a type 3.4 ordinary chondrite before and after annealing at 900°C for 200 h and in Figure 12 laboratory annealing data are compared with the type 3 ordinary chondrite data. Whatever the detailed explanation for peak shape changes, the annealing data confirm the idea that the variations in TL peak shape are related to thermal (i.e. metamorphic) history. The increase in peak temperature and width occurs at temperatures similar to the transition temperature for low-temperature (ordered) feldspar to high-temperature (disordered) feldspar, between 500 and 700°C (20), so the simplest explanation for the changes in peak shape would be that types 3.2-3.5 ordinary chondrites contain feldspar in the low form, while types 3.6-3.9 contain feldspar predominantly in the high form.

Physical separation of the feldspar in types 3.2-3.5 ordinary chondrites is extremely difficult since it is very fine-grained (<1 μm) and mixed with other phases. We have therefore performed similar annealing experiments with terrestrial feldspars, fully cognizant of the differences in formation conditions and trace element chemistry of these feldspars and meteoritic feldspar (21). Several terrestrial feldspars in the low-temperature form (ordered Si-Al chain) have peak temperatures and widths similar to those of type 3.2-3.4 ordinary chondrites. Furthermore, and like the meteorites, they undergo an increase in peak temperature when annealed in the laboratory. The degree of disordering in the terrestrial oligoclase increases slowly as the TL peak temperature increases, and at higher annealing temperature the disordering increases rapidly with small increases in peak temperature (Figure 13). The activation energy for disordering is greater than for the

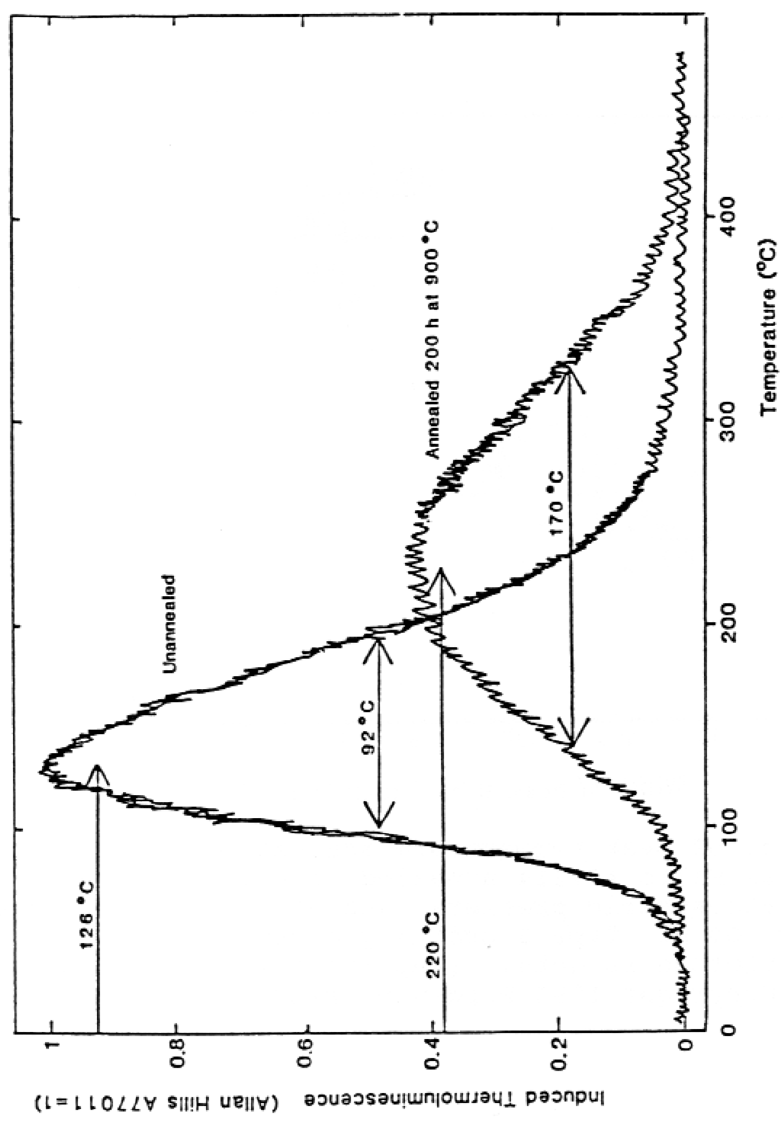


Figure 11. Two glow curves for the type 3.4 ordinary chondrite Allan Hills A77011 (which may actually be a fragment of the same meteorite as Allan Hills A77214) before and after annealing at 900°C for 200 h in a dry nitrogen atmosphere at atmospheric pressure. (Reprinted by permission from Ref. 33. Copyright 1984 MacMillan Journals.)

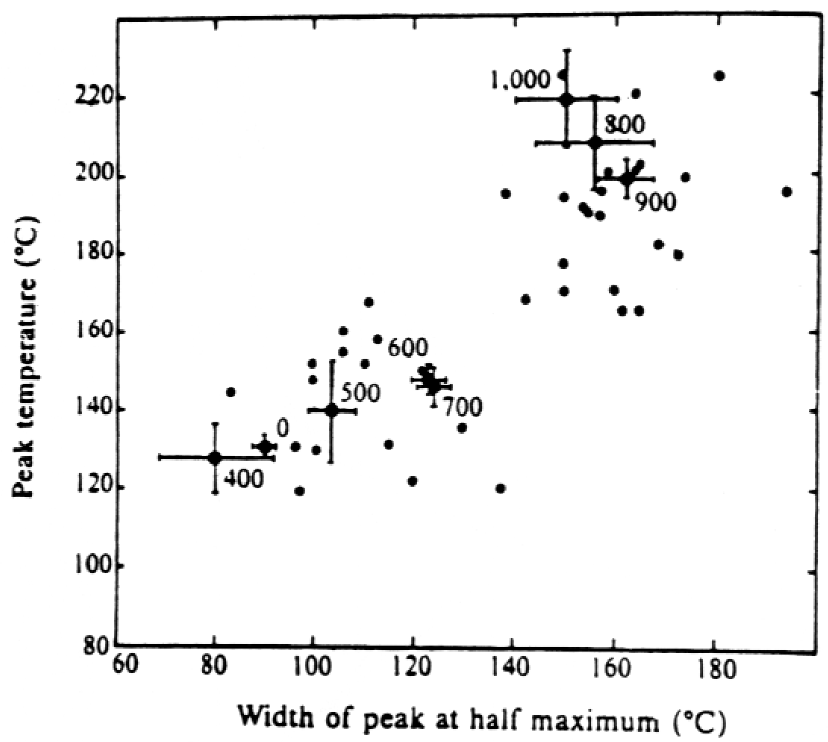


Figure 12. Plot of peak temperature against peak width for samples of Allan Hills A77214 annealed in a dry nitrogen atmosphere at atmospheric pressure, and at the temperatures indicated, for 100 h. Type 3 ordinary chondrites (c.f. Figure 3) are plotted as dots. (Reprinted with permission from Ref. 9. Copyright 1985 Pergamon Press.)

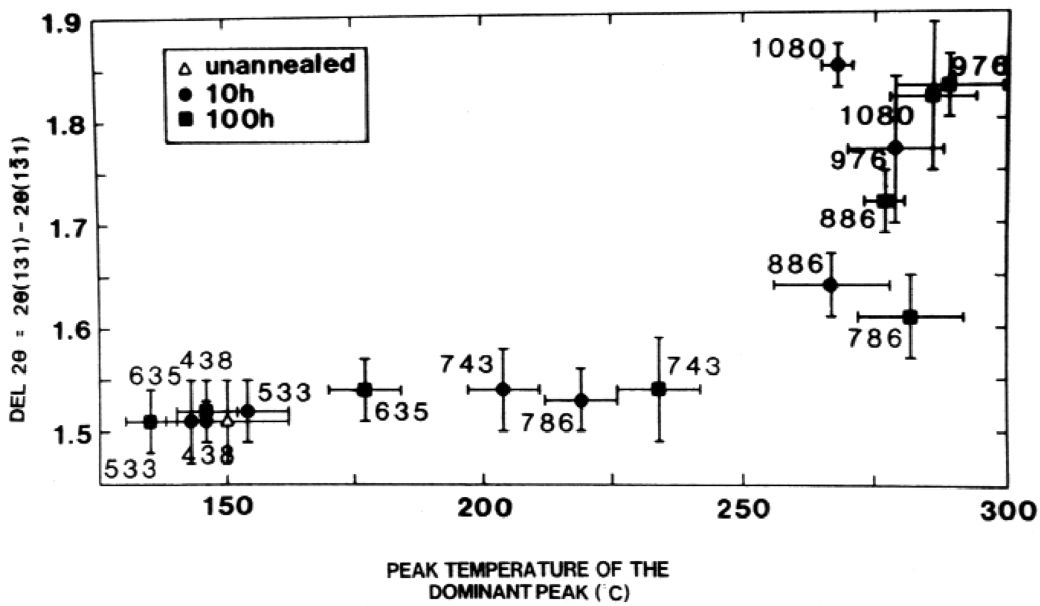


Figure 13. The difference in 2θ angle for the 131 and 1$\bar{3}$1 reflections in the X-ray diffraction patterns for the plagioclase oligoclase (~1.5° for the ordered and ~2.0° for the disordered phases) plotted against TL peak temperature for samples annealed at the temperatures (°C) and the times indicated. (Reprinted with permission from Ref. 21. Copyright 1987 Lunar and Planetary Institute.)

change in TL peak shape, 21 kcal/mol compared with 74 kcal/mol (9). Pasternak suggested that the TL changes were caused by changes in lattice defect structure which preceded, but were associated with, disordering (22). We have also synthesized doped-feldspars in the laboratory, to explore the TL and structural relationships (35), and the data similarly suggest that the relationship between peak temperature and disordering is not straight-forward, and that intermediate feldspars, for example, may be involved. A major study of the TL properties of terrestrial and synthetic feldspars is warranted, but it is clear from existing data that annealing not only affects disordering, but it also affects peak temperatures and that the two are somehow related.

Other Studies

We end this review of meteorite TL and CL and their relationship with feldspar properties with a brief description of some applications to several meteorite problems not previously mentioned. The details presented here are minimal, and intended to illustrate that even though our understanding of some of the basics is still incomplete, there is considerable potential for the application of the work to a variety of geological problems.

Shock Studies. Many meteorites suffered a shock event at a time they were located on their parent bodies. This left many petrographic signs of alteration, but estimating the temperatures and pressure involved has proved fairly difficult. Figure 14 shows a histogram of TL sensitivities for meteorites of type 5 and 6 with petrologic shock classifications (i.e. "facies") indicated; facies a is unshocked and facies f is heavily shocked. The heavily shocked individuals have lower TL sensitivities than the others, since shock pressures in excess of 30 GPa cause the feldspar to convert the glass to maskelynite, either by melting or via a solid state transformation. Samples of the unshocked Kernouve meteorite, after annealing at a variety of temperatures for 10 h, showed a decrease in TL sensitivity, especially after annealing at 1100°C (sodic feldspar melts at 1120°C); the data are shown across the top of Figure 14 (23). These data confirm petrologic estimates for the post-shock temperature for facies e-f of around 1100°C.

Induced thermoluminescence measurements on a suite of artificially shocked terrestrial low-feldspar samples were reported by Hartmetz et al. (24). There were changes in the induced TL peak shape comparable to those discussed above, suggesting that either disordering, or the changes in defect structure preceding disordering, occurred during the shock process. There has been considerable discussion in the literature as to whether the shock process causes disordering of ordered feldspars, and of its significance

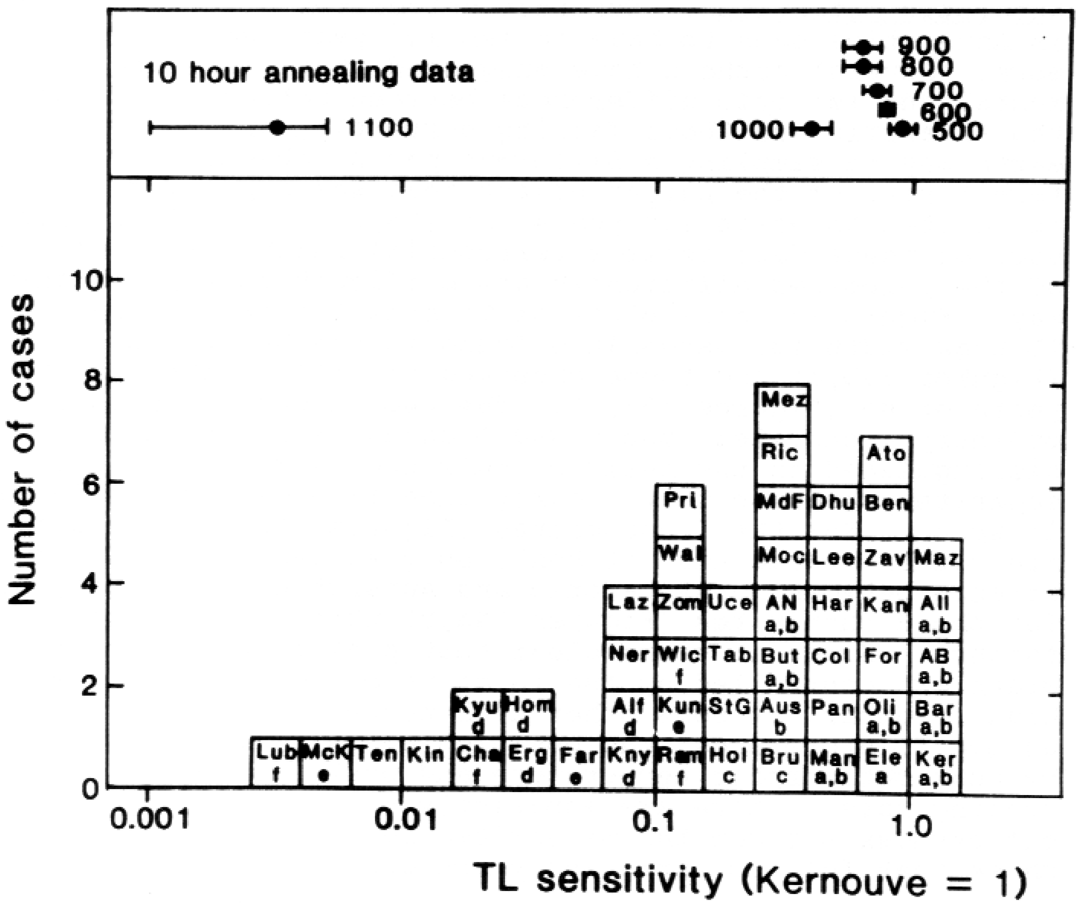


Figure 14. Histogram of TL sensitivity values for type 5,6 ordinary chondrites. The meteorites are identified by the first three letters of their names, and the letter under the name refers to a qualitative ranking according to the intensity of shock experienced; a is unshocked and f is most heavily shocked. The data along the top of the figure refer to observed TL sensitivities for samples of the Kernouve meteorite annealed for 10 h at the temperatures indicated (°C). (Reprinted with permission from Ref. 23. Copyright 1984 Pergamon Press.)

for understanding the shock history of feldspar-bearing rocks from terrestrial craters. Efforts to measure disordering directly, using X-ray diffraction and spectroscopic methods, are of marginal success because of the small amounts of feldspar surviving conversion to glass by shock.

Antarctic Meteorites. Numerous meteorites being recovered in Antarctica seem to have fallen 10^5 years ago, maybe more. Several authors have suggested that there are elemental and isotopic differences between meteorites found in the Antarctic and those falling currently, and that the earth may be sampling a different parent object or a different part of the parent object that was supplying meteorites to earth 10^5 years ago (25). It is clear that some of these data reflect terrestrial weathering, but some of the purported differences are difficult to explain this way. Figure 15 shows plots of TL peak temperature against TL peak width for meteorites found in the Antarctic (Figures 15b,d) and those observed to fall in the last 250 years or so (Figures 15a,c). The two largest classes of ordinary chondrites, the H and L chondrites, which are distinguished on the basis of bulk chemistry, are plotted separately because they clearly came from separate objects in space. For the L chondrites (Figures 15c,d), the data are rather sparse and, at best, only suggestive of a difference between non-Antarctic and Antarctic meteorites, but for the H chondrites (Figures 15a,b) there is a marked difference. Since it seems clear that peak temperature and width are controlled by the relative proportions of low and high feldspar, or some other high temperature phase with unique TL properties, the position on this plot is governed by peak metamorphic temperature and post-metamorphic cooling rate. There are apparently metamorphically-related differences between the meteorites currently falling and those that fell to earth 10^5 years ago.

Chondrules. There are systematic differences in the thermoluminescence properties of chondrules physically separated from meteorites. Figure 16 shows plots of TL sensitivity against peak temperature and peak width for chondrules separated from the Dhajala ordinary chondrite (type 3.8). The TL sensitivities of individual chondrules in Dhajala range over about two orders of magnitude and show a factor of two range in their peak temperatures and widths. About 80% of the chondrules have relatively low TL sensitivity and broad peaks at high glow curve temperatures; much like the type 3.5-3.9 chondrites or samples of the Allan Hills A77214 meteorite annealed above 700°C (Figure 12). The feldspar in these chondrules presumably crystallized at temperatures >700°C, or the feldspar in the chondrules formed at lower temperatures and has subsequently been heated to temperatures >700°C. The remaining 20% of the chondrules separated from Dhajala have rela-

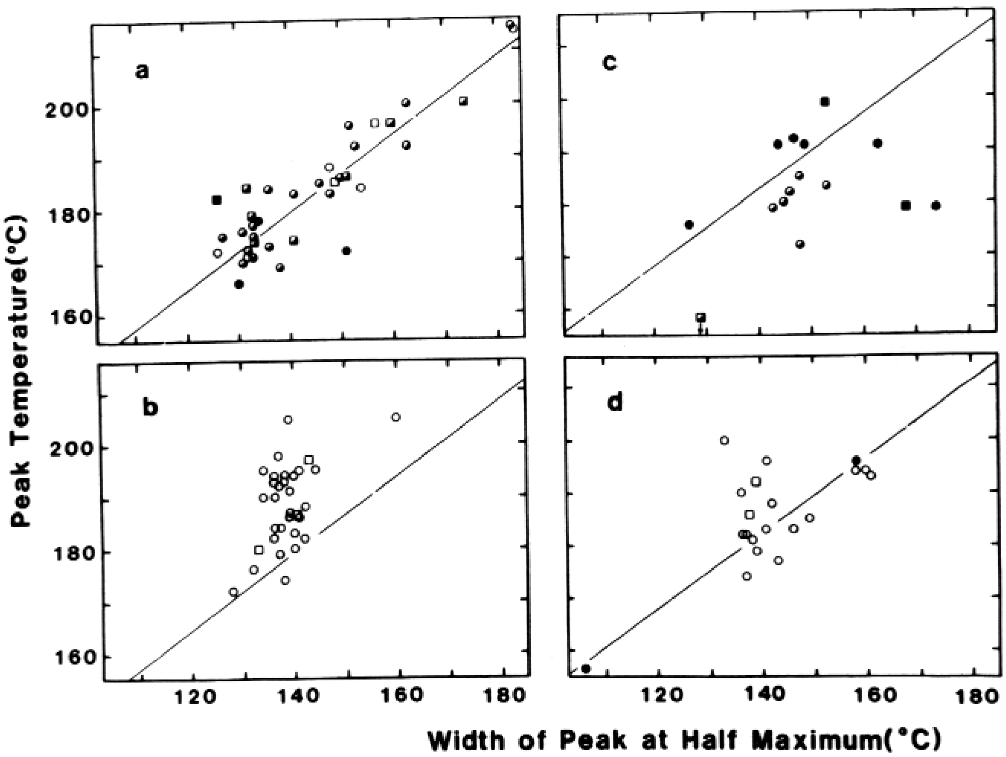


Figure 15. Plots of peak temperature against peak width for meteorites collected in the Antarctic (figures b and d) and for meteorites observed to fall elsewhere in the world (figures a and c). Two classes of ordinary chondrite are plotted separately, H chondrites (figures a and b) and L chondrites (figures c and d). Shock classes are indicated, where known, by the shading of the symbols (shock classes a-c, half filled; shock classes d-f, filled; shock class unknown, open). A few type 4 chondrites are plotted as squares. (Reprinted with permission from Ref. 34. Copyright 1988 Pergamon Press.)

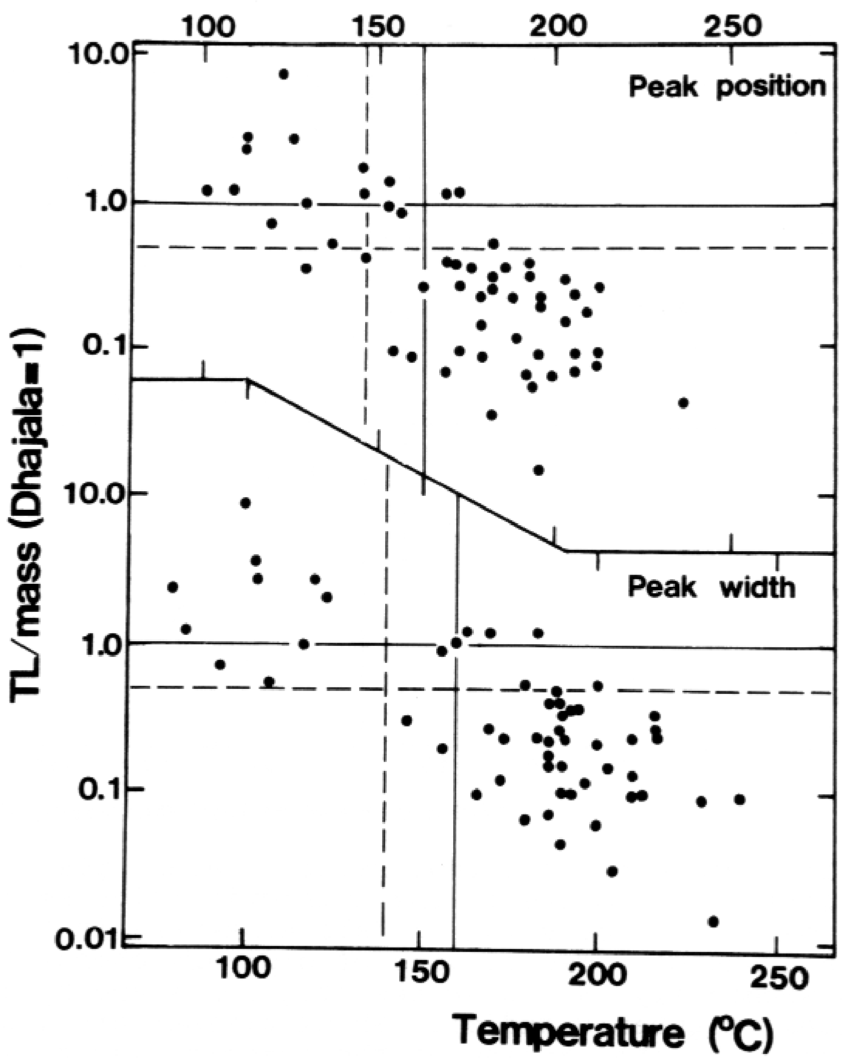


Figure 16. Plot of TL sensitivity against peak temperature and peak width for chondrules separated from the Dhajala meteorite (type 3.8). Because the chondrule masses vary over several orders of magnitude, their TL data have been divided by mass. (Reprinted with permission from Ref. 26. Copyright 1984 Pergamon Press.)

tively high TL sensitivities and they have narrow TL peaks at low glow curve temperatures; much like the type 3.2-3.5 chondrites in Figure 12. It is clear that the crystallization of feldspar has taken place over a variety of temperatures and has occurred to different extents in different chondrules. Some authors have suggested that chondrules in these meteorites suffered metamorphism prior to being incorporated into the meteorite, and these data seem to confirm that idea. However, there are relationships between TL properties and the composition of the mesostases in the Dhajala chondrules which suggested to Sears et al. that the facility of crystallization affects TL sensitivity (26). Each chondrule therefore experienced the same metamorphic history, but while the glass in some chondrules crystallized relatively little, and became closed systems at high temperatures, other chondrules continued to crystallize as the post-metamorphic temperature fell into the fields of lower-temperature forms of feldspar. We have recently extended this study to other type 3 ordinary chondrites of various petrologic types and found that the distribution of data over plots analogous to Figure 16 varies with type in the way expected for crystallization of the glass during various metamorphic regimes.

CO Chondrites. The CO chondrites are a class of carbonaceous chondrites, whose bulk composition distinguishes them from ordinary chondrites, but which are mineralogically and petrologically somewhat analogous to the ordinary chondrites. For example, they are petrologic type 3, and have experienced a range of metamorphic intensities; McSween divided them into petrologic subtypes I, II, and III (27). One of the petrologic trends observed by McSween is the crystallization of primary glass to form feldspar. Unlike the ordinary chondrites, the CO chondrites contain numerous inclusions of Ca,Al-rich minerals, among which is plagioclase.

The induced TL curves consist of two peaks, one at peak temperatures corresponding to the low form and one at a peak temperature corresponding to the high form. Annealing causes the low peak to disappear and merge with the high peak. The low peak varies in intensity with McSween's petrologic subtype, and the numerous petrologic data on which they are based, while the high peak is independent of metamorphism experienced (28; Figure 17). It was suggested that the low peak was due to feldspar formed by crystallization in the low field and that the high peak was due to primary feldspar in the Ca,Al-rich inclusions.

Shergottites. The shergottite meteorites are a rare class of meteorites which consist essentially of pyroxene and maskelynite. Their composition, petrography, age and gases trapped within the fabric of the meteorite have led to a widespread idea that these meteorites, and the related nakhlites and Chassigny meteorites, were ejected from Mars,

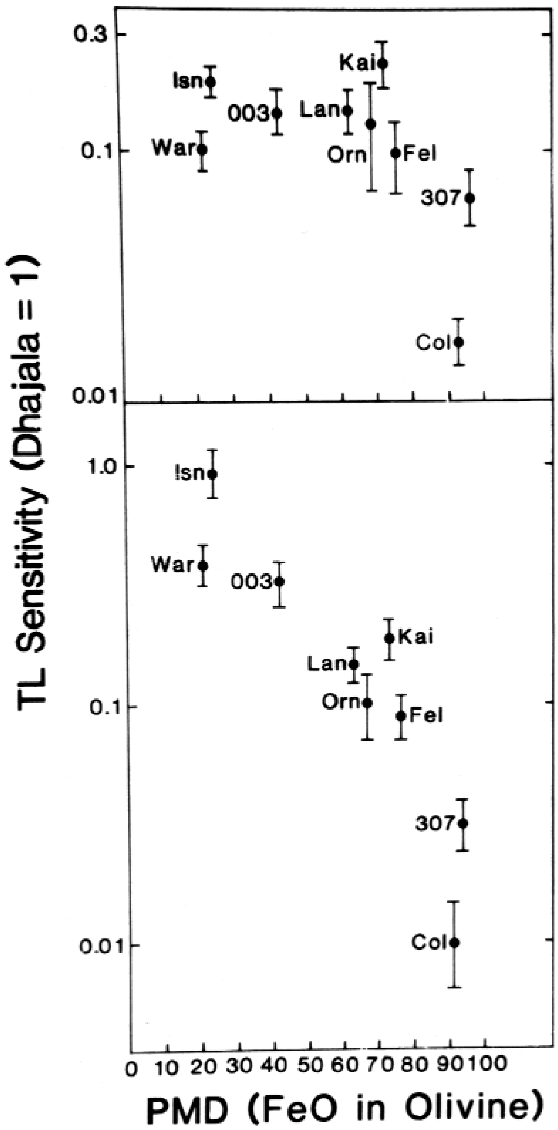


Figure 17. TL sensitivity against silicate heterogeneity (a measure of metamorphic intensity since metamorphism homogenizes silicate compositions) expressed as percent mean deviation from the mean for the CO chondrite class. The 130°C peak is plotted in the lower portion of the diagram and the 250°C peak is plotted in the upper part of the diagram. The meteorites, which are identified by the first three letters or last three numbers of their names, have been assigned to petrologic (metamorphic) types I-III (I low) on the basis of petrologic data by McSween (27) and others as follows: Isna III, Warrenton III, Allan Hills A77003 II, Ornans II, Lance II, Felix II, Allan Hills A77307 I, Kainsaz I, Colony I. (Reprinted with permission from Ref. 28. Copyright 1987 Pergamon Press.)

and it was the force of ejection that converted their feldspar into maskelynite (29). The biggest difficulty in understanding such an origin concerns the feasibility of ejecting large objects from the surface of a planet. Plausible mechanisms have been devised that might explain the ejection of meter-sized objects, but not the 10-100 m objects the shergottites were thought to be at the time of ejection. The estimated ejecta size is based on diffusion calculations for the loss of argon from the meteorites, and such calculations are critically dependent on the assumed value for the temperature following the formation of maskelynite by shock. A value of 400°C is suggested by annealing experiments on shergottites and the associated changes in refractive index, and this leads to calculated ejecta sizes in the 10-100 m range. The arguments have been succinctly summarized by McSween (29).

The shergottites show trends in TL peak temperature, peak width and TL sensitivity which are most readily interpreted in terms of the TL being produced by trace amounts of feldspar in the maskelynite (30). Maskelynite crystallizes very readily, and laboratory heating for an hour at 900°C is sufficient to cause 10-fold increases in TL sensitivity. If, as seems likely, the feldspar in the maskelynite formed during post-shock cooling, then the existence of a high form of feldspar that can be produced in the laboratory by annealing above 600°C, suggests that post-shock heating of the shergottites as they were ejected from Mars was in excess of 600°C. The situation is summarized by Figure 18. The corresponding estimated size for the ejecta is in the meter range, and current theories are well capable of accounting for the ejection of objects this small from Mars.

Summary and Concluding Remarks

In this brief review of the induced TL and CL properties of meteorites we have summarized the factors accounting for TL sensitivity and the main features of the peak shape (peak temperature and peak width). The TL sensitivity of meteorites is governed primarily by the amount of feldspar; in all but a few meteorites, the TL is produced almost exclusively by plagioclase. This has been demonstrated by mineral separation experiments, by petrographic and electron microprobe studies of the cathodoluminescence properties of meteorites, and by annealing experiments with meteorites and terrestrial feldspars. The shape of the TL peak is also governed by thermal history. Most probably, the conversion of the low temperature, ordered form of feldspar to the high temperature, disordered form of feldspar is responsible for the considerable increases in peak temperature and width observed with increasing metamorphism or laboratory annealing. However, the relationship between TL properties and disordering is not simple; the TL changes

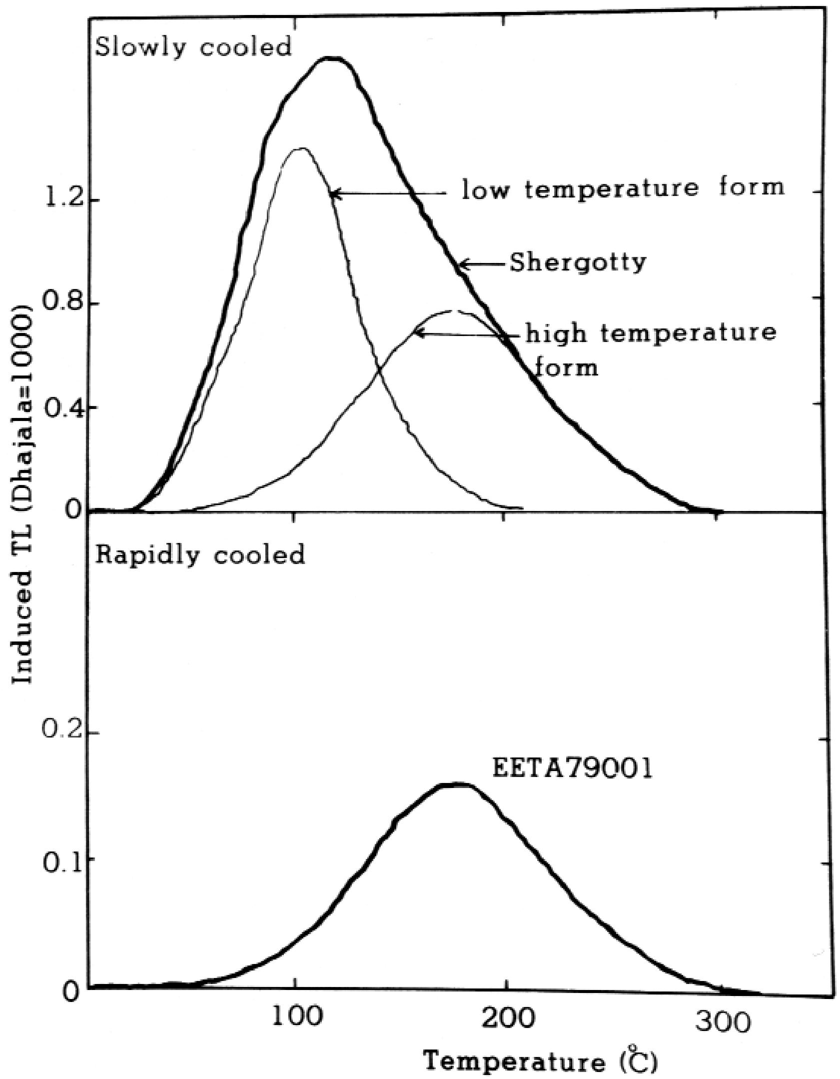


Figure 18. Glow curves for two Shergottite meteorites with an explanation for the differences in glow curve shape based on two components whose relative abundance depends on maximum temperature and cooling rates. (Reprinted with permission from Ref. 30. Copyright 1986 Pergamon Press.)

appear to occur more readily than disordering and may be associated with processes preceding disordering.

Several studies of various kinds of meteorites have shown that induced TL properties provide new insights into these processes, sometimes in a quantitative way. This is despite the uncertainty in the details of the peak shape - disordering relationship, because even an empirical application of laboratory data leads to many useful conclusions. To date, the applications have been mainly to meteoritic problems, but there are many instances in which one can envisage useful application to terrestrial problems. Low grade metamorphism and weathering are examples of processes that might reasonably be addressed using induced TL properties.

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Literature Cited

1. Herschel, A.S. Nature 1899, 60, 29.
2. Howard, E. Phil. Trans. 1802, 92, 168-212.
3. Hasan, F.A.; Haq, M.; Sears, D.W.G. Proc. 17th Lunar Planet Sci. Conf., Part 2, J. Geophys. Res. 1987, 92, E703-9.
4. Antarctic Meteorite Newsletter, Johnson Space Center, Houston, TX, 1988
5. Van Schmus, W.R.; Wood, J.A. Geochim. Cosmochim. Acta 1967, 31, 747-65.
6. Sears, D.W.; Grossman, J.N.; Melcher, C.L.; Ross, L.M.; Mills, A.A. Nature 1980, 287, 791-95.
7. Lalou, C.; Nordemann, D.; Labyrie J. C.r. hebd. Seanc. Acad. Sci. (Paris) Serie D 1970, 270, 2104-2401.
8. Sears, D.W.; Grossman, J.N.; Melcher, C.L. Geochim. Cosmochim. Acta 1982, 46, 2471-81.
9. Guimon, R.K.; Keck, B.D.; Weeks, K.S.; DeHart, J.; Sears, D.W.G. Geochim. Cosmochim. Acta 1985, 49, 1515-24.
10. DeHart, J.; Sears, D.W.G. Lunar and Planetary Science XVII, 1986, pp 160-61.
11. DeHart, J.M.; Lofgren, G.E.; Sears, D.W.G. Lunar and Planetary Science XVIII, 1987, pp 225-26.
12. DeHart, J.M.; Lofgren, G.E.; Sears, D.W.G. Lunar and Planetary Science XIX, 1988, pp 259-60.

13. Steele, I.M. Geochim. Cosmochim. Acta 1986, 50, 1379-95.
14. Sears, D.W.G.; Weeks, K.S. Proc. 14th Lunar Planet. Sci. Conf., Part 1, J. Geophys. Res. 1983, 88, A773-78.
15. Lofgren, G.E. Bull. Geol. Soc. Amer. 1971, 82, 111-24.
16. Hutchison, R.; Alexander, C.M.O.; Barber, D.J. Geochim. Cosmochim. Acta 1987, 51, 1875-82.
17. McNaughton, N.J.; Barthwicks, S.; Fallick, A.K.; Pillinger, C.T. Nature 1981, 294, 639-641.
18. McNaughton, N.J. Proc. Lunar Planet. Sci. Conf. XIII, J. Geophys. Res. 1982, 87, A297-302.
19. Sears, D.W.G.; Morse, A.D.; Hutchison, R.; Guimon, R.K.; Alexander, C.O.; Wright, I.P.; Pillinger, C.T. Lunar and Planetary Science XIX, 1988, pp 1051-52.
20. Smith, J.V. Feldspar Minerals; Springer-Verlag: New York, 1974.
21. Hartmetz, C.P.; Sears, D.W.G. Lunar and Planetary Science XVIII, 1987, pp 397-98.
22. Pasternak, E.S. Ph.D. Thesis, University of Pennsylvania, Philadelphia, 1978.
23. Sears, D.W.G.; Bakhtiar, N.; Keck, B.D.; Weeks, K.S. Geochim. Cosmochim. Acta 1984b, 48, 2265-72.
24. Hartmetz, C.; Ostertag, R.; Sears, D.W.G. Proc. 17th Lunar Planet. Sci. Conf., Part 1, J. Geophys. Res. 1986, 91, E263-74.
25. Dennison, J.E.; Lingner, D.W.; Lipschutz, M.E. Nature 1986, 319, 390-92.
26. Sears, D.W.G.; Sparks, M.H.; Rubin, A.E. Geochim. Cosmochim. Acta 1984, 48, 1189-1200.
27. McSween, H.Y. Geochim. Cosmochim. Acta 1977, 41, 477-91.
28. Keck, B.D.; Sears, D.W.G. Geochim. Cosmochim. Acta 1987, 51, 3013-22.
29. McSween, H.Y. Geology 1984, 12, 3-6.
30. Hasan, F.A.; Haq, M.; Sears, D.W.G. Geochim. Cosmochim. Acta 1986, 50, 1031-38.
31. Guimon, R.K.; Lofgren, G.E.; Sears, D.W.G. Geophys. Res. Lett. 1986, 13, 969-72.
32. Guimon, R.K.; Lofgren, G.E.; Sears, D.W.G. Geochim. Cosmochim. Acta 1988, 52, 119-27.
33. Guimon, R.K.; Weeks, K.S.; Keck, B.D.; Sears, D.W.G. Nature 1984, 311, 363-65.
34. Haq, M.; Hasan, F.A.; Sears, D.W.G. Geochim. Cosmochim. Acta 1988, 52, 1679-89.
35. Guimon, R.K.; Lofgren, G.E.; and Sears, D.W.G. Lunar and Planetary Science XVIII, pp. 374-75.

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