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Chemical and physical studies of type 3 chondrites. IX: Thermoluminescence and hydrothermal annealing experiments and their relationship to metamorphism and aqueous alteration in type <3.3 ordinary chondrites

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Abstract—Samples of four type 3 chondrites have been annealed at 400–850°C and 0.77–1 kbar for 10–500 h in the presence of various amounts of water (0–10 wt.%) and sodium disilicate (0–2 molal) and their thermoluminescence properties measured. After annealing for >20 h at temperatures >600°C, the TL sensitivity of the samples increased by factors of up to 40. After annealing at <600°C for 10–500 h, or relatively short periods at high temperatures (*e.g.*, ≤20 h at 850°C), the TL sensitivity of the samples decreased by up to 2 orders of magnitude (depending on the original value). The TL peak temperatures observed in the present experiments are consistent with a low form of feldspar (the TL phosphor) being produced at <800°C and a high form being produced at >800°C. When both high and low forms were present originally, the low-form was destroyed preferentially. We suggest that these data are consistent with the TL-metamorphism trends observed in type >3.2 chondrites, being due to the formation of feldspar (with structural details being dependent on formation temperature) by the devitrification of chondrule glass during metamorphism. For types <3.2, the TL data are equally consistent with these types experiencing lower levels of metamorphism than the higher types, or with type 3.0 being produced from higher types by aqueous alteration. The presence of water with non-terrestrial D/H ratios, and petrographic evidence for aqueous alteration in Semarkona, lead us to favour the aqueous alteration hypothesis.

INTRODUCTION

THE ORDINARY CHONDRITES are a unique source of information about the earliest period of solar system history and the processes experienced by the first solids to form. Most ordinary chondrites show variations in certain petrologic and mineralogic properties which reflect varying degrees of metamorphism. These are summarised in VAN SCHMUS and WOOD's (1967) scheme of petrologic types. The least metamorphosed ordinary chondrites, and in this sense the "most primitive", are type 3, while the most metamorphosed are type 6. With increasing metamorphism, volatile elements and compounds become less abundant, Ca-poor clinopyroxene is replaced with orthopyroxene, igneous glass becomes less abundant, feldspar becomes more abundant and coarsens, mineral compositions become increasingly homogeneous, and chondrule textures are obliterated (VAN SCHMUS and WOOD, 1967; DODD, 1969). Within the type 3 ordinary chondrites, systematic changes in some of these properties suggest that further subdivision is desirable (DODD *et al.*, 1967; WOOD, 1967; HUSS *et al.*, 1981; AFIATTALAB and WASSON, 1980), and hence subdivision into types 3.0–3.9 (SEARS *et al.*, 1980).

The thermoluminescence (TL) properties of ordinary chondrites are also strongly related to metamorphism. The ordinary chondrites as a whole show a 10^5 fold range in TL sensitivity, while the type 3 chondrites show a 10^3 fold range (SEARS *et al.*, 1980). For types 3.3 and above, the temperature at which maximum TL emission occurs (the "peak temperature"), and the range of temperatures over which TL is emitted (the "peak width" or, more precisely, the full width of the TL peak at half its maximum intensity, FWHM), increase with increasing metamorphism; types 3.3–3.5 have TL peak temperatures and widths of 120–160 and 70–140°C, respectively, while types 3.6–3.9 have TL peak temperatures and widths of 160–220 and 140–200°C, respectively (SEARS *et al.*, 1982). These changes in TL peak temperature and width can be reproduced by annealing the appropriate meteorites or terrestrial feldspar samples (feldspar is the major producer of TL in meteorites: LALOU *et al.*, 1970), so that TL peak shape, as well as TL sensitivity, is apparently reflecting thermal history. The peak shape changes seem to be related to disordering since they occur near the order/disorder transformation temperature for feldspar. However, kinetic studies and X-ray diffraction data show that the relationship is not straight forward (GUIMON *et al.*, 1985; HARTMETZ and SEARS, 1987). For types <3.3, the TL glow curves are broad and characteristically hummocky, and cathodoluminescence images show that a great many phosphors are probably producing the TL in addition to those which dominate in the higher types (DEHART and SEARS, 1986).

We have argued that the metamorphism-dependence of TL sensitivity reflects crystallisation of feldspar from primary, feldspathic, igneous glass abundant in the lowest petrologic types (SEARS *et al.*, 1980; GUIMON *et al.*, 1986). We have attempted to test this idea by performing a series of annealing experiments in which water, sodium disilicate (Nadisi) and high pressures enable devitrification to occur at measurable rates (LOFGREN, 1971). Preliminary experiments on Sharps showed that under certain conditions an increase in TL sensitivity could be produced and that a detailed study was justified (GUIMON *et al.*, 1986). Samples of the TL curves from our preliminary work are shown in Fig. 1; means and standard deviations for the full data set are given in Table 1. When only ~2 wt.% water was added to the samples, prior to annealing, the annealing caused the TL peak to broaden and

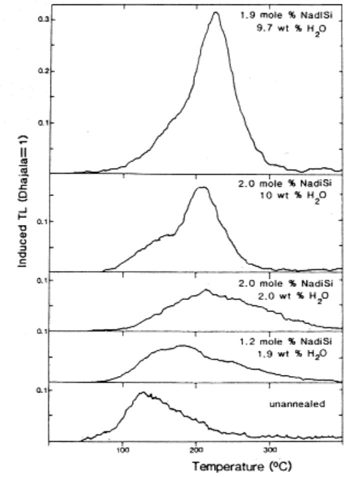

FIG. 1. Representative glow curves (TL *vs.* temperature) for samples of the Sharps meteorite annealed at 700–847°C and at 1 kbar pressure in the presence of water and sodium disilicate (means ± 1σ for 3–5 curves for each sample appear in Table 1). Annealing in the presence of small amounts of water causes the peak to broaden and move to higher temperature, but to slightly decrease in TL sensitivity. However annealing in the presence of ~10 wt.% water causes a narrow peak to appear at 220°C with a significant increase in TL sensitivity (from GUIMON *et al.*, 1986).

move to higher temperatures in a way similar to that observed for samples of meteorite annealed dry above the order/disorder temperature. However, when 10 wt.% water was added to the samples prior to annealing, the treatment caused a significant increase in TL sensitivity. In the present paper we report on a detailed study of the effects of hydrothermal annealing on a type 3.0 ordinary chondrite, Semarkona, and a type 3.4 ordinary chondrite, Allan Hills A77214 (ALHA77214). We also report, more fully, the data from our preliminary study of Sharps, and discuss these in the light of our new data, and we report two runs with the Dhajala (type 3.8) ordinary chondrite. Dhajala is significant in the present context as its TL properties suggest that, as with equilibrated ordinary chondrites (VAN SCHMUS and RIBBE, 1968), it contains feldspar in the high-form.

EXPERIMENTAL TECHNIQUES

Samples of Semarkona, ALHA77214, Sharps and Dhajala, typically 1.5 g, were ground, the magnetic material removed with a hand-magnet, and the non-magnetic material gently re-ground so as to pass through a 100-mesh sieve. After drying overnight in a vacuum oven at 85°C, 20–50 mg aliquants were sealed in gold capsules with predetermined amounts of sodium disilicate (Nadisi) and/or water. The capsules were then placed, four at a time, in externally heated pressure vessels (TUTTLE, 1949; LOFGREN, 1971). The run times and temperatures are listed in Table 1, with pressures of ~1 kbar and argon as the pressure-medium. The thermocouples were calibrated

Table 1. Conditions of annealing and thermoluminescence properties of Allan Hills, Semarkona, Dhajala and Sharps meteorites.*,+

Name	T_a (°C)	t_a (h)	H_2O (wt%)	NDS	100 - 175°C Peak TL sens#	T_m (°C)	FWHM (°C)	175 - 225°C Peak TL sens#	T_m (°C)	FWHM (°C)
SEM	Natural							.0049±.0008	214±15	179± 8
SEM	400	168	9.2	1.9	<.0008	ND	ND	-	-	-
SEM	400	168	11.1	3.2	-	-	-	.0040±.0006	207± 3	52± 3
SEM	450	168	11.1	2.8	<.0004	ND	ND	-	-	-
SEM	450	168	11.0	2.8	<.0005	ND	ND	-	-	-
SEM	500	168	9.6	2.7	.073±.013	157± 9	66± 6	-	-	-
SEM	500	168	8.7	1.9	<.0008	ND	ND	-	-	-
SEM	500	168	8.6	2.4	<.0004	ND	ND	-	-	-
SEM	500	168	11.2	2.9	<.0008	150±20	ND	-	-	-
SEM	500	168	11.8	0	<.0006	ND	ND	-	-	-
SEM	500	168	8.3	0	<.0006	ND	ND	-	-	-
SEM	500	168	11.0	1.0	<.0008	ND	ND	-	-	-
SEM	500	168	11.5	0.9	<.0008	ND	ND	-	-	-
SEM	550	168	11.1	2.6	<.0006	ND	ND	-	-	-
SEM	600	168	9.7	1.8	.006±.001	147± 5	108±11	-	-	-
SEM	600	168	10.6	1.7	-	-	-	.015±.002	207± 2	158± 5
SEM	700	168	11.0	1.8	-	-	-	.053±.008	206± 2	78± 2
SEM	700	168	9.9	2.1	-	-	-	.087±.013	219± 4	68± 2
SEM	800	168	10.9	2.0	-	-	-	.10 ±.05	210± 4	62± 2
SEM	800	168	10.4	2.1	-	-	-	.04 ±.02	204± 4	56± 3
SEM	900	168	9.8	2.1	-	-	-	.23 ±.03	204± 4	49± 1
ALHA	Natural				.058±.013	122± 6	88± 6	-	-	-
ALHA	500	10	10.5	2.3	.040±.006	115± 2	86± 3	-	-	-
ALHA	500	10	10.5	2.5	.0048±.0006	123± 3	82± 3	-	-	-
ALHA	500	10	5.7	2.4	.021±.003	122±11	87± 4	-	-	-
ALHA	500	10	5.0	4.8	.025±.004	130± 5	88± 4	-	-	-
ALHA	500	20	9.7	2.0	.0064±.0011	143± 6	84± 3	-	-	-
ALHA	500	20	9.9	1.6	.0068±.0013	131± 4	101± 2	-	-	-
ALHA	500	20	5.1	2.3	.016±.003	139± 6	97± 3	-	-	-
ALHA	500	20	4.9	1.8	.014±.002	121± 5	75± 3	-	-	-
ALHA	500	100	10.4	1.9	.0087±.0029	131± 5	77± 3	-	-	-
ALHA	500	100	9.4	1.9	.014±.004	127± 5	80± 2	-	-	-
ALHA	500	100	5.1	2.0	.009±.003	123± 5	60± 4	-	-	-
ALHA	500	100	5.1	4.7	.0010±.0002	126± 5	ND	-	-	-
ALHA	†500	100	5.0	0	.040±.004	101± 3	70±10	-	-	-
					.0044±.0007	125± 5	60±10	-	-	-
ALHA	500	100	5.5	0	.0057±.0008	111± 5	50±10	-	-	-
ALHA	500	200	11.0	1.8	<.0008	ND	ND	-	-	-
ALHA	500	200	10.7	2.7	.0018±.0002	135± 5	93± 4	-	-	-
ALHA	500	200	10.7	2.7	.0049±.0009	135± 5	70± 4	-	-	-
ALHA	500	200	5.0	4.2	.0014±.0004	160±15	105±21	-	-	-
ALHA	500	200	5.2	1.9	.054±.008	140± 5	99± 7	-	-	-
ALHA	500	500	9.9	2.1	-	-	-	.0003±.0008	240± 5	119±28
ALHA	500	500	9.8	1.7	.0010±.0001	172± 6	ND	-	-	-

continued/...

Table 1. (contd.)

	T_a	t_a	H_2O	NDS	100 - 175°C Peak			175 - 225°C Peak		
Name	(°C)	(h)	(wt%)		TL sens#	T_m (°C)	FWHM (°C)	TL sens#	T_m (°C)	FWHM (°C)
ALHA	500	500	9.6	2.2	-	-	-	.0024±.0005	181± 5	ND
ALHA	500	500	5.1	1.7	<.0008	ND	ND	-	-	-
ALHA	500	500	4.8	1.6	<.0008	ND	ND	-	-	-
ALHA	850	10	9.6	2.9	<.0008	ND	ND	-	-	-
ALHA	850	10	5.1	1.8	.0043±.0007	160±10	125± 5	-	-	-
ALHA	850	10	5.1	2.7	-	-	-	.0024±.0005	176± 6	ND
ALHA	850	10	10.0	1.9	<.0008	ND	ND	-	-	-
ALHA	850	20	10.3	2.3	-	-	-	.0095±.0014	193± 3	44± 2
ALHA	850	20	9.8	7.5	-	-	-	.013±.002	191± 1	43± 1
ALHA	850	20	5.2	1.9	.0056±.0008	171± 6	135±16	-	-	-
ALHA	850	20	7.1	2.6	-	-	-	.0031±.001	206± 4	ND
ALHA	850	100	10.9	2.7	.014±.002	149± 6	ND	.011±.001	187± 5	ND
ALHA	850	100	10.3	2.0	.011±.001	141± 3	ND	.0057±.0008	181± 3	ND
ALHA	850	100	5.1	1.8	.014±.002	170± 5	ND	.012±.002	200± 5	ND
ALHA	850	100	5.3	1.8	.013±.001	143± 3	ND	.010±.001	180± 2	ND
ALHA	850	100	5.0	0	.033±.003	152± 3	ND	.014±.001	189± 3	ND
ALHA	850	100	5.5	0	.036±.004	145± 3	ND	.014±.002	181± 2	ND
ALHA	850	200	10.0	2.5	.052±.008	156± 3	35± 1	.020±.003	192± 2	ND
ALHA	850	200	10.0	2.1	.075±.01	149± 3	ND	.19 ±.02	196± 5	43± 1
ALHA	850	200	4.9	3.1	-	-	-	.039±.005	194± 3	83± 9
ALHA	850	200	4.9	1.8	.057±.011	154± 4	47± 6	.035±.008	186± 5	43± 3
ALHA	850	500	11.1	2.3	.015±.002	145± 3	ND	.013±.002	184± 2	ND
ALHA	850	500	11.0	2.0	.016±.003	161± 3	ND	.017±.002	203± 2	ND
ALHA	850	500	5.0	2.2	.011±.001	109± 1	50± 5	-	-	-
ALHA	850	500	5.3	1.8	.028±.004	142± 2	ND	.013±.001	179± 1	ND
ALHA	850	500	5.3	3.1	.030±.003	143± 3	ND	.012±.002	179± 1	ND
SHA	Natural				.11 ±.003	145± 4	84± 7	-	-	-
SHA	700	100	0	0	.17 ±.015	154± 3	126± 5	-	-	-
SHA	755	168	0.	0	.18 ±.02	141± 3	118± 3	-	-	-
SHA	755	168	0	0	.15 ±.02	156± 4	122± 2	-	-	-
SHA	755	168	2	0	.050±.001	167±11	147±10	-	-	-
SHA	755	168	2	0	-	-	-	.067±.006	184± 2	142± 3
SHA @	800	100	0	0	.13 ±.01	171± 5	158± 7	-	-	-
SHA @	800	100	0	0	.13 ±.01	160± 5	159± 5	-	-	-
SHA	847	174	2	2	-	-	-	.075±.008	218± 5	157±10
SHA	847	174	1.9	1.2	-	-	-	.068±.008	187±12	136± 6
SHA	845	174	10	2.0	-	-	-	.15 ±.02	210± 4	63± 3
SHA	845	174	9.7	1.9	-	-	-	.33 ±.02	225±11	72± 9
DHA	Natural				1.00	168±10	168±10			
DHA	850	168	7.6	2.1	-	-	-	.20 ± .02	194± 3	50± 9
DHA	850	168	9.9	2.0				.45 ± .10	189± 1	52±10

* Uncertainties are standard deviations of 3-5 replicate measurements.

+ Name refers to meteorite names, abbreviated as follows: DHA, Dhajala; ALHA, Allan Hills A77214; SHA, Sharps; SEM, Semarkona. Other symbols and abbreviations as follows: T_a, annealing temperature; t_a, annealing time; NDS, sodium disilicate (molal); T_m, TL peak temperature; FWHM, full width of the TL peak at half its maximum intensity; ND, instances where a peak is present but this parameter is difficult to determine, usually due to interference by another peak; hyphen indicates that the peak is absent.

Normalized to Dhajala = 1.

† Capsule sealed in a manner which separated part of the sample, that with high TL, from the fluxes. Only the low TL sample is plotted in Fig. 4a.

@ Annealed at atmospheric pressure using the techniques of Guimon et al. (1985).

against the melting point of NaCl and enabled temperatures to be determined with 1σ uncertainties of ~5%.

After annealing, the charges were lightly re-ground and 4 mg aliquants placed in copper dishes for TL measurement using the apparatus and techniques of GUIMON (1987). TL sensitivities were normalized to that of Dhajala. The values quoted are means of 3–5 measurements on the same sample and the quoted uncertainties are the standard deviations, compounded with the uncertainty for Dhajala in the case of TL sensitivity.

RESULTS

The results are listed in Table 1. The present Semarkona sample had a peak temperature higher than the literature values, but since 1σ uncertainties for this meteorite are rather large (~15°C), the difference is probably not significant. The data for the annealed Semarkona samples are shown in Fig. 2. The TL sensitivities of eleven of the thirteen samples of Semarkona annealed at or below 550°C were below detection limits, indicating at least a 6-fold decrease from the unannealed value. One sample had a peak temperature of 150 ± 20°C, but, with two exceptions, the TL signals of the others were too weak to enable peak temperatures and widths to be determined. The exceptions were: (1) a sample annealed at 400°C, which had TL properties unchanged from the original sample—this value is probably best explained as due to a poor capsule seal so that the sample was effectively annealed dry; and (2) a sample annealed at 500°C which had a peak temperature of 157 ± 9°C and a TL sensitivity 14 times that of the unannealed sample. This sample was particularly coarse-grained, and it was possible to hand-pick several individual grains which were found to have higher TL sensivitity than the remaining powder; that with highest TL value was clearly a chondrule fragment. Cathodoluminescence photographs have shown that Semarkona contains several large, and highly luminous, chondrules (DEHART and SEARS, 1986)

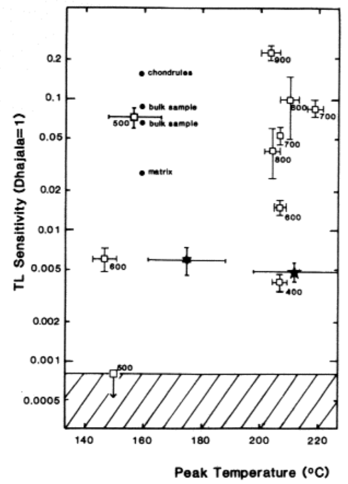

FIG. 2. TL sensitivity *vs.* peak temperature for samples of the Semarkona meteorite annealed for 168 h at 1 kbar in the presence of ~10 wt.% water and ~2 molal sodium disilicate (see Table 1 for precise experimental conditions and data). The values by each data point refer to the annealing temperature in °C; duplicate samples were run at most temperatures. The cross-hatched field refers to 10 samples annealed at 400, 450, 500 and 550°C whose TL sensitivities were ≤0.0008 and whose peak temperatures were indeterminate. The large star refers to the unannealed sample used for the present study, and the small star refers to literature data (SEARS *et al.,* 1982). The samples annealed at 600°C showed either a modest change or no change in TL sensitivity, but while one sample had a peak temperature of 147 ± 5°C, the other had a peak temperature of 207 ± 2°C. Samples annealed at >600°C showed an increase in TL sensitivity with increasing annealing temperature, by up to a factor of ~40, and had peak temperatures of 200–220°C. The anomalous 500°C sample was separated into (i) chondrules and chondrule fragments, (ii) two splits of bulk powder and (iii) "matrix" (*i.e.* fine-grained powder remaining after the chondrules and chondrule fragments had been removed); data for these separates are plotted as filled circles.

and the anomalous TL properties of this sample may reflect the presence of an atypical chondrule.

The two samples annealed at 600°C had TL sensitivities similar to, or a little greater than, the unannealed samples, but one had a peak at 147 ± 5°C while for the other it was 207 ± 2°C. Samples annealed above 600°C had peak temperatures of 200–220°C and TL sensitivities which increased with increasing annealing temperature by up to a factor of about 40 times that of the unannealed sample. Fig. 3 compares the peak widths and the peak temperatures for the annealed Semarkona samples with those of other type 3 ordinary chondrites. The data for the unannealed sample, and one of the samples annealed at 600°C, fall in the field of the type 3.6–3.9 chondrites, while the other 600°C sample and the anomalous 500°C samples plot in or near the field occupied by the 3.3–3.5 chondrites. The Semarkona samples annealed at or above 700°C, which showed significant increases in TL sensitivity, plot in a tight cluster with peak widths of 49–78°C and temperatures of 204–219°C.

After annealing at 500°C for up to ~200 h, the TL sensitivity of ALHA77214 decreased by a factor of about 10 and the TL peak moved from 122 ± 6°C to 120–140°C. Annealing for longer times caused a further order of magnitude decrease and an increase in peak temperature to 160–180°C (Fig. 4a). Thus in general, longer annealing times favoured lower TL sensitivities and higher peak temperatures. Annealing at 850°C caused the peak to move from 122 ± 6 to 140–160°C with, in general, up to a factor of 5 decrease in TL sensitivity (Fig. 4b). Additionally, a second discrete peak formed at 180–200°C which usually had a TL sensitivity ~1/5 the original value, but on occasion was comparable or greater in TL sensitivity than the original value.

The time dependency of the TL sensitivity data for ALHA77214 can be judged better using Fig. 5. The samples annealed at 500°C show a simple time-dependency in the TL sensitivity decrease, which is indepedent of the amount of water added (Fig. 5a). The samples annealed at 850°C show more complicated behaviour than the 500°C series (Fig. 5b). Short annealing times (10 and 20 h in the case of samples with 5 wt.% water, 10 h in the case of samples with 10 wt.% water) cause 25-fold decreases in TL sensitivity. However, longer annealing times produce a factor of only 5, or less, decrease in TL sensitivity compared to the annealed value.

To help establish the cause of the TL sensitivity decreases, a series of 500°C annealing experiments were performed on ALHA77214 with various amounts of water present but without Nadisi (Fig. 6 and Table 2). Samples containing 5 wt.% water showed a decrease in TL sensitivity comparable to that observed in Fig. 5a, but samples annealed in their "as received" state decreased in TL sensitivity by only a factor of 2. Samples dried in a vacuum oven at 85°C for one month showed a decrease in TL sensitivity by only 30%. Water is apparently the active agent causing decreases in TL sensitivity; even indigenous and/or absorbed atmospheric water is capable of causing an effect.

The Sharps data are qualitatively similar to those of ALHA77214 (Fig. 7, *cf.* Fig. 4b), showing a decrease in TL sensitivity and movement in peak temperature from 145 ± 4 to 160–185°C and then a new peak appearing at 200–220°C with TL sensitivities comparable to or higher than the original value. Also shown in Fig. 7 are data for several samples an-

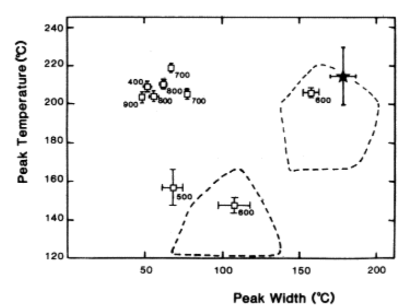

FIG. 3. TL peak temperature *vs.* peak width for samples of the Semarkona meteorite annealed at 1 kbar for 168 h. The star refers to the unannealed sample, and the values alongside the data points refer to annealing temperatures in °C, duplicates normally being measured. The two fields marked by broken lines are from GUIMON *et al.,* (1985) and refer to type 3.3–3.5 ordinary chondrites (lower field) and type 3.6–3.9 ordinary chondrites (upper field).

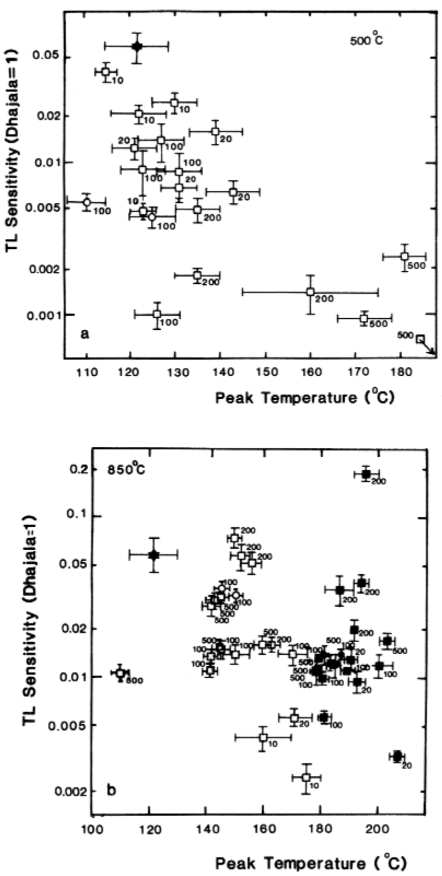

FIG. 4. TL sensitivity *vs.* peak temperature for samples of ALHA 77214 annealed at (a) 500°C and (b) 850°C for the time indicated (in hours). The star refers to the unannealed sample, the circles to samples containing water and the square to samples containing water and sodium disilicate. Peak temperatures appear to increase and TL sensitivity to decrease after annealing at 500°C, both in a time-dependent fashion. Annealing at 850°C caused similar changes in peak temperatures, but most samples produced glow curves with a second peak at 175–210°C (filled symbols). (Two samples annealed at 500°C, and two annealed at 850°C, have been omitted from these plots as only upper limits for TL sensitivity, and no peak temperatures, were obtained.)

nealed dry which showed a modest increase in TL sensitivity; this probably reflects heterogeneity in the original sample as the material was taken from a separate chip.

The TL peak temperature and peak widths for the annealed Sharps samples are compared in Fig. 8. The samples annealed dry at 700 and 755°C stayed in the field occupied by type 3.3–3.5 ordinary chondrites, but samples annealed dry at 800°C and all those annealed with 2 wt.% water had moved to the field of type 3.6–3.9 ordinary chondrites. As observed above, the Sharps samples annealed with 10 wt.% water had especially narrow peaks at 220°C. Water and/or Nadisi are also apparently catalysing the conversion of low to high feldspar.

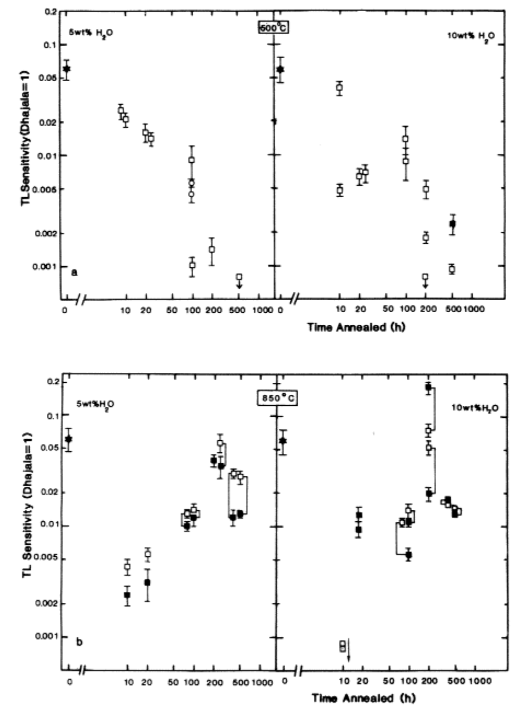

FIG. 5. TL sensitivity *vs.* annealing time for samples of Allan Hills A77214 annealed at 500 and 850°C, with ~5 and ~10 wt.% water. Symbols as in Fig. 4. Symbols linked with tie-lines represent samples whose TL glow curve consists of two peaks, the filled symbols referring to the higher temperature peak. Samples annealed at 500°C (Fig. 5a) showed a time-dependent (and water-independent) decrease in TL sensitivity, falling almost 100-fold after 500 h. The samples annealed at 850°C for 10–20 h (Fig. 5b) showed a decrease in TL sensitivity by more than an order of magnitude, but after annealing for longer periods the samples had TL sensitivities within a factor of 5 of the unannealed values.

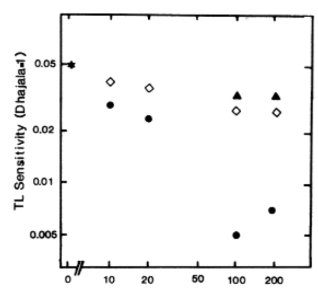

FIG. 6. The effect of various water contents on TL sensivity during annealing of Allan Hills A77214. Samples were annealed (i) with 5 wt.% H_2O (filled circles), (ii) in the "as received" state (open diamonds), and (iii) after drying in a vacuum oven at 85°C for one month (filled triangles). The star refers to the unannealed sample. The data show that it is the water that causes the TL sensitivity decreases observed in Figs. 4 and 5. Even the small amounts of absorbed atmospheric and indigenous water seem to have an effect. One sigma experimental uncertainties for the TL data are comparable with the size of the symbols.

Table 2 Thermoluminescence sensitivity data for samples of Allan Hills A77214 annealed at 500°C after extensive drying, in the "as received" state, and in the presence of 5 wt% water.

Annealing time (h)	H_2O (wt.%)	TL Sensitivity* (Dhajala = 1)
0	as received	0.052 ± 0.003
10	as received	0.040 ± 0.002
10	5	0.029 ± 0.002
20	as received	0.037 ± 0.002
20	5	0.024 ± 0.001
100	as received	0.027 ± 0.001
100	5	0.0057± 0.0008
100	dried	0.035 ± 0.002
200	as received	0.027 ± 0.001
200	5	0.0068± 0.0004
200	dried	0.034 ± 0.002

* Uncertainties are standard deviations based on triplicate measurements of a single sample.

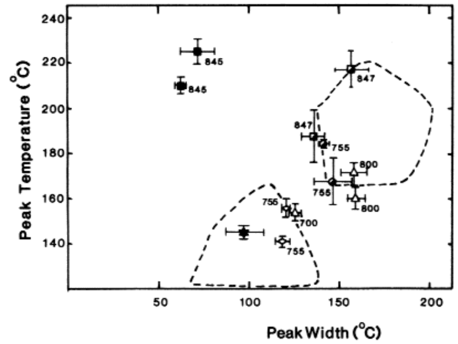

FIG. 8. Peak temperature *vs.* peak width for samples of the Sharps meteorite annealed at the temperatures indicated (°C) under a variety of conditions. Symbols as in Fig. 7. The broken lines indicate the fields of type 3.3–3.5 (lower field) and type 3.6–3.9 (upper field) ordinary chondrites. The TL peak tends to broaden and move to higher glow curve temperatures as the "severity" of the annealing conditions increase. However, samples annealed with ~10 wt.% water had very narrow peaks at ~220°C.

Dhajala is the only meteorite in the present study containing appreciable amounts of feldspar in the high form; 80% of the chondrules in Dhajala contain feldspar in the high form, while the remainder, which have TL sensitivities 10–100 times the others, contain feldspar in the low form (KECK *et al.,* 1986). The two annealing experiments on Dhajala produced decreases in TL sensitivity by factors of 2–5 and the peak moved to higher temperatures and decreased considerably in width. However, the TL intensity at higher glow curve temperatures did not change as much as that at low glow curve temperatures (Fig. 9), indicating that with a meteorite whose feldspar is a mixture of high and low forms it is the low form which is preferentially destroyed.

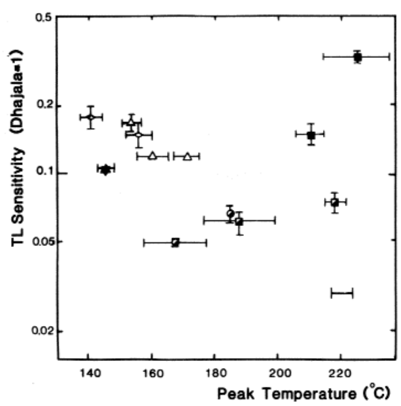

FIG. 7. TL sensitivity *vs.* peak temperature for samples of Sharps annealed at 700–850°C for 100–174 h under a variety of conditions. Open symbols indicate samples annealed in their natural state at 1 kbar (diamonds) and at atmospheric pressure (triangles, see GUIMON *et al.,* 1985). The "error bar" without a symbol refers to the induced TL at 220°C in the glow curve of the unannealed sample, while the star refers to the TL sensitivity of the unannealed sample. Samples to which water has been added are indicated by circles, those to which water and Nadisi have been added are indicated by squares: the filling indicates amount of added water; open, none; half-filled, ~2 wt.%; filled, ~10 wt.%. Samples containing no added water showed a modest increase in TL sensitivity with little or no change in peak temperature, samples with ~2 wt.% water showed a 1.5-fold decrease in TL sensitivity and 20–60°C increase in peak temperature, while samples containing ~10 wt.% water had TL peaks near 220°C with TL sensitivities up to 10 times that of the 220°C region in this glow curve before annealing. (Selected glow curves from these samples are shown in Fig. 1).

DISCUSSION

There are clearly several processes occurring in the samples during the annealing treatments which result in changes to their TL characteristics. We will discuss the lowering of TL sensitivity of certain samples, its increase in others, changes in TL peak positions and peak widths, and the relevance of these data to our understanding of the secondary alteration processes experienced by type 3 ordinary chondrites.

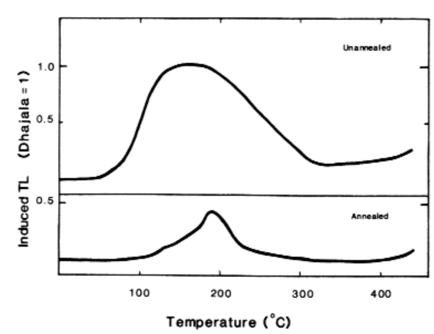

FIG. 9. Glow curves for the Dhajala meteorite, before (upper curve) and after annealing at 850°C for 168 h at 1 kbar in the presence of 7.6 wt.% water. The TL sensitivity decreased by a factor of 2–5 and the peak moved to high temperatures and became much narrower. We interpret this as the preferential destruction of the low-temperature feldspar component of the phosphor responsible for the TL.

Decreases in TL sensitivity

All meteorites in the present study showed a decrease in TL sensitivity under certain conditions of annealing. In general, low annealing temperatures and/or short annealing times favour the destruction of TL, and the low temperature part of the glow curve is usually affected preferentially. A factor of only 2 decrease in the TL sensitivity of ALHA72214 was produced by dry annealing for 100 h at temperatures $<1000°C$; a major drop in TL sensitivity occurred only after annealing $>1000°C$ (GUIMON *et al.,* 1985). The process causing the decreases in TL sensitivity in the present experiments is therefore associated with the fluxes. The annealing experiments on ALHA77214, in which samples were annealed with various amounts of water (Fig. 6), indicated that it is the water that is causing the decreases in TL sensitivity, and even the small amounts of absorbed atmospheric and indigenous water are sufficient to have an effect. A 40% decrease in TL sensitivity was also observed in samples of ALHA77011 and Kernouve after "dry" annealing; absorbed water might also be responsible in these cases (GUIMON *et al.,* 1985; SEARS *et al.,* 1984a).

Plausible mechanisms by which water could cause TL sensitivity decreases are the physical destruction of the feldspar (or other phosphor) responsible for the TL, the low-temperature feldspar being preferentially affected, or that the hydrothermal treatments destroy the lattice sites responsible for the TL ("the luminescence centers"), without destroying the feldspar, preferentially affecting sites associated with the low feldspar. The luminescence centers in feldspar are probably Mn^{2+} substituting for Ca^{2+} (GEAKE *et al.,* 1971), although other transition metals are known to be associated with TL and CL of feldspars (MARIANO *et al.,* 1973).

Increases in TL sensitivity

The amount of the increase in TL sensitivity depended on the original level, varying from little or none for Dhajala to a factor of 40 for Semarkona. This process also appears to be strongly dependent on temperature (Figs. 2, 5) and required $>2\%$ water (Fig. 7).

In keeping with our earlier work (SEARS *et al.,* 1982; DEHART and SEARS, 1986), we think that these data are best explained by crystallisation of feldspar in chondrule glass. We would expect the process to be temperature-dependent, catalysed by water, and to be displayed most readily by meteorites with the lowest original TL sensitivity. SPARKS *et al.* (1983) briefly reviewed the existence of feldspar and glass in chondrites, and noted the widely accepted conclusion that it was the dry conditions in which the type 3 chondrites have been stored for the last 4.6 Ga that has ensured the preservation of glass. In the case of Semarkona, where some of the Na is located in the hydrous silicates (ALEXANDER *et al.,* 1986), the process of feldspar formation would also involve the transport of Na.

The situation in our experimental charges is, therefore, a competitive one, with the destruction of the feldspar (or its TL centers) by reactions with water dominating at low temperatures (and at high temperatures for short times), and with the crystallisation of glass becoming important at high temperatures, given sufficient time (>20 h).

Peak temperatures and widths

The fields marked in Figs. 3 and 8 indicate the regions occupied by types 3.3–3.5 ordinary chondrites (lower field) and types 3.6–3.9 ordinary chondrites (upper field); type 3.0–3.2 scatter over the plot. A meteorite originally in the low field can be moved to the higher field by annealing at $>700°C$, suggesting that the fields are probably associated, with ordered and disordered feldspar being the dominant TL phosphor. However the activation energy for the changes in peak shape is only ~8 kcal/mole, compared with ~80 kcal/mole for disordering (GUIMON *et al.,* 1985). Furthermore, terrestrial ordered feldspars (albite, oligoclase and bytownite), which have been annealed sufficiently to cause these peak-shape changes to occur, have undergone only small degrees of disordering (HARTMETZ and SEARS, 1987). Existing data therefore indicate that TL peak temperature and width are determined by thermal history, but the detailed mechanisms are unclear.

The conclusions of the previous section concerning TL sensitivity, and the above data and ideas, lead to several predictions as to what should happen to TL peak temperature and width during the present annealing experiments. Low temperatures ($\leq 700°C$), in which the preferential decrease in TL sensitivity of the low form is the major or only process, will cause the resultant TL "peak" to appear at higher temperatures and TL sensitivity to be lower than originally. This is essentially observed in the present data for ALHA77214 (Fig. 4a), Sharps (Fig. 1) and Dhajala (Fig. 9). Peak temperature and width data are not available for Semarkona samples showing significant decreases in TL sensitivity, but, in any case, we doubt that low-feldspar is the major phosphor in this meteorite.

Annealing $\geq 800°C$ under conditions insufficient to cause the formation of significant amounts of new feldspar would probably result in even more effective destruction of low form and the conversion of the low form to the high form (the process analogous to that observed in our previous annealing experiments on dry samples). This seems to be the case with Sharps data plotting in or near the upper field in Fig. 8. Annealing under conditions suitable for the production of new feldspar probably produces a single type of feldspar such as a readily-produced metastable form or the equilibrium form. In cases where new feldspar appears to have been formed, the annealing temperature was above the transformation temperature and the peak temperature was ~200°C. However, the peaks were much narrower than observed for type 3 ordinary chondrites (Figs. 3, 8), suggesting that the peaks observed for the type 3 chondrites are due to mixtures of feldspar in various structural forms and perhaps also with a variety of lattice defects.

The data for ALHA77214 annealed at 850°C may be particularly significant in this connection, as most of the samples produced TL curves with a peak at 140–160°C in addition to the expected peak at 180–210°C. This appears to be a discrete peak from those corresponding to the two fields in Figs. 3 and 8. It is possible that it is entirely an artifact of the experiments, but it could also be that it is present at much lower intensities in natural samples and is partly responsible for their broadness compared to the peaks in synthetic samples.

Relevance to secondary processes in meteorites—metamorphism

A variety of petrologic data have shown that the TL sensitivity of type 3 ordinary chondrites is strongly related to metamorphism (SEARS *et al.,* 1980). There has been some debate as to whether the metamorphism was "prograde" or "autometamorphism", and we have argued that it was probably the former (GUIMON *et al.,* 1985). However, for the purposes of the present paper this point is mute. The present data demonstrate that the cause of the TL sensitivity increase may well involve the formation of feldspar through the crystallisation of glass. Peak temperatures and widths are also dependent on thermal history of the meteorite, in a way indirectly associated with the state of ordering of the Al/Si framework in the feldspar. Thus, type 3.6 and above experienced the major period of crystallisation of their feldspar at temperatures above the order-disorder transformation temperature. We have not yet managed to synthesise any feldspar below 600°C, where we expect to produce the ordered form, presumably because of kinetic difficulties (MARTIN, 1969).

Our previous interpretations of the thermal history of separated chondrules from Dhajala and of shergottites are strengthened by the present data, in that they indicate that TL sensitivity reflects the amount of feldspar present in the igneous glass of the chondrules and the maskelynite of the shergottites, and that peak positions can be used to infer the presence of low and high temperature forms of the feldspar (SEARS *et al.,* 1984b; KECK *et al.,* 1986; HASAN *et al.,* 1986). The postulated presence of high feldspar in shergottites has relevance to the post-shock temperature and the plausibility of a Martian origin, and the presence of low temperature feldspar in chondrules in ordinary chondrites shows that some remained open systems to low temperatures.

The present work also bears on questions of the stability of chondritic glass and the inferred dryness of the chondritic environment for glass-bearing meteorites. It is clear that when water is present in amounts greater than 2 wt.%, metamorphism of glass-bearing chondrites will cause crystallisation in very short time intervals; smaller amounts of water would probably suffice during actual metamorphism. The presence of glass in type 3 chondrites is therefore rightly considered as evidence for a very dry environment. We can now turn this argument around for the type <3.3 chondrites; since there is evidence for indigenous water in these types (MCNAUGHTON *et al.,* 1982; HUTCHISON *et al.,* 1987), these meteorites could not have experienced even the mildest levels of metamorphism since the water was acquired, as they contain a great many glassy chondrules.

In principle, TL data have the possibility of providing cooling rate estimates. If one assumes that pure high and low feldspars have very narrow TL peaks, then the relatively broad peaks observed in type >3.5 ordinary chondrites are due to the presence of mixtures. The relative proportions of high and low forms will have been dictated by the maximum temperatures encountered during metamorphism and post-metamorphic cooling rates. If the two are to be related, for example through burial depth, it should be possible to find relationships between peak width or peak temperature and cooling rate. Attempts to use the relative proportions of high and low feldspars to deduce the thermal histories of terrestrial systems have proved difficult because of the effect of solutions of unknown composition (PARSONS and BROWN, 1984), but the presence of glass in type 3 chondrites indicates that this should not be a problem in the present case.

Relevance to secondary processes in meteorites–aqueous alteration

A surprise finding in the present study was that relatively mild annealing conditions caused a considerable decrease in TL sensitivity, so that it was not only possible for metamorphism to increase TL sensitivity, but for aqueous attack to lower it several orders of magnitude. This raises the question of to what extent could the TL range measured in type 3 ordinary chondrites reflect aqueous alteration. For all but a few type 3 ordinary chondrites, the evidence overwhelmingly favours metamorphism as the major process determining TL sensitivity levels; aside from a considerable amount of petrographic data (DODD *et al.,* 1967; DODD, 1969; WOOD, 1967; HUSS *et al.,* 1981), the TL data rule out a conversion of types >3.5 to 3.2–3.4 by aqueous alteration because it preferentially attacks the low form (*i.e.,* it would not produce narrow peaks at ~140°C). The point really at issue is the role of aqueous alteration in the history of types 3.0 and 3.1 ordinary chondrites (which at the present time are Semarkona, Krymka and Bishunpur).

The TL trends are equally consistent with conversion of a type 3.0 to a type 3.3 ordinary chondrite by metamorphism or by the production of type 3.0 from type 3.3 by aqueous alteration. Aqueous alteration effects have been observed in Semarkona (NAGAHARA, 1984; HUTCHISON *et al.,* 1987): (1) calcite has been observed, sometimes with a distribution suggestive of deposition as veins in the center of the opaque matrix; (2) the outer regions of some chondrules contain altered mesostases which yield low sums upon electron-microprobe analyses; (3) water with higher than terrestrial D/H ratios is released by stepwise heating (MCNAUGHTON *et al.,* 1982).

Cathodoluminescence (CL) images show that there are a wide variety of phosphors in type 3.0–3.1 ordinary chondrites that are not significant in higher types (possibly Fe-free olivine and pyroxene, silica and anorthite). It is the abundance of diverse phosphors that is probably responsible for the hummocky shape of the Semarkona, Bishunpur and Krymka glow curves and the heterogenity in their TL properties. If their unusual CL properties can be ascribed to aqueous alteration, then the order of the degree of alteration is Semarkona ≫ Bishunpur > Krymka. Aqueous alteration is, of course, well-documented for the carbonaceous chondrites, probably including some type 3 carbonaceous chondrites (DU FRESNE and ANDERS, 1962; BUNCH and KERRIDGE, 1979; MCSWEEN, 1979).

Which are the most primitive ordinary chondrites?

In studies of type 3 ordinary chondrites, it would be useful to identify those which most closely resemble the solid material that originally gathered together in the nebula. The aqueous alteration effects described by HUTCHISON *et al.,* (1987) appear to be parent body effects, which implies that the starting material was drier than the present types 3.0–3.1, *i.e.* similar to the type 3.2–3.3 chondrites. The results of this study indicate that types 3.0–3.1 could be aqueously altered versions of types ≥3.2. It could be relevant that the types 3.0–3.1 are not the type 3 chondrites whose composition most closely resembles cosmic; ANDERS and ZADNIK (1985) pointed out that in their proportions of several highly volatile elements, type 3.3–3.4 chondrites more closely resemble CI chondrites than the known types 3.0–3.1. However, it is possible that volatile-loss could accompany aqueous alteration.

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