

THE THERMOLUMINESCENCE SENSITIVITY - METAMORPHISM RELATIONSHIP IN ORDINARY CHONDRITES:
EXPERIMENTAL DATA ON THE MECHANISM AND IMPLICATIONS FOR TERRESTRIAL SYSTEMS

R. Kyle Guimon and Derek W.G. Sears

Department of Chemistry and Biochemistry, University of Arkansas at Fayetteville

Gary E. Lofgren

SN2, NASA Johnson Space Center

Abstract. Hydrothermal annealing experiments have been performed on samples of the Sharps meteorite in order to investigate the mechanism responsible for the metamorphism-related, 10^5 -fold range in the thermoluminescence (TL) sensitivity in ordinary chondrites. Duplicate 50 mg samples of meteorite were annealed under the following conditions: (a) 168 h at 785°C and 1 kbar; (b) the same time, temperature and pressure, but with 2 wt% water; (c) 174 h at 855°C and 0.77 kbar with 2 wt% water and 2 molal sodium disilicate (NadiSi); (d) the same time, temperature and pressure as the preceding samples, but with 10 wt% H₂O and 2 molal NadiSi. Samples annealed under the first three sets of conditions showed little or no change in their TL sensitivities, however the samples annealed with 10 wt% water and 2 molal NadiSi showed a 3 to 10-fold increase in TL sensitivity, and the temperature of the TL peak was suggestive of feldspar in the high-temperature form. We suggest that these data are consistent with the TL sensitivity-metamorphism relationship in ordinary chondrites being due to the formation of the TL phosphor, feldspar, by the crystallization of chondrule glass.

Introduction

We have found that the thermoluminescence (TL) phenomenon provides a unique means of determining the presence and relative amounts of the mineral feldspar, and indications of its crystallographic form, in a complex natural rock mixture with a sensitivity not available with any other technique. In an earlier report we showed that the detailed TL emission characteristics are related to the degree of disorder in the Al-Si framework of the feldspar [Guimon et al., 1985]. In the present report, we show that experimental devitrification of feldspar-rich glasses in the presence of alkali solutions, a technique known to increase the amount of crystalline feldspar in such materials [Lofgren, 1971], causes the TL sensitivity to increase, even though the amounts of feldspar involved are well below the detection limits of other techniques.

Our studies have concerned the ordinary chondritic meteorites, but the conclusions should be applicable to almost any rock system where the feldspar levels are low and vary in response to geological processes. This class of meteorite consist predominantly of olivine (Mg,Fe)₂SiO₄,

pyroxene (Mg,Fe)SiO₃, metal (Ni,Fe alloy), sulfide (FeS), and a sodic feldspar (NaAlSi₃O₈ in solid solution with 10-15 mole% CaAl₂Si₂O₈ and 1-6 mole% KAlSi₃O₈) [Van Schmus, 1969]. The assemblage seems to be the result of the aggregation of diverse material from various locations and processes in the primordial solar nebula, 4.6 x 10⁹ years ago [e.g. Anders, 1964]. About 30 ordinary chondrites do not contain petrographically observable feldspar, but instead contain a glass of approximately feldspathic composition. They are also unusual in a number of petrological and mineralogical properties [Dodd et al., 1967; Scott et al., 1981; Rambaldi et al., 1980], which reflect relatively low levels of parent body metamorphism. In the classification scheme devised by Van Schmus and Wood, the level of metamorphism experienced is indicated by a petrologic type 3-6, and the glass-bearing meteorites are type 3 [Van Schmus and Wood, 1967]. Thermoluminescence sensitivity has been found to be strongly related to metamorphism experienced, especially at the lowest levels of intensity [Sears et al., 1980]. Types 3-6 display a 10⁵-fold range in TL sensitivity, while type 3 alone displays a 10³-fold range. Using a variety of petrologic properties in combination with TL the type 3 chondrites can be subdivided into types 3.0-3.9 [Sears et al., 1980]. We have suggested that this increase in TL sensitivity with metamorphism reflects the formation of feldspar by crystallization of the glass, which is largely in the chondrules [Sears et al., 1984], the most common constituent of the chondrites.

We have also observed that, as the degree of metamorphism and TL sensitivity increase throughout types 3.3-3.9, the temperature at which the maximum TL is emitted increases from ~100 to ~200°C [Guimon et al., 1985]. The work to date is summarized in Figure 1. The samples with TL peaks between ~120 and 160°C occur in the interval indicated by cross-hatching. These samples have very narrow peaks (80-120°C). At higher TL sensitivities (corresponding to types 3.6-3.9), peaks occur at 180-220°C and are broad (140-180°C), while at lower TL sensitivities (corresponding to types <3.2) the TL peaks can occur at a variety of temperatures and widths and the glow curve (TL against temperature) has a characteristically hummocky shape. Cathodoluminescence studies (CL) have shown that the source of the luminescence in these very low TL meteorites is no longer the mesostasis glass with blue-green CL, but is a variety of other materials usually displaying red or yellow CL [DeHart and Sears, 1986]. If we assume for types >3.2 that the TL sensitivity reflects the amount of

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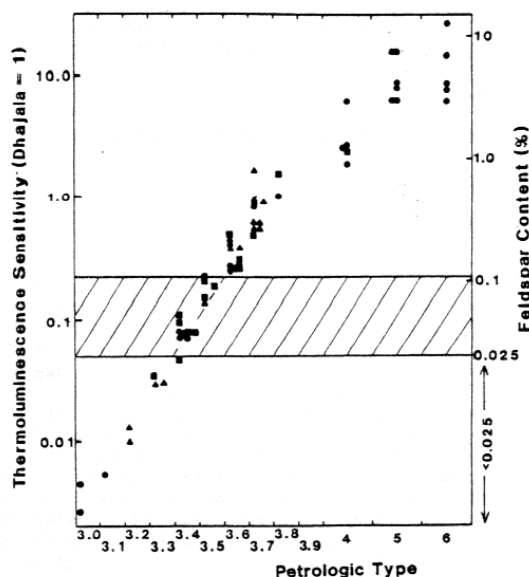


Fig. 1. The thermoluminescence sensitivity of ordinary chondrites as a function of metamorphism experienced (3.0 low, 6 high). The hatched area indicates meteorites with feldspar in the low temperature form. The right-hand scale indicates feldspar abundance as calculated from the TL sensitivity.

crystalline feldspar, and that amount of feldspar in a type 6 is 8%, then we arrive at the feldspar scale in Figure 1.

The change in peak temperature from ~ 100 to $\sim 200^\circ\text{C}$ can be reproduced in the laboratory by annealing experiments. Both quantitatively and qualitatively, the increase in peak temperature closely resembles that displayed by Amelia albite, where the change is associated with the onset of disorder [Guimon et al., 1985]. For some time, we have been attempting to also reproduce the increase in TL sensitivity by laboratory annealing experiments to further elucidate the factors governing the TL sensitivity-metamorphism relationship. The present paper reports our first successful attempt to increase TL sensitivity in a chondrite by laboratory annealing experiments.

Experimental

The glass in type 3 chondrites has survived geological time because, in the absence of water, sodic glasses are very slow to devitrify [Sears et al., 1984]. Our experimental charges were therefore fluxed with water and sodium disilicate ($\text{Na}_2\text{Si}_2\text{O}_5$) which is also known to catalyze the devitrification process [Lofgren, 1971; Martin, 1969]. Two grams of the Sharps (type 3.4) meteorite were ground and the metal removed with a hand-magnet. Aliquants of 20–50 mg were then placed in gold capsules, weighed, dried in a vacuum oven at 100°C overnight to remove any indigenous or atmospheric water and then reweighed. The predetermined amounts of sodium disilicate and/or water were then added. The

capsules were sealed by arc welding and placed, four at a time, in externally heated pressure vessels using argon as the pressure medium [Lofgren, 1971]. The following annealing conditions were chosen: (1) 168 hours at $755\pm 5^\circ\text{C}$ and 1.0 ± 0.1 kbar pressure with no added water or $\text{Na}_2\text{Si}_2\text{O}_5$; (2) the same time, temperature, and pressure as set 1 but with 2 wt% H_2O added; (3) 174 hours at $855\pm 5^\circ\text{C}$ and 0.77 ± 0.04 kbar with 2 wt% H_2O and 2 mole% $\text{Na}_2\text{Si}_2\text{O}_5$ added; (4) the same time, temperature, pressure and amount of $\text{Na}_2\text{Si}_2\text{O}_5$ as group 3 but with 10 wt% H_2O added. After annealing, the TL sensitivity of each sample was measured with apparatus and techniques of Sears and Weeks [1983].

Results

Figure 2 shows some of the data obtained in this experiment presented as glow curves, plots of TL emitted against temperature. The overall effects of annealing were to move the peak temperature from 145 ± 3 to $218\pm 10^\circ\text{C}$ and increase the TL sensitivity from 0.097 ± 0.003 to 0.33 ± 0.02 . In fact, it is somewhat misleading to compare TL sensitivities at different glow curve temperatures, it is meaningful to note that the increase in TL sensitivity at the 220°C region of the glow curve was about an order of magnitude. The details are as follows. The TL peak for the unannealed Sharps material, curve (a), peaks at relatively low temperature ($128\pm 5^\circ\text{C}$) and is relatively narrow ($94\pm 4^\circ\text{C}$). After annealing at 755°C and 1 kbar without any devitrification catalyst (curve b), the TL sensitivity increased approximately 2-fold but the peak position and peak width remained very similar to their natural values. The sample similarly annealed, but with 2 wt% H_2O added (curve c), showed an increase in peak temperature to $167\pm 11^\circ\text{C}$ and FWHM (full-width at half maximum intensity) to $122\pm 2^\circ\text{C}$ but similar TL sensitivity to that of the unannealed sample. The addition of a 2 wt% of a 2 molal solution of $\text{Na}_2\text{Si}_2\text{O}_5$, produced no further changes in the glow curve for one charge (curve d) but caused the peak temperature to increase from $187\pm 12^\circ\text{C}$ to $218\pm 5^\circ\text{C}$ in the other (curve e). Increasing the amount of water to about 10 wt% produced major changes to the glow curves. A sharp peak appeared at $210\pm 4^\circ\text{C}$ in one charge (curve f) and at $225\pm 2^\circ\text{C}$ in the other (curve g), with the result that the TL sensitivity of the 200°C region of the glow curve increased by factors of 3 and 10, respectively, compared with that of the unannealed material. We doubt that the difference in the intensity of curves 2f and 2g can be reasonably attributed to differences in annealing conditions, but rather to sample heterogeneity. Minor differences in glass structure, such as the type and number of nucleation sites for instance, will be of major importance.

Discussion

Two first order effects are apparent in these results: (1) the dominant peak in the untreated sample is at 120°C while the dominant peak in the annealed samples is at 220°C ; (2) the intensity of the TL in the fluxed and annealed samples is significantly higher than that of the untreated samples. The first effect has been observed in all our annealing experiments at temperatures in

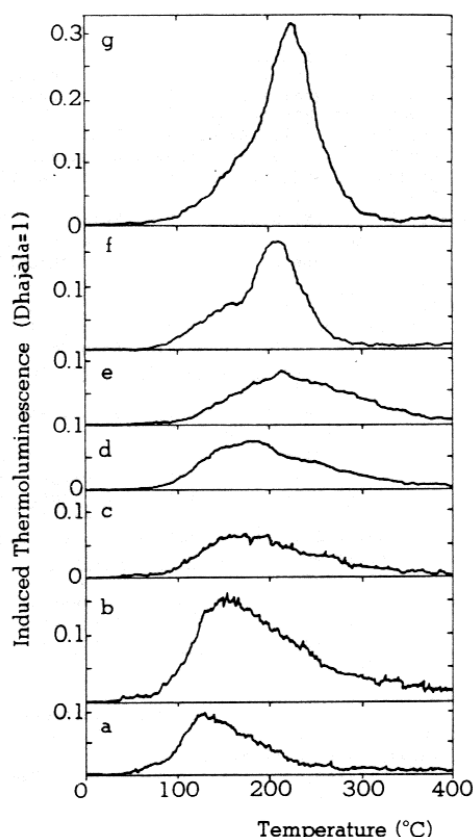


Fig. 2. Glow curves (plots of thermoluminescence against temperature) for samples of the Sharps H3.4 chondrite annealed under a conditions with various amounts of devitrification catalysts (water and sodium disilicate, Na₂Si₂): a) unannealed sample; b) 775°C, 168 h, 1 kbar; c) 755°C, 168 h, 1 kbar, 2 wt% H₂O; d) 855°C, 174 h, 0.77 kbar, 2.0 wt% H₂O, 1.2 mole % Na₂Si₂; e) 855°C, 174 h, 0.77 kbar, 2 wt% H₂O, 2.0 mole % Na₂Si₂; f) 855°C, 174 h, 0.77 kbar, 10 wt% H₂O, 2.0 mole % Na₂Si₂; g) 855°C, 174 h, 0.77 kbar, 9.7 wt% H₂O, 1.9 mole % Na₂Si₂.

excess of 800°C and is associated with the onset of disordering [Guimon et al., 1985]. The second effect has not been observed in our previous annealing experiments with type 3 ordinary chondrites, and is clearly related to the addition of water and Na₂Si₂ to the charges; most plausibly the increase in TL sensitivity was caused by the formation of feldspar in the glassy material in the meteorite samples. We suggest that this is compelling evidence for our earlier suggestion that the TL-metamorphism relationship in ordinary chondrites reflects the formation of feldspar through the devitrification of glass, glass being a characteristic feature of primitive (i.e. little metamorphism) meteorites. It is significant to note, if this is correct, that our TL measurements detected an increase in the feldspar content from 0.025% to 0.075% in a 4 mg bulk

sample, and we found evidence concerning a change in its structural form. These values are well below the detection limits of x-ray diffraction and optical methods and the feldspar grains are almost certainly well below the resolution of the optical microscope were they to be present in greater amounts. Furthermore, Ashworth has been able to detect secondary feldspar in the glass of Tieschitz (3.6) and Bremervorde (3.9) using TEM, but not in lower types [Ashworth, 1981].

A further example of thermoluminescence being very highly sensitive to changes in the amount of feldspar is provided by the shergottite class of achondrite meteorites [Hasan et al., 1986]. Meteorites in this class appear to be igneous rocks, with a strong possibility that they originated in the lava flows on Mars. Mineralogically, they contain olivine, pyroxene, and maskelynite, the latter being a diaplectic glass produced from feldspar by intense shock. The TL is extremely low, consistent with the thorough maskelynitization of the feldspar, and it shows a 10-fold range which we have argued reflects varying degrees of crystallization during the post-shock cooling period. Samples of a shergottite meteorite annealed for 10-100 hours at 900°C, but without added catalysts, also exhibited up to a 10-fold increase in TL sensitivity. Mineral separation experiments indicated that the TL phosphor in shergottites is associated with maskelynite, presumably as nanogram per gram quantities of crystalline feldspar in the glass. Although the shergottite and ordinary chondrite classes of meteorites are very different in origin and history, and their feldspathic material is very different in composition, their TL properties contain remarkable similarities, not the least of which is that treatments which cause crystallization of the feldspathic material increase the TL. The difference in the ease with which the crystallization can be induced in these classes is noteworthy and consistent with what is known about the relative stabilities of the diaplectic glass in shergottites [Duke, 1968] and the igneous glass in type 3 ordinary chondrites [Sears et al., 1984].

It seems feasible in principle to use changes in thermoluminescence sensitivity to monitor quantitatively any process which causes variations in the amount and structural data of feldspar. Furthermore, the feldspar need be present in only trace amounts. The ability to measure quickly the quantitatively trace quantities of feldspar in bulk samples may have application to many terrestrial systems. Weathering of basalts [Ehlers and Blatt, 1982, pages 269-275] or granites [Goldich, 1938] could be followed this way, since feldspar is destroyed to form clay minerals. Conversely, contact metamorphism of clay minerals results in the formation of feldspars and could be followed at even the mildest levels of metamorphic intensity [Ehlers and Blatt, 1982, pages 585-587]. In principle, the phenomenon could be used with rock systems in which minerals other than feldspar are the major source of luminescence, especially if they exhibit phase changes which influence the fine details of the TL emission.

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R.K. Guimon and D.W.G. Sears, Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701.
G.E. Lofgren, SN2, NASA Johnson Space Center, Houston, TX 77058.

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