

Chemical and physical studies of type 3 chondrites—IV: Annealing studies of a type 3.4 ordinary chondrite and the metamorphic history of meteorites

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Abstract—Samples of a type 3.4 chondrite have been annealed at 400–1000°C for 1–200 hours, their thermoluminescence properties determined and analyzed for K, Na, Mn, Sc and Ca by instrumental neutron activation analysis. After annealing at $\leq 900^\circ\text{C}$, the samples showed a 50% decrease in TL sensitivity, while after annealing at 1000°C it fell to 0.1–0.01 times its unannealed value and loss of Na and K occurred. The TL and compositional changes resemble those observed for the equilibrated Kernouve chondrite after similar annealing treatments, except that the sharp TL decrease, and element loss, occurred at $\sim 1100^\circ\text{C}$; this difference is presumably due to petrographic differences in the feldspar of the two meteorites. The temperature and the width of the TL peak showed a discontinuous increase after annealing at 800°C; peak temperature jumped from 130 to 200°C and peak width increased from 90 to 150°C. The activation energies for these TL changes are 7–10 kcal/mole. Similar increases in the TL peak temperature have been reported in TL studies of Amelia, VA, albite, where they were associated with the low to high-temperature transformation. However, the activation energy for the transformation is ~ 80 kcal/mole. These changes in TL emission characteristics resemble trends observed in type 3 ordinary chondrites and it is suggested that type 3.3–3.5 chondrites have a low-feldspar as TL phosphor and >3.5 have high-feldspar as the phosphor. Thermoluminescence therefore provides a means of palaeothermometry for type 3 ordinary chondrites.

INTRODUCTION

WE HAVE REPORTED that the thermoluminescence (TL) sensitivity of type 3 ordinary chondrites (or unequilibrated ordinary chondrites, UOC) is acutely sensitive to low-grade metamorphism (SEARS *et al.*, 1980) and may be used for the assignment of precise petrologic types which aid in the interpretation of many metamorphism-sensitive properties (GRADY *et al.*, 1982; MCNAUGHTON *et al.*, 1982; SCOTT, 1984). Other properties of the TL emission may also have important implications for the history of ordinary chondrites and, in particular, their palaeothermometry. The temperature at which the maximum TL emission occurs (the peak temperature) and the temperature range over which emission occurs (full-width at half maximum height, FWHM) may be related to the crystallography of the TL phosphor (SEARS *et al.*, 1982; SEARS and WEEKS, 1983). The basis for this suggestion is that (1) the TL phosphor in an equilibrated chondrite is feldspar, and consistent with this, the chondrule-to-chondrule TL variability in Dhajala is related to the amount and composition of the chondrule mesostasis (SEARS *et al.*, 1984b),

and (2) PASTERNAK (1978) observed changes in the TL properties of Amelia, Virginia, albite which were associated with the transformation from the low-temperature to the high-temperature form. Qualitatively and quantitatively, the TL changes induced by annealing Amelia albite resemble the TL trends observed in UOC.

In the present paper, we report annealing experiments on a type 3.4 ordinary chondrite and compare the changes which were produced with Pasternak's albite data and with the TL trends in UOC, and we discuss the implications. A preliminary announcement of some of the main features of our results was published by GUIMON *et al.* (1984).

EXPERIMENTAL

Chips of Allan Hills 77249,21 (469 mg) and 77214,14 (433 mg), which are both of petrologic type 3.4 ± 0.1 and thought by SCOTT (1984) to be paired with Allan Hills A77011 (3.5 ± 0.1), were prepared for annealing by grinding, removal of the magnetic portion, regrinding to pass through a 100 mesh sieve, and 20 mg aliquots placed in high-purity SiO_2 glass vials. The vials were three times evacuated to 100 μm Hg, refilled with high-purity N_2 and heat sealed. They were then annealed in a wire-wound tube furnace for 1–1000 hours and at 600 to 1000°C (Table 1), a duplicate being run at each time and temperature.

After annealing, 4 ± 0.1 mg of sample was placed in a Cu pan and the TL properties determined with the apparatus and techniques of SEARS and WEEKS (1983).^{*} For the purpose of tabulation, our TL sensitivity data are normalized to the TL of the Dhajala meteorite to enable interlaboratory comparison, but for the purposes of plotting the data are normalized to the data for the unannealed sample to better enable comparison with the unannealed material. After it was discovered that annealing of Allan Hills A77011 produced systematic changes in peak temperature and width, these parameters were measured for the Kernouve H6 chondrite

^{*} Some definitions: "TL" is the phenomenon, "natural TL" is the TL present in the sample when it reaches our laboratory, "induced TL" is the TL which can be induced in the sample after draining its natural TL by momentary heating to 500°C (usually in the TL apparatus) and exposing the sample to ionizing radiation. "TL sensitivity" is the induced TL at the maximum emission as the sample as heated in the TL apparatus; usually it is normalized to the same quantity for the Dhajala meteorite. The TL peak width and temperature measurement are described in Fig. 1 of SEARS and WEEKS (1983).

Table 1. Data on the effect of annealing for various times and temperatures on the TL sensitivity, peak temperature and FWHM of Allan Hills A77011.*

Annealing Temperature (°C)	Annealing Time (hr)	TL Sensitivity (Dhajala=1)	Peak Temperature (°C)	FWHM† (°C)
Natural	---	0.054 ± 0.005 0.059 ± 0.004	136 ± 6 126 ± 2	88 ± 4 92 ± 2
600	10	0.026 ± 0.003	148 ± 10	116 ± 2
	100	0.027 ± 0.006	152 ± 8	122 ± 3
	100	0.026 ± 0.005	144 ± 3	124 ± 4
700	10	0.026 ± 0.002	156 ± 5	124 ± 8
	100	0.035 ± 0.005	146 ± 5	124 ± 5
800	10	0.047 ± 0.003	150 ± 6	118 ± 7
	10	0.041 ± 0.013	156 ± 19	118 ± 5
	100	0.033 ± 0.005	208 ± 12	156 ± 9
900	1	0.026 ± 0.003	150 ± 15	122 ± 4
	1	0.017 ± 0.002	136 ± 16	116 ± 3
	10	0.026 ± 0.004	152 ± 9	146 ± 4
	100	0.012 ± 0.001	204 ± 9	166 ± 6
	100	0.019 ± 0.003	194 ± 6	152 ± 3
	200	0.015 ± 0.002	190 ± 19	166 ± 17
1000	10	0.008 ± 0.0008	218 ± 11	162 ± 12
	100	0.004 ± 0.0004	210 ± 21	148 ± 15

* Uncertainties are 1 σ based on 3-5 replicate measurements.

† Full-width-half-maximum.

from the glow curves of a separate study (SEARS *et al.*, 1984a).

After TL measurement the samples were transferred to clean, high density polyethylene vials and irradiated for 30 minutes at the University of Missouri Research Reactor for neutron activation analysis for Mn, Ca, Sc, Na and K. Synthetic standards and the Allende meteorite and unannealed 77011 were included. Four counts of 2.5 to 10 hours duration were made at Fayetteville and the data reduced using BAEDCKER's (1976) SPECTRA program; the Ca and K peaks were hand-plotted and the program's value adjusted. The agreement between our data and Allende literature values was good. 1 σ uncertainties expressed as a percentage

of the mean and based on the samples for which no element loss was suspected (<700°C for 100 h and <20 h at 900°C for K, <1000°C for Na and all Ca, Mn, and Sc data) are 11, 15, 8.4, 9.5 and 11 for K, Na, Ca, Mn and Sc, respectively. These errors are larger than normally obtainable because of the small sample size and the errors introduced by removal of the magnetic fraction, the latter are minimized by Sc-normalization.

RESULTS

Our TL data are presented in Table 1 and Figs. 1-5. Fig. 1 shows glow curves for an unannealed sample and a sample that had been severely annealed. The peak temperature of the sample which had been annealed for 200 hours at 900°C was 220°C, compared with 126°C for the unannealed sample, and the peak width increased from 92 to 170°C in response to the annealing. At the same time, the TL sensitivity decreased to about 40% of its unannealed value.

The effect of annealing for 10 and 100 h at various temperatures on the TL sensitivity is shown in Fig. 2. In samples annealed at or below 900°C, the TL sensitivity is slightly lower than the unannealed value, but after annealing at 1000°C it is almost 100 times less than the unannealed value. Kernouvé showed a similar 100-fold decrease in TL sensitivity after annealing at 1100°C (SEARS *et al.*, 1984a). No time dependency in TL sensitivity decreases after annealing at 900°C has been detected, however, at 1000°C samples annealed 1 or 2 hours are lower than the unannealed values by a factor of 2, whereas samples annealed for 10 and 20 hours are lower by factors of 10 and 100, respectively (Fig. 3).

The TL peak temperature and width of samples

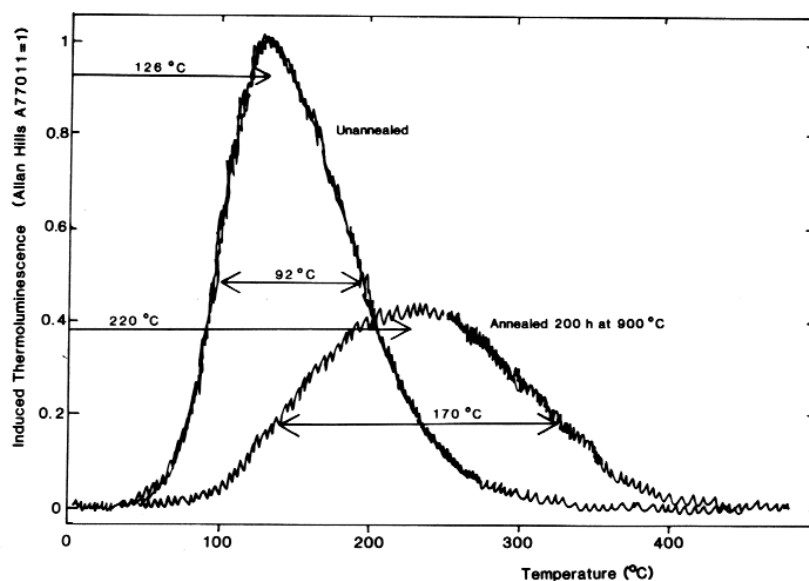


Fig. 1. Glow curves for an unannealed sample of Allan Hills A77011 and for a sample annealed at 900°C for 200 hours. The annealing treatment has caused a 60% decrease in the TL sensitivity, a 94°C increase in the peak temperature and a 78°C increase in the width of the peak.

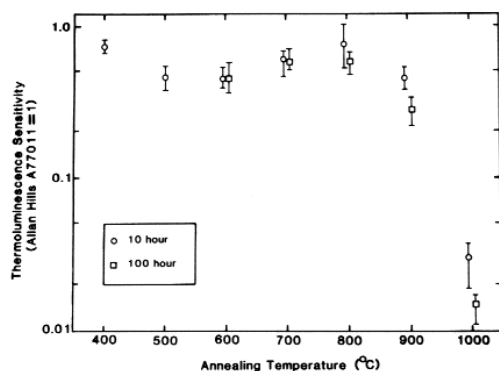


FIG. 2. Plot of the TL sensitivity of samples of Allan Hills A77011 annealed at various temperatures for 10 and 100 h. A ~50% decrease in TL sensitivity is observed for samples annealed up to ~900°C, and a 10–20 fold decrease is observed for samples annealed at 1000°C.

annealed for 100 h at various temperatures are presented in Fig. 4. Samples annealed at 400–700°C have peak temperatures and widths close to their unannealed values, but samples annealed 800–1000°C have peaks at about 200°C and widths of about 160°C. The increase in both parameters, especially peak temperature, is rather abrupt and occurs mainly between 600 and 800°C. The increases in peak temperature and width show a fairly regular time-dependency on a semi-log plot (Fig. 5). Annealing at 900°C produced a 20°C peak temperature shift after 10 h and a 70°C shift after 100 h. The peak width increased by 30°C after 1 h, 50°C after 10 h and 70°C after 100 h of annealing at 900°C.

In Table 2 we present our data for the Na, K, Mn and Ca content of our samples determined by INAA after the annealing treatment and TL measurement. To allow for the mass of metal that was removed at the beginning of sample preparation, the data have been divided by 1.12. This value was calculated from KEIL's (1962) planimetric data for the weight of metal and sulfide in L chondrites. Excluding those data which are thought to exhibit element loss, the mean value for each element is in good agreement with MASON's (1979) L group mean value. In Fig. 6 the data are normalized to Sc to remove the scatter produced by the poorly-reproducible metal separation necessary for TL measurement. Calcium and Mn showed no significant variation. Sodium concentrations dropped 30–40% from the original value after annealing for 100 h at 1000°C (or 200 h at 900°C), while K was similarly lost after annealing for 100 h at 800°C. We also detected significant time-dependency in the loss of Na and K, the latter being the more readily lost.

DISCUSSION

Cause of the TL sensitivity changes

The 50% decrease in TL sensitivity of the samples annealed <1000°C resembles that observed for the

Kernouve meteorite and we presume it has similar causes. For Kernouve, the 40% decrease in TL sensitivity after annealing at 1000°C, had a low activation energy (~8 kcal/mole) and followed very closely the pattern of Cs loss following similar annealing treatment by IKRAMUDDIN *et al.* (1977a,b) of the Tieschitz and Krymka ordinary chondrites. We suggested that the TL decrease was associated with diffusional processes or crystallographic changes which facilitated the loss of Cs from the feldspar or feldspathic mesostasis. While there is evidence that feldspar is the TL phosphor in equilibrated meteorites, this is not necessarily the case for type 3 chondrites although the present data are consistent with the idea. We were unable to obtain activation energies for the TL decreases observed in the present study, since the Arrhenius plots did not yield statistically significant lines. This may be because Allan Hills A77011 is considerably more heterogeneous than Kernouve, although the scatter in Figs. 2 and 3 is larger than the 1 σ uncertainties which suggests that other effects may be responsible.

The TL sensitivity changes for Allan Hills A77011 differ from the Kernouve data in that the abrupt decrease occurred around 1100°C for Kernouve but 1000°C for 77011. SEARS *et al.* (1984a) suggested that the abrupt decrease at 1100°C in the TL sensitivity of Kernouve was associated with fusion of the feldspar, accompanied by some decomposition. A possible explanation for the lower stability of the TL in Allan Hills A77011, based on the assumption that the TL phosphor is feldspar, concerns the petrographic siting of feldspar. For a meteorite of a low petrologic type, like Allan Hills A77011, the feldspar exists as submicron crystallites set in a glass, rather than ≥ 10 micron-sized crystals. Perhaps at some temperature during the annealing process the glass dissolved the feldspar microcrystals, and this would probably occur

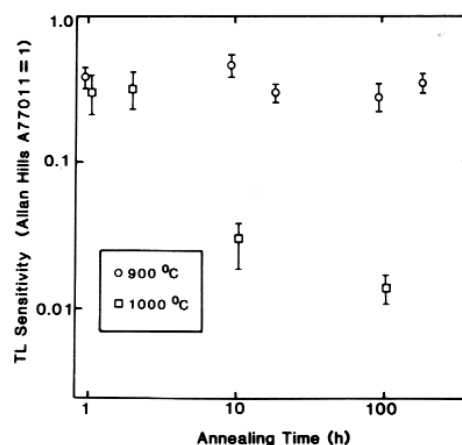


FIG. 3. Plot of the TL sensitivity of samples of Allan Hills A77011 as a function of annealing time at 900 and 1000°C. There is little or no time dependency apparent in the 900°C runs, but at 1000°C the time dependency is very strong.

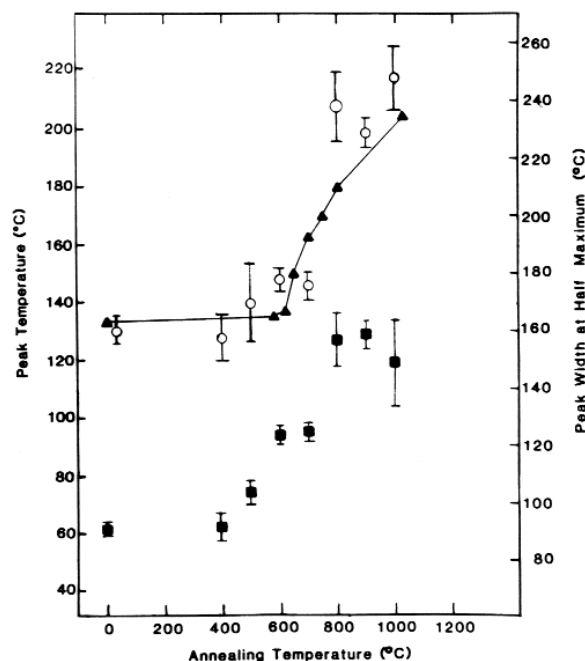


FIG. 4. Plots of TL peak temperature (circles, left-hand scale) and width (squares, right-hand scale) as a function of annealing temperature for the samples annealed for 100 h. Little or no significant shift in peak temperature occurs until samples are annealed at 800°C, when the peak jumps about 60°C. Thermoluminescence peak temperature data for Amelia albite, taken from PASTERNAK (1978), are also indicated (triangles, left-hand scale); the similarity in the behavior of the TL peak temperature for the two materials is striking. The trend in peak width resembles that shown by peak temperature, but the increase starts at ~500°C. The peak almost doubles in width after annealing at 900°C for 100 h.

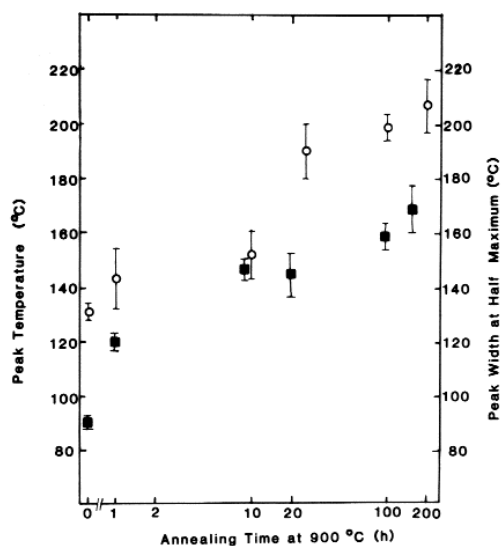


FIG. 5. Plots of the TL peak temperature (circles, left-hand scale) and width (squares, right-hand scale) as a function of the time annealed at 900°C. There is a steady increase in the peak temperature, from 130 to 210°C, and the peak width increases from 90 to 170°C after 200 h of annealing.

below the melting point of feldspar (~1120°C). Other explanations exist, for example, maybe another mineral is responsible for the TL which undergoes some major physical change that destroys its phosphor capabilities at 1000°C; however we know no potential phosphors with melting points ~1000°C.

Table 2. The abundance of Na, K, Mn, Sc and Ca in annealed Allan Hills A77011 samples after T1 measurement.*

	Mean L Group†	Annealing Temperature for 100 hours (°C)				
		600	700	800	900	1000
Na (mg/g)	6.5	5.11	4.28	5.67	6.39	4.30
K (mg/g)	870	782	478	482	534	507
Mn (mg/g)	2.46	1.96	1.53	2.10	2.20	2.10
Ca (mg/g)	12.8	11.0	9.20	11.6	12.7	12.5
Sc (µg/g)	8.2	7.04	5.76	7.83	8.40	8.08
Mass (mg)	--	26.9	11.3	12.4	29.7	15.2

	Unannealed	Time Annealed at 900°C (h)				
		1	10	20	100	200
Na (mg/g)	6.63	6.02	4.95	6.51	6.39	6.89
K (µg/g)	826	695	633	812	534	553
Mn (mg/g)	2.30	2.04	2.09	2.21	2.20	2.16
Ca (mg/g)	12.9	12.4	12.2	12.1	12.7	11.3
Sc (µg/g)	8.16	7.98	7.90	8.16	8.40	9.28
Mass (mg)	23.1	12.6	22.8	23.0	29.7	5.5

* Analyses were made on the non-magnetic extracts used for T1 measurements and have been corrected to bulk values by dividing all data by 1.12 (see text).

† Mason (1979).

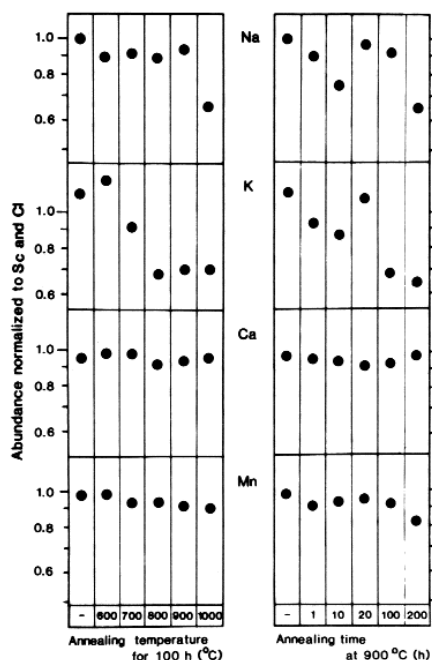


FIG. 6. Plot of the CI and Sc normalized abundances of Na, K, Ca and Mn in samples of the Allan Hills A77011 meteorite after annealing for various times and temperatures and after TL measurement. Sodium and K show evidence for loss following sample annealing at high temperatures, and loss of both shows a time dependency.

Compositional data

The sharp decrease in the TL sensitivity of Allan Hills A77011 after annealing at 1000°C for 10 or

100 h is accompanied by a 40% loss of Na and K (Fig. 6). The Kernouve meteorite showed 20–30% loss of these elements after annealing at 1100°C for 10 h and this accompanied a ~10-fold decrease in TL sensitivity (SEARS *et al.*, 1984a). Apparently, element loss, like the TL sensitivity decrease, occurred more readily in Allan Hills A77011 than in Kernouve and the reason may also involve the petrographic siting of the feldspar. If element loss is a diffusion controlled process, then loss from a microcrystalline mesostasis would occur more readily than from ~100 μm grains since the latter requires considerable volume diffusion while loss from a fine-grained mesostasis would be considerably facilitated by grain boundary diffusion.

Cause of the TL peak temperature and peak width variations with annealing

We were able to obtain activation energies (E_a) for the processes responsible for the peak temperature and peak width variations using the data in Fig. 5 and the method described by SEARS *et al.* (1984a) (substitution of the first-order kinetics equation into the Arrhenius equation). The resulting Arrhenius plot for the 10 and 100 hour series of annealings produces lines with correlation coefficients of 0.87 to 0.94 (Fig. 7). For the peak temperature, the 10 and 100 hour data yielded E_a values of 7.1 ± 2.7 and 10.9 ± 4.5 kcal/mole, respectively, and for peak width the values were 6.3 ± 1.3 and 4.0 ± 1.8 kcal/mole. (The uncertainties are $\pm 1\sigma$.) The agreement in the values obtained for different annealing runs is reassuring. The similarity in E_a for the peak shift and peak broadening indicates that the same mechanism is probably re-

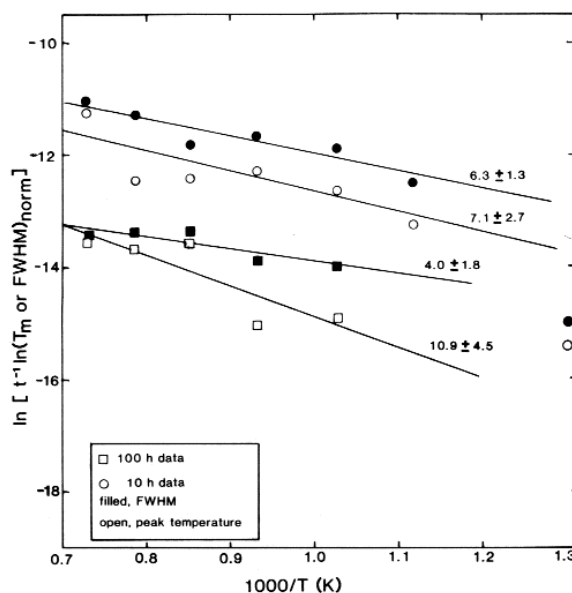


FIG. 7. Arrhenius plots for the TL peak temperature and width following annealing. The values indicate the calculated activation energies (kcal/mole) with 1σ uncertainties.

sponsible for both effects. The smallness of the values precludes any fusion process (~ 25 kcal/mole) or any chemical process involving the breakage of Si-O bonds (~ 100 kcal/mole). We are left with diffusional processes as the most likely cause.

Superimposed on the plot of our data for the peak temperature change (Fig. 4) are data obtained by PASTERNAK (1978; page 226) for annealed samples of the Amelia albite ($\text{An}_{0.5}\text{Or}_{1.3}\text{Ab}_{98.2}$). Pasternak's annealing conditions were comparable to ours, except that his samples were placed in a Pt crucible and annealed for 1 day in an He atmosphere, and we assume comparable errors. Pasternak used X-ray diffraction to show that in the parameter $2\theta(131) - 2\theta(1\bar{3}1)$ increased from $1.084 \pm .007$ to $1.208 \pm .011$, indicating that the annealing had caused a measurable transformation of the albite from the low temperature (ordered) to the high temperature (disordered) form. However, transformation was not complete, as this would have yielded a value of 2.0 for $2\theta(131) - 2\theta(1\bar{3}1)$. The simplest interpretation of our data, therefore, is that the TL phosphor in Allan Hills A77011 is feldspar in the low temperature form and that the annealing treatment has caused some transformation to the high-temperature form. If this is correct, then it is the first indication of the presence of low-temperature feldspar in any chondritic meteorite, and indicates that during metamorphism the plagioclase in type <3.5 ordinary chondrites was able to achieve the equilibrium structure at very low temperatures.

The activation energy for the low to high temperature transformation was determined from X-ray diffraction measurements to be 74.3 ± 1.4 kcal/mole (MCKIE and MCCONNELL, 1963). Pasternak found that E_a for the transformation based on the TL data for Amelia albite in Fig. 4 was 21 ± 5 kcal/mole. This is somewhat greater than our value but still significantly less than the McKie and McConnell's value. Although the movement in the TL peak position and the broadening of the TL peak are associated with the low to high temperature transformation, apparently it is not actually the transformation that is responsible for the changes; Pasternak suggested that defect formation which precedes the transformation may actually be responsible for the TL changes. The composition of the secondary feldspar in type 3 chondrites is not known, but it is doubtful that it is albite since in equilibrated L chondrites the feldspar is oligoclase ($\text{Ab}_{84}\text{An}_{10}\text{Or}_6$, VAN SCHMUS and RIBBE, 1968). However, compositional differences between albite and meteoritic feldspar probably do not explain the difference in the two TL-derived values, since our analysis of the data of SCHNEIDER (1957) indicates that oligoclase probably undergoes the low to high transformation with the same E_a as albite. (Extracting the data from Schneider's Fig. 1, we calculate 59 ± 54 kcal/mole for his albite sample and 63 ± 11 kcal/mole for his oligoclase sample; details are available from the authors.)

Palaeothermometry

Palaeothermometry of type 3 chondrites has proved very difficult. The use of mineral pairs is precluded because of the absence of equilibration in type 3 chondrites and the exchange of oxygen isotopes between minerals cannot be used because of the discovery of significant amounts of an ^{16}O -rich component. The absence of composition-dimension relationships in the taenite grains indicates that certain type 3 chondrites, Bishunpur (type 3.1) and Krymka (type 3.0) have not experienced temperatures above 400°C (WOOD, 1967; RAMBALDI and WASSON, 1981; DODD, 1981). The distribution of Fe and Ca between orthopyroxene and diopside has been used to determine equilibration temperatures for type 6 chondrites of all classes, and for petrologic types 4 and 5 for LL chondrites (see DODD, 1981, for a review, and OLSEN and BUNCH, 1984). The results depend critically on the calibration curve assumed, and there appears to be systematic differences between estimates based on the Ca distribution and those based on the Fe distribution. The oxygen isotope thermometer has been applied to seven type 5 and 6 chondrites and one type 4 chondrite (ONUMA *et al.*, 1972). DODD (1981) summarizes the data as suggesting the following metamorphic temperature ranges: 3, 400–600 (a few type 3, <400); 4, 600–700; 5, 700–750; 6, 750–950°C. However, it is clear from his discussion that these are far from certain.

The present results suggest that TL sensitivity measurements may enable a new approach to the palaeothermometry of chondrites. Fig. 8 presents three plots of peak temperature against peak width; Fig. 8a shows the present data for Allan Hills A77011, Fig. 8b presents the data we obtained from the glow curves of SEARS *et al.* (1984a) for the Kernouve H6 chondrite (Table 3), and Fig. 8c presents the data for 42 type 3 ordinary chondrites from SEARS and WEEKS (1983) and SEARS *et al.* (1982). (Previously unpublished peak temperature and peak width data for type 3 ordinary chondrites are presented in Table 4.)

In both Fig. 8a and 8c the data tend to form two clusters, one at the lower left, which we think is associated with the low temperature feldspar, and one at the upper right, which we think is associated with the high temperature feldspar. VAN SCHMUS and RIBBE (1968) performed X-ray diffraction studies on feldspar separated from a number of equilibrated chondrites and found that it was always in the high temperature form. Consistent with this, the Kernouve data plot in the upper right portion of Fig. 8b. If type > 3.5 have high temperature feldspar and type < 3.5 have low temperature feldspar as their TL phosphor and then laboratory data on the transformation temperature indicate equilibration temperatures for the type ~ 3.5 meteorites of $500\text{--}600^\circ\text{C}$ (SMITH, 1972). However, some caution is necessary since chondritic feldspar is oligoclase, for which little laboratory data exist, and there are trace and minor

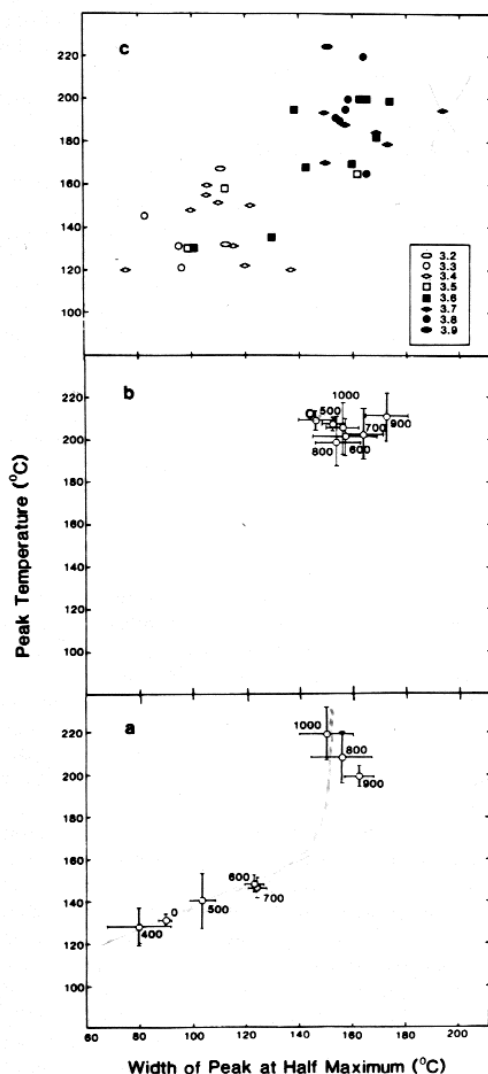


FIG. 8. Thermoluminescence peak temperature against width of the peak for (a) samples of Allan Hills A77011 and annealed at the temperatures indicated (°C; 0 = unannealed), (b) samples of the Kernouve equilibrated chondrite annealed over a similar range of temperatures and times, and (c) 38 type 3 ordinary chondrites (Table 4; SEARS and WEEKS, 1983). The petrologic type of each sample is indicated. There is a bimodal distribution in the data with type ≤ 3.5 in the lower cluster and type > 3.5 in the upper cluster, and 77011 can be transferred from one cluster to the other by annealing. All the Kernouve data plot in the upper cluster and annealing at temperatures below 700°C does not transfer points to the lower cluster.

element differences between meteoritic and the synthetic feldspars used for laboratory investigations. Assuming that the TL changes induced in Allan Hills A77011 by our annealing treatments had all achieved equilibrium, then our data indicate an equilibration temperature for the type 3.5 chondrites of 700–

Table 3. Effect of annealing for 10 and 100 hour on the TL peak temperature and FWHM for the Kernouve H6 chondrite (measured from the glow curves of SEARS *et al.*, 1984a).*

Annealing Temperature (°C)	Peak Temperature (°C)		FWHM† (°C)	
	10h	100h	10h	100h
Unannealed	217 ± 5		167 ± 7	
500	234 ± 3		193 ± 7	
	196 ± 2		153 ± 2	
600	209 ± 8		170 ± 9	
	208 ± 7		185 ± 15	
700	212 ± 2	253 ± 3	178 ± 6	223 ± 5
	208 ± 12	229 ± 10	187 ± 9	188 ± 10
800	199 ± 12		177 ± 2	
	217 ± 12		179 ± 10	
900	210 ± 12		179 ± 10	
	228 ± 9		209 ± 2	
1000	203 ± 3	234 ± 10	174 ± 6	178 ± 7
	222 ± 12		179 ± 2	

* Uncertainties are 1 σ based on 3–5 replicate measurements.

† Full-width-half-maximum.

800°C. However, we cannot be sure that longer times at 700°C would not produce the TL changes. It seems safe to conclude, however, that the equilibration temperature for type 3.5 ordinary chondrites is $\leq 800^\circ\text{C}$. This conclusion is consistent with the results of ASHWORTH *et al.* (1984) who found that striations in the pyroxenes of a type 4 H chondrite, Quenggouk, disappeared after annealing at 800°C for one week, whereas no change occurred after annealing at 650°C.

Also indicated in Fig. 8c is the petrologic type of the chondrites. As expected, the type 3.2–3.5 constitute the lower cluster and the type 3.6–3.9 constitute the upper cluster. The meteorites which appear to be

Table 4. Unpublished data from the studies of SEARS *et al.* (1980; 1982) on the TL peak temperature and FWHM for type 3 ordinary chondrites with TL sensitivity > 0.05 (where Dhajala = 1).

Meteorite*	Type	Peak Temperature (°C)		FWHM† (°C)
St. Mary's County	3.3	145		83
Chalpinur	3.4	120		77
77038	3.4	150		122
77214	3.4	148		100
77249	3.4	152		105
77260	3.4	155		105
77167	3.4	152		110
Sharps	3.4	122		120
77011	3.5	130		100
77050	3.5	160		105
77015	3.5	158		112
Willaroy	3.5	195		157
Tieschitz	3.6	130		100
Parnallee	3.6	135		130
Brownfield	3.6	195		138
Yamato 74191	3.6	168		142
Clovis	3.6	170		160
77278	3.6	200		162
Kohar	3.6	200		162
Mezö Madaras	3.7	190		155
Hedjaz	3.7	200		157
77299	3.7	220		162
Prairie Dog Creek	3.8	170		150
Dhajala	3.8	165		165
78084	3.9	225		150

* Five digit numbers should be prefixed with "Allan Hills A".

† Full-width-half-maximum.

discordant are the two type 3.6 plotting in the lower cluster and the individual type 3.5 chondrite plotting in the upper cluster. Since petrologic type assignments made on the basis of TL are thought to be within ± 0.1 (this is the 1σ estimate for the TL data, see SEARS *et al.*, 1980), the discordancies are not significant.

Thermal history of type 3 ordinary chondrites

There are several implications of our suggestion that the least metamorphosed type 3 chondrites contain the ordered form of feldspar and from our ability to cause, by simple thermal treatments, TL changes similar to the trends observed in UOC. These implications may be discussed in the context of the following related questions: 1) why did the high form, present in >3.5 chondrites, not revert to the low form on cooling; 2) are the data consistent with the concept of the UOC as a single metamorphic sequence, whereby a petrologic type 3.0 chondrite is related to type 6 by closed-system, post-accretionary metamorphism; 3) was the metamorphism experienced by chondrites progressive metamorphism or autometamorphism (as defined by DODD, 1969); 4) did the metamorphism pre- or post-date agglomeration; 5) do these data provide any insights into post-metamorphism cooling rates?

The data in Fig. 8b bear on the questions 1 and 5. We found that while the low to high temperature transformation could be performed in the laboratory, the reverse process could not. It may be relevant that MACKENZIE (1957) and MARTIN (1969) found that the high temperature form of albite is metastable in the field of the low form over a wide temperature interval. In terms of TL and thermal history, three groups of type 3 chondrites can be distinguished; types 3.0–3.2, types 3.3–3.5 and types ≥ 3.6 (see Fig. 3 of SEARS *et al.*, 1982). The thermal history of each group could be inferred to be as follows: a) For types 3.0–3.2, the formation of grains and chondrules in the nebula was followed by agglomeration with little or no subsequent or attendant metamorphism. The feldspathic material present was almost entirely glass, and the TL observed is due to primary feldspar or other phosphors. GOODING (1979) and SEARS *et al.* (1984b), for example, have observed that the glass in type 3 ordinary chondrites is feldspathic in composition. b) For types 3.3–3.5, the formation of grains and chondrules in the nebula produced glasses with essentially feldspathic composition, but subsequent or attendant metamorphism produced secondary feldspar *via* the devitrification of glass at temperatures below the order-disorder transition. c) For the remaining types, the formation and agglomeration of glassy feldspathic grains and chondrules in the nebula was associated with metamorphism above the order-disorder transformation temperature. Subsequent cooling did not cause a reversion to the low form because of the metastability of the high form, pre-

sumably because of the lower probability of the transition state forming in the high state than in the low state (MCKIE and MCCONNELL, 1963).

We assume, therefore, that the TL data for Kernouvé did not move to the lower left part of Fig. 8b after annealing below 700°C, and the high form did not revert to the low form in UOC on cooling, because of the kinetics of the process. The situation may afford an opportunity for estimating an upper limit for the cooling rate of type ≥ 3.6 chondrites through the temperature range in which the high to low transformation occurred. Unfortunately, the high to low transformation is so sluggish that it does not appear to have been studied kinetically in the laboratory; indeed a major problem has been explaining the abundance of low temperature feldspars terrestrially. Water and $\text{Na}_2\text{Si}_2\text{O}_5$ catalyse the transformation and are assumed to account for the terrestrial abundance of low-feldspar (MARTIN, 1969). It does appear, however, that the metastability of the high form of feldspar in type ≥ 3.6 chondrites reflects a dry, $\text{Na}_2\text{Si}_2\text{O}_5$ -free environment.

We believe the metamorphism experienced by the UOC occurred after agglomeration because it is difficult to see how some structures (*e.g.* intergrown metal) could not have occurred after agglomeration. The main indicator of pre-agglomeration metamorphism is the variable equilibration of individual chondrules, but this could reflect differences in the amount and composition of the chondrule mesostasis (SEARS *et al.*, 1984b).

One of the questions which has proved most difficult to resolve is whether the meteorites experienced metamorphism following their formation at high temperatures (autometamorphism) or whether they experienced metamorphism during a heating episode subsequent to their formation (progressive metamorphism) (*e.g.* DODD, 1969; TAYLOR and SCOTT, 1984). ASHWORTH *et al.* (1984) recently argued that progressive metamorphism could not have homogenized silicate compositions in type 4 chondrites without destroying lamellae of clinopyroxene which have been observed in the orthopyroxene. Their argument is based on a poor estimate for the activation energy for the clinopyroxene removal and ignores the possibility that clinolamellae may have formed on cooling; this process has been demonstrated in the laboratory (SMYTH, 1974). The present TL data seem more consistent with progressive metamorphism. If the meteorites agglomerated hot and the petrologic type sequence reflects agglomeration temperatures, as required by autometamorphism, then the meteorites must have experienced a two stage cooling history; stage 1, associated with agglomeration has a slow cooling rate so that equilibrium could be achieved (*e.g.* high-temperature feldspar form) and minerals homogenized, followed by a second, rapid cooling stage, so that the equilibria were frozen (*e.g.* the high form of feldspar did not convert to the low form). The same two stage history would have been

experienced by all petrologic types, so that a range of equilibria would be obtained. Progressive metamorphism offers a simpler interpretation, since the equilibria would be fixed at or near the maximum temperature experienced during metamorphism, where elevated temperatures were experienced for the longest times as the temperature-time curve leveled off, prior to falling.

The idea that the UOC are a single metamorphic sequence (question 2 above), was advocated by DODD *et al.* (1967) and, more recently, HUSS *et al.* (1981) and others. Since we have been able to reproduce the TL peak temperature and peak width relationships observed in the type 3.5–type 6 series in the laboratory by simple closed-system processes on the agglomerated material, our data are consistent with this idea. However, if our interpretations are correct, the TL changes reflect internal crystallographic rearrangements in a particular component acting independently of the rest of the meteorite and could therefore have occurred prior to accretion. In short, a null result would have argued against the metamorphic sequence idea, but a positive result is consistent with either possibility.

The strongest evidence against a single metamorphic sequence for the UOC is provided by the oxygen isotope data of CLAYTON *et al.* (1981). The type 3 ordinary chondrites contain oxygen which is 1‰ higher in ^{18}O (and 0.5‰ higher in ^{17}O) than the equilibrated chondrites. SEARS and WEEKS (1983) found that it was difficult to explain this in terms of the loss of CO , the most probable mechanism so far proposed, because of the lack of sufficient C. There is no such mass balance problem for Si, and we suggest that the oxygen isotope difference between UOC and equilibrated chondrites may involve the formation of SiO , but then one might expect Si isotope differences between UOC and the equilibrated chondrite and this is not observed (CLAYTON *et al.*, 1983). However, the possibility remains to be quantitatively explored.

A final point we wish to discuss concerns the spectacular 10^3 -fold range of TL sensitivities observed in type 3 chondrites. We have not, in our annealing experiments on a type 3.4 chondrite, produced any significant increase in the TL sensitivity of our samples. This is consistent with our interpretation of the increase being due to the devitrification of glass (SEARS *et al.*, 1980; 1982; 1984b) as laboratory experiments involving the formation of crystalline feldspar from glasses typically require 1 kbar of encumbent pressure for 1000 h, and the presence of water or $\text{Na}_2\text{Si}_2\text{O}_5$ as a catalyst. The absence of a big TL sensitivity increase in our data is not therefore evidence against a single metamorphic sequence of UOC.

CONCLUSIONS

The thermoluminescence sensitivity changes induced in Allan Hills A77011 are similar to those

induced in the Kernouve equilibrated chondrite except that the abrupt TL sensitivity decrease observed to occur after annealing 77011 at 1000°C , and associated alkali loss, occurred at 1100°C for Kernouve. This difference is thought to be associated with differences in the petrographic setting of the feldspathic material in the two meteorites.

The thermoluminescence peak temperature and the peak width of Allan Hills A77011 show changes on annealing which resemble those shown by Amelia albite and type 3 ordinary chondrites. The peak temperature and width changes have similar activation energies, indicating a common process, probably involving diffusion. The changes are associated with the low to high temperature transformation in feldspar, but the transformation is not the cause of the TL change since their activation energy is lower. The data indicate that certain type 3 ordinary chondrites (type < 3.5) have not experienced temperatures above 800°C . Annealing an equilibrated meteorite at low temperatures did not produce decreases in TL peak temperature and width, consistent with literature data that the high form tends to exist metastably in the field of the low form.

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