

## Thermoluminescence and the shock and reheating history of meteorites—II: Annealing studies of the Kernouve meteorite

DEREK W. G. SEARS, NOROUZ BAKHTIAR, BRADLY D. KECK and KAREN S. WEEKS

Department of Chemistry, University of Arkansas, Fayetteville, AR 72701

(Received May 11, 1984; accepted in revised form August 1, 1984)

**Abstract**—Samples of the unshocked, equilibrated chondrite, Kernouve (H6), have been annealed for 1–100 hours at 500–1200°C, their thermoluminescence sensitivity measured and Na, K, Mn, Ca and Sc determined by instrumental neutron activation analysis. The TL sensitivity decreased with temperature until by 1000°C it had fallen by 40%. The process responsible has an activation energy of  $\sim 8$  kcal/mole and probably involves diffusion. Samples annealed 1000–1200°C had TL sensitivities  $10^{-2}$  times the unannealed values, most of the decrease occurring  $\sim 1100^\circ\text{C}$ . This process has an activation energy of  $\sim 100$  kcal/mole and is probably related to the melting of the TL phosphor, feldspar, with some decomposition and loss of Cs, Na and K. Meteorites whose petrography indicates heating  $> 1100^\circ\text{C}$  by natural shock heating events (shock facies d–f), have TL sensitivities similar to samples annealed  $> 1100^\circ\text{C}$ . Our own and literature compositional data indicate that TL is more stable to annealing than Ag, In, Tl, Bi, Zn and Te and less stable than Na, K, Mn, Ca, Se and Co, while the TL decrease resembles very closely the pattern of Cs loss on annealing.

### INTRODUCTION

AN IMPORTANT type of event in the history of chondritic meteorites is that responsible for the violent shock processes many of them have experienced; often the shock event is thought to have been associated with the break-up of the meteorite parent body or with the change in orbit that made it possible, ultimately, for the meteorite to find its way to earth. The shock event caused mineralogical and petrological changes, inert gas loss and mobile element redistribution and loss (e.g. HEYMANN, 1967; SMITH and GOLDSTEIN, 1977; DODD and JAROSEWICH, 1979; WALSH and LIPSCHUTZ, 1982; SEARS *et al.*, 1984).

The  $^{40}\text{Ar}$ – $^{39}\text{Ar}$  method indicates that shock events occurred between 50 and 750 Ma ago, with the majority occurring between 250 and 550 Ma ago (TURNER, 1969; TURNER *et al.*, 1978; BOGARD *et al.*, 1976; BOGARD and HIRSCH, 1980). Estimates of the magnitude of the shock, and the post-shock cooling rates, have been made using petrographic techniques. DODD and JAROSEWICH (1979) defined 6 shock “facies”, a–f, based on the texture of the olivine, the presence of vein and melt pockets, the deformation of plagioclase and the extent to which it has been converted to maskelynite. They estimated that the following pressures were associated with each shock level: a,  $<50$ ; b, 50–200; c, 200–220; d, 220–350; e, 350–570 and f,  $>570$  kbar. HEYMANN (1967) had previously assigned 19 meteorites to 5 shock classes according to their metallography, sulfide texture, veins and olivine x-ray diffraction patterns. Where the two studies overlap there seems to be a reasonable correspondence between them. Heymann’s “heavily shocked” and “very heavily shocked” classes correspond to facies e,f; his “moderately to heavily shocked” class to facies d, his “moderately shocked” to facies b, or possibly c, and his “lightly shocked”

to a. Meteorites of facies d–f have typically experienced peak temperatures of 1000–1200°C and cooling at rates of between 500°C/day and  $3 \times 10^{-4}$  °C/day (HEYMANN, 1967; TAYLOR and HEYMANN, 1969, 1970, 1971; SMITH and GOLDSTEIN, 1977).

The K–Ar age of equilibrated ordinary chondrites varies systematically with their ability to display thermoluminescence, *i.e.* their TL sensitivity (KOMOVSKY, 1961; LIENER and GEISS, 1968; SEARS, 1980). Liener and Geiss suggested this relationship was associated with the production of TL traps by a mechanism involving radiation damage. However, SEARS (1980) was unable to induce TL sensitivity changes in powder from the Kernouve meteorite with high doses of  $\alpha$ ,  $\beta$ ,  $\gamma$  or proton radiation, although he was able to cause a *decrease* TL sensitivity by subjecting meteorite samples to shock pressures in excess of 270 kbar or by annealing at temperatures in excess of  $\sim 1000^\circ\text{C}$  for 1 hour. He therefore suggested that a shock and/or reheating event had caused a lowering of TL sensitivity, and that the relationship with K–Ar age is a consequence of the meteorites with low K–Ar age having been severely shocked. SEARS *et al.* (1984) recently reported a study of the petrologic and TL changes occurring in response to shock pressures of 70, 165, 270, 390 kbar, and higher. At pressures  $> 270$  kbar, 10 to 100-fold decreases in TL sensitivity were observed and conversion of the feldspar to glass occurred, olivine became mosaiked, pyroxene was severely deformed, kamacite acquired the shock transformation structure and the sulphides experienced incipient melting.

The present paper is a continuation of work described by SEARS (1980). We report new data on the effect of annealing on the TL sensitivity of the Kernouve meteorite which better define the TL–reheating relationship. By such a study we hope to improve both our understanding of the TL changes

TABLE 1. Thermoluminescence sensitivity of Kernouve meteorite powder after annealing for various times and temperatures. Data normalized to the unannealed Kernouve value.\*

Time (h)	Temperature (°C)								
	500	600	700	800	900	1000	1100	1150	1200
1	1.05±0.08	0.71±0.07	0.73±0.05	0.63±0.17	0.65±0.10	0.54±0.10	0.15±0.07	0.075±0.05	<0.004
2			0.73±0.14			0.51±0.15	0.12±0.09		
10	0.91±0.11	0.77±0.30	0.70±0.08	0.64±0.11	0.65±0.05	0.39±0.13	0.003±0.002		0.003±0.002
20			0.60±0.12			0.44±0.07	0.0009±0.0005		
100			0.52±0.10			0.24±0.16	0.0003±0.0002		

\* Errors are standard deviations based on at least three experiments. Exceptions are the 1150°C data for which only one vial was annealed and the error is a guess.

associated with shock/reheating and of the reheating history of chondrites.

### EXPERIMENTAL

The Kernouve meteorite (H6) was used for this study because it is a well-studied and essentially unshocked and unheated chondrite. About 2.0 g of material, taken from a variety of locations on the original 70 g fragment used by SEARS (1980; British Museum catalog number BM48400), was ground (<100 µm), the magnetic material removed with a hand magnet, and 20 mg aliquots placed in 100 high-purity quartz vials. (The magnetic separation aids in the homogenization; it is well known that metal and FeS are not phosphors.) The vials were evacuated to  $10^{-6}$  µm, filled to 1 atmosphere with nitrogen, heat sealed, and annealed in a manually controlled, wirewound tube furnace for 1–100 h at 500–1200°C. The temperature was monitored at the sample vial location with a chromel-alumel thermocouple. The standard deviation of 12 readings of the temperature was <5% for the ≤1000°C experiments and about 5% for the 1100, 1150 and 1200°C experiments. Except for the 1150°C measurements, 3 vials were annealed at each time and temperature; the experimental uncertainties quoted for the TL sensitivity refer to the standard deviation displayed by the 3 vials.

For TL measurements,  $4 \pm 0.1$  mg samples were placed in a 5 mm diameter Cu dish, exposed to  $^{90}\text{Sr}$   $\beta$  source for 2 minutes (~25 krad absorbed dose), and the induced TL was measured in modified Daybreak apparatus (SEARS and WEEKS, 1983). The induced TL of each sample was measured at least three times, typically yielding standard deviations of <5%. Before and after each set of TL measurements, the TL values of unannealed powder were determined: average values were used for normalization.

Our annealing results led us to suspect compositional changes in our samples, which we checked by instrumental neutron activation analysis. Annealed samples, synthetic standards and control samples (Allende and BCR-1) were irradiated in the University of Missouri research reactor for 30 minutes and counted five times at Fayetteville over 4 weeks. Data were reduced with the SPECTRA program (BAEDECKER, 1976); the Ca and K data were also hand-plotted. Our data and literature values for Allende and BCR-1 agreed very well. Because of the small sample size, our Kernouve data have slightly lower precision than our control samples. Mn, Sc and Ca are unaffected by annealing and have relative standard deviations of 9.9, 10.7 and 15.0%, respectively. For the <1000°C data of Na, and <800°C data of K, the standard deviations are 9.4 and 9.6%, respectively. Sample heterogeneity is clearly the major cause of uncertainty, since  $1\sigma$  statistical uncertainties are <1% for Na, Mn and Sc and only a few percent for Ca and K. Sc-normalization minimizes the effects of sample heterogeneity; hence variations in Fig. 5 are ~5% rather than ~10%.

### RESULTS

The data are presented in Table 1. Figure 1 shows the relationship between TL sensitivity and annealing

temperature for the 1 and 10 hour series, and Fig. 2 shows the effect of annealing at different times for the 700, 1000 and 1100°C series.

Annealing at 500°C produced no significant change in TL sensitivity. Between 600 and 1000°C there was fairly gradual decrease in TL, reaching about 60% of its original value after 1 hour of annealing and slightly less after 10 hours of annealing. Above 1000°C, the TL sensitivity dropped abruptly to  $10^{-2}$  to  $10^{-3}$  times its unannealed value. These data are in reasonable agreement with the less precise data of SEARS (1980) who measured the effect on TL sensitivity of annealing for 1 hour at 400–1200°C.

There is a small but perceptible time-dependence in the annealing experiments at 700 and 1000°C, but at 1100°C and 1150°C the effect is very marked (Table 1, Fig. 2). After annealing at 1200°C for 1 and 10 hour the TL sensitivity had fallen to 0.4% of its unannealed value.

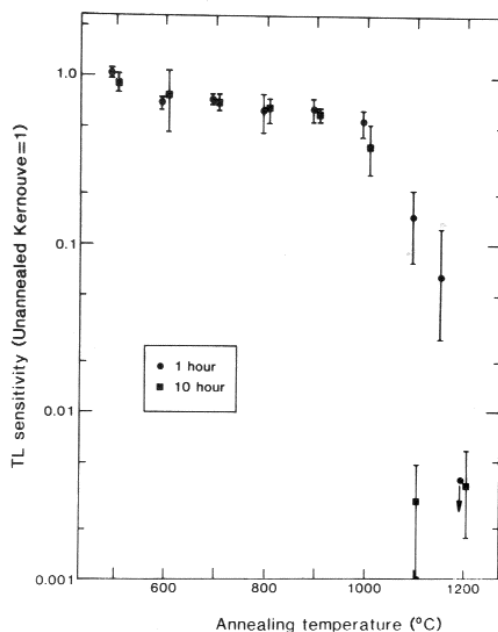


FIG. 1. Plot of the TL sensitivity of Kernouve meteorite samples after annealing for 1 hour and 10 hours at temperatures of 500 to 1200°C. The data are normalized to the TL sensitivity of unannealed Kernouve material. Each point is the mean of at least three samples and the error bars refer to  $\pm 1\sigma$ .

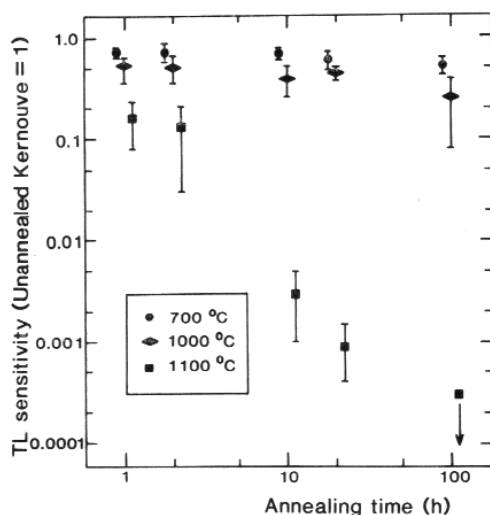


FIG. 2. Plot of the TL sensitivity of Kernouve meteorite samples after annealing at 700, 1000 and 1100°C for times between 1 hour and 100 hours, normalized to the data for unannealed Kernouve. Each point is the mean of at least three samples and the error bars refer to  $\pm 1\sigma$ .

### DISCUSSION

#### a) Cause of the TL sensitivity changes associated with annealing

The TL phosphor in the equilibrated Saint Severin meteorite is located in the low-density, feldspar-rich fraction (LALOU *et al.*, 1970), and it seems likely that the phosphor in most equilibrated meteorites is feldspar. A reasonable interpretation for the abrupt 1100°C decrease in TL sensitivity is that it is associated with fusion of the feldspar. Pure albite melts at 1120°C (SMITH, 1972); the addition of ~10 mole percent An (chondritic feldspar is  $\text{Ab}_{82}\text{An}_{12}\text{Or}_6$ , VAN SCHMUS and RIBBE, 1968) increases the melting point a few degrees, while the influence of other silicates may lower it a little. Certainly, melting the TL phosphor would destroy its TL sensitivity which depends on the semi-conductor properties of the crystalline material.

We have attempted to estimate activation energies ( $E_a$ ) for the TL destruction process in the hope that it would shed some light on the processes. The first-order rate constants were estimated from the slope of the semi-log version of Fig. 2 (correlation coefficients for  $\ln \text{TL}$  vs. time were 0.82, 0.95, and 0.96 for the 700, 1000 and 1100°C, respectively) and the Arrhenius equation was used to calculate the activation energies. The 700 and 1000°C data yield a value of  $6.6 \pm 3.4$  kcal/mole for  $E_a$ , while the 1000 and 1100°C data gave a value of  $12.5 \pm 10.2$  kcal/mole. (The errors quoted are for the  $1\sigma$  level and are based on the uncertainties in the slopes of the  $\ln \text{TL}$  vs. time curves.) These would be reasonable determinations of  $E_a$  for the two processes producing the TL decrease only if the 1000°C data were truly applicable

to both processes, which is highly unlikely. In fact, because of the relative slopes of the curves in Fig. 2, our estimate for the higher value is much more uncertain than for the lower value. A move of 50°C in the temperature at which the sharp decrease is assumed to occur changes our estimated  $E_a$  by ~40 kcal/mole, so that our most optimistic estimate for the higher temperature process is 85–145 kcal/mole.

A better estimate of the activation energy of the 500–1000°C drop could be calculated if use could be made of the data in Fig. 1. Substitution of the first-order (exponential) decay equation into the Arrhenius equation yields the relationship

$$\ln[-t \ln(\text{TL})] = \ln A - \frac{E}{RT}$$

where  $t$  is the annealing time, TL is the TL sensitivity normalized to the unannealed TL sensitivity and  $A$  is the pre-exponential factor in the Arrhenius equation. Figure 3 is the resulting plot of  $\ln[-t \ln(\text{TL})]$  against  $1/T$  for the 1 and 10 hour annealing data. The 10 h data yield a good correlation ( $r = 0.97$ ), but for the 1 hour data the correlation is rather weak ( $r = 0.86$ ). The activation for energies calculated from the slopes are  $7.7 \pm 1.8$  kcal/mole for the 10 hour data and  $11.0 \pm 6.5$  kcal/mole for the 1 hour data, in agreement with the values calculated above.

Although our estimate of  $E_a$  for the high temperature process is a poor one, it does seem to indicate a process involving reasonable amounts of energy. The enthalpy of fusion of most silicates, including

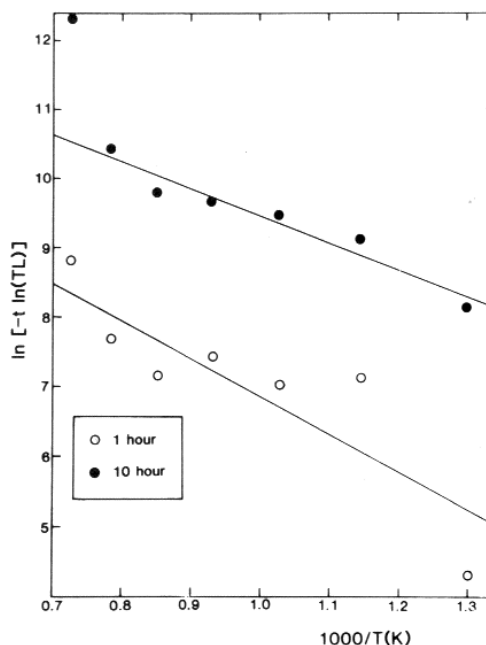


FIG. 3. Arrhenius plots using the data in Fig. 1 yield activation energies of  $7.7 \pm 1.8$  kcal/mole for the 10 hour data and  $11.0 \pm 6.5$  kcal/mole for 1 hour data.

feldspars, are in the range of 15–25 kcal/mole while processes involving the breakage of bonds are somewhat higher, for example the strength of the Si-O bond is  $96.0 \pm 11.0$  kcal/mole. It may be, therefore, that the  $E_a$  we estimate for the higher temperature process is more consistent with decomposition of the TL phosphor, rather than with simple melting.

Values as small as 7 kcal/mole are not consistent with the breakage of bonds, or with vaporization or fusion of silicates, as they are much too small. They are consistent with certain diffusion processes so that the decrease in TL between 500 and 1000°C may be associated either with the redistribution of the impurities responsible for the TL or with crystallographic changes.

*b) TL sensitivity and compositional variations during annealing studies*

IKRAMUDDIN *et al.* (1977a,b) have demonstrated that the ordinary chondrites Krymka and Tieschitz suffer considerable mobilization and loss of highly volatile trace elements as a result of annealing at temperatures between 500 and 1200°C for one week. The annealing conditions used in the Ikramuddin *et al.* work differ slightly from those used here in that (1) the annealing atmosphere was  $H_2$  at  $10^{-5}$  atmospheres and (2) their apparatus incorporated a cold trap. Annealing atmosphere had little or no influence on the TL sensitivity changes produced by the annealing experiments of SEARS (1980), who performed

some runs in a hydrogen atmosphere and others in a vacuum. IKRAMUDDIN *et al.* (1979) similarly found that there was little or no indication of a major effect when various atmospheres were used. The absence of a cold trap in our apparatus is not an important difference because recondensation of evaporated materials should still leave the meteorite depleted since the surface area of the inside of our vials is very much greater than that of the relatively small samples. For the TL study the lack of a cold trap is not a problem at all, since the likelihood of evaporated atoms recondensing in their original lattice sites is negligible.

IKRAMUDDIN *et al.* (1977a,b) found that Bi, Tl, In, Te, Zn and Ag were readily mobilized by annealing. They are apparently more sensitive to the annealing treatment than we found TL to be in our experiments. In contrast, Co and Se were more stable than TL at all temperatures. Gallium and Cs are the only elements whose behavior resembles TL in any way (Fig. 4). Gallium is present in its unannealed proportions in the samples annealed at <1000°C, but after annealing at 1000°C it had fallen to about 60% of its unannealed value in Krymka and to about 80% of its original value for Tieschitz. The decrease in Cs abundance in response to annealing follows that of TL remarkably closely. The correlation coefficients for Cs and TL (after 10 hours of annealing) were 0.95 for Krymka and 0.90 for Tieschitz. The annealing experiments on Tieschitz and Krymka did not go above 1000°C, but BART *et al.* (1980) and

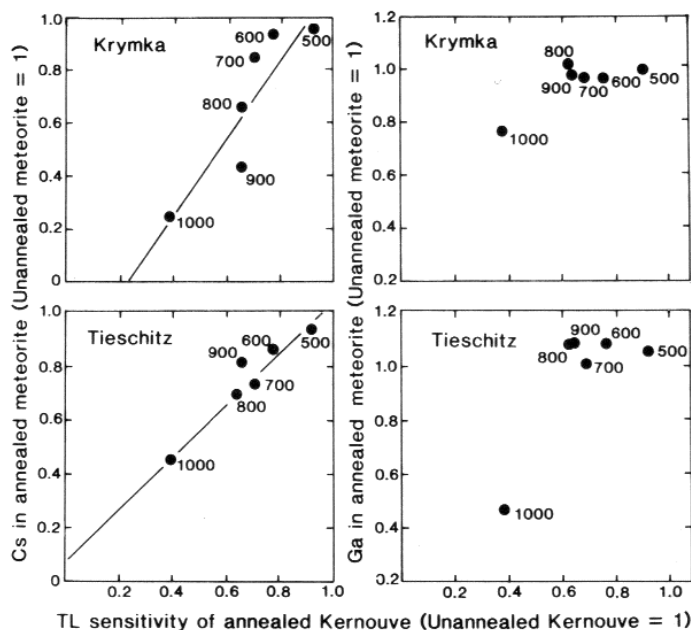


FIG. 4. Plots of Cs and Ga against TL sensitivity in two ordinary chondrites after annealing at temperatures between 500 and 1000°C. The other eight elements determined by IKRAMUDDIN *et al.* (1977a,b) were either appreciably less stable than thermoluminescence (Ag, Te, Zn, Bi, Tl, In) or more so (Co and Se).

TABLE 2. The abundance of Na, K, Mn, Sc and Ca in annealed Kernouve samples after TL measurement.\*

	-----Annealing Temperature for 10 hours (°C)-----							
	500	600	700	800	900	1000	1100	1200
Na (mg/g)	5.79	5.29	4.48	5.91	5.85	5.01	4.82	3.11
K (mg/g)	0.875	0.719	0.530	0.717	0.706	0.578	0.563	0.392
Mn (mg/g)	3.50	3.17	2.64	3.48	3.40	2.82	3.26	3.07
Ca (mg/g)	13.8	11.2	9.84	13.2	13.2	9.68	13.2	9.07
Sc (μg/g)	8.72	7.83	7.18	8.64	9.84	7.32	8.56	7.14
Mass (mg)	17.4	20.1	17.1	24.6	13.6	18.9	21.8	7.9

	Mean H Group†	Unannealed	-----Time annealed at 1000°C (h)-----				
			1	2	10	20	100
Na (mg/g)	5.7	5.82	5.64	5.00	4.03	5.01	5.41
K (mg/g)	0.800	0.750	0.857	0.672	0.549	0.549	0.574
Mn (mg/g)	2.26	3.30	3.48	3.03	2.70	2.82	3.21
Ca (mg/g)	11.9	12.5	13.4	11.0	9.06	9.68	13.4
Sc (μg/g)	7.6	8.56	9.20	7.92	6.18	7.32	8.64
Mass (mg)		25.0	18.7	22.6	23.9	18.9	23.6

\* Analyses were made on the non-magnetic extracts used for TL measurements and have been corrected to bulk values by dividing all data by 1.25 (see text).

† Mason (1979).

NGO and LIPSCHUTZ (1980) have reported data for Allende heated to 1400°C in which the Cs trend continues to follow TL.

The correlation between TL and Cs may be a further indication that the TL phosphor is feldspar. As an alkali metal, one would expect Cs to reside with Na and K in feldspar in ordinary chondrites. Presumably Cs is either associated with the TL mechanism directly or the changes in the feldspar responsible for its decrease in TL also increase the facility by which Cs can migrate through the crystal and escape. Gallium, being chemically similar to Al, might also be expected to be associated with feldspar. However, it is appreciably less volatile than Cs and would also reside in different lattice sites which are less labile.

We have checked for major changes in the composition of our samples by performing an INAA on the material after annealing and TL measurement. We analyzed for Na and K, which are intermediate in volatility between Cs and Ga and also may have been volatilized during our experiments, and we measured Ca, the most refractory feldspathic element. In addition, we determined Mn and Sc. Manganese is an element which is of moderate volatility and is often associated with luminescence in Ca-bearing minerals since it may substitute for Ca. Scandium is a refractory lithophile we can analyze with high precision and wanted to use as a normalization element, since our analysis was made on magnetic extracts and we wanted to remove the effect of poorly-reproducible metal separations.

Our INAA data are given in Table 2 and Fig. 5. For the purposes of tabulation we have divided all our data by 1.25 to remove the effect of metal extraction from the homogenized sample at the be-

ginning of our work. The factor of 1.25 is the mean ratio of our data and literature H group averages (MASON, 1979), excluding the samples which we think showed element loss. The value of 1.25 is close

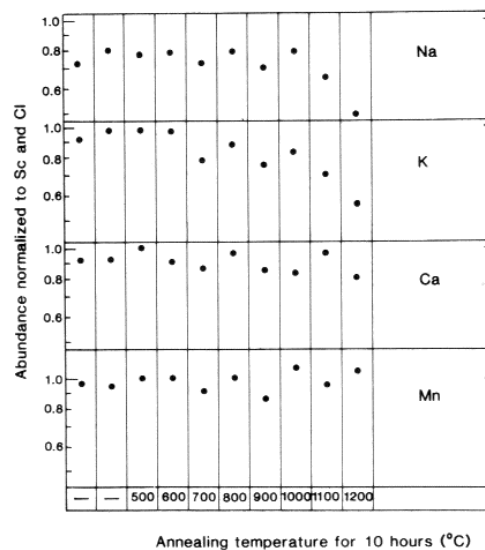


FIG. 5. Bulk compositions of four elements thought to be associated with meteorite TL in samples which have been annealed for 10 hours at a variety of temperatures. Calcium, Na and K are located in large part in the TL phosphor, feldspar, and Mn is often responsible for TL of Ca-bearing minerals. Calcium and Mn are uniformly abundant in all the samples, whereas Na and K show loss in samples annealed above 1000°C, K perhaps showing some loss at lower temperatures. The data have been Sc-normalized to remove the effects of sample heterogeneity.

to that calculated from literature values for the weight of metal plus sulfide in H chondrites (KEIL, 1962). As expected, Ca showed no variation except that due to sample heterogeneity and analytical errors, and neither did Mn. However, we did detect some loss of Na and K at temperatures in excess of 1000°C, where we think the feldspar was melted by annealing. There is also some suggestion of a small loss of K at lower temperatures (~800°C). It is possible, therefore, that the 40% decrease in TL at lower temperatures may be associated with the loss of the more volatile alkali metals. The 100-fold drop in TL sensitivity at temperatures above 1000°C, which had an activation energy which is rather large for simple melting, may be associated with loss of Na and K, as well as Cs.

### c) TL sensitivities of shocked meteorites

Figure 6 is a histogram of the TL sensitivities of 16 chondrites from the study of SEARS (1980) and 32 from that of LIENER and GEISS (1968). The two sets of data have been expressed in common units by using the five samples common to both studies and then normalizing all data to Kernouve. For the sake of internal consistency, the TL sensitivity shown by powders has been used, even though better data are obtained when the samples are prepared as  $\leq 10$   $\mu$ m grains deposited on disks (SEARS, 1980). We have

omitted meteorites of petrologic types 3 and 4 because these meteorites have low TL associated with their low petrologic type (SEARS *et al.*, 1980). The histogram is highly skewed, even using logarithmic intervals of TL sensitivity, with a mode of somewhere between 0.3 and 1.0 and extending down to nearly 0.003.

We have superimposed on the histogram the shock classes based on the work of DODD and JAROSEWICH (1979) and HEYMANN (1967). We found a discrepancy in the published shock classifications for Bruderheim which the former authors call facies d but the latter calls class 2, moderately shocked. On the basis of other meteorites common to both studies we think Heymann's class 2 is equivalent to facies b, or c at highest. We have compromised and called Bruderheim facies c. Only a few of the non-heavily shocked meteorites for which we have TL data have been assigned shock classes by DODD and JAROSEWICH (1979). The unshocked samples in the SEARS (1980) study were chosen on the basis of good 4.6 aeon  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  plateaux and we have assigned these meteorites an a,b in the histogram.

Of the meteorites which plot in the low TL sensitivity tail of the histogram (TL < 0.15), those for which data exist are members of shock facies d-f. Meteorites with TL sensitivities > 0.15 are facies c (near the bottom of the TL range) and facies a (near the top of the TL range).

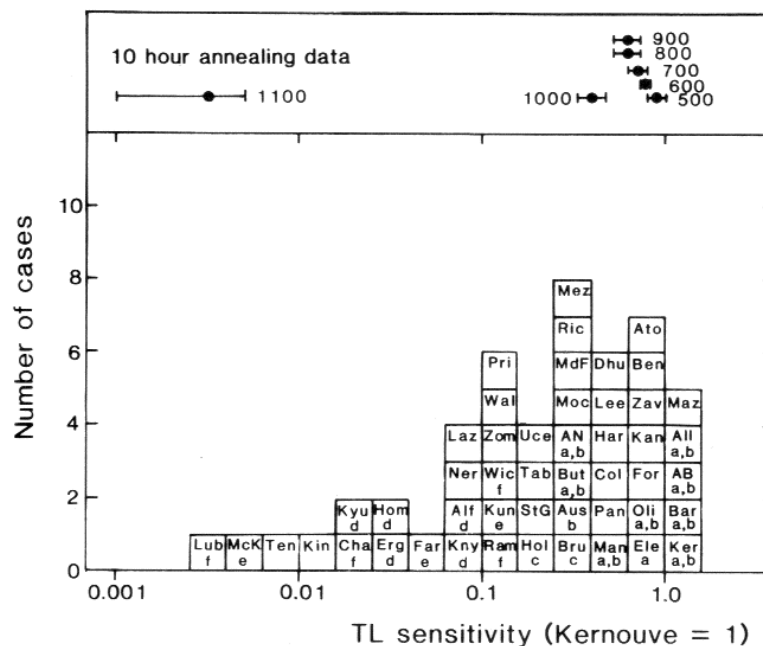


FIG. 6. Histogram of the TL sensitivities of 48 ordinary chondrites, measured by SEARS (1980) and LIENER and GEISS (1968), compared with the TL sensitivity observed after annealing for 10 hours at a variety of temperatures. The histogram is skewed, with a peak including unshocked or little shocked meteorites (facies a-c), and a tail which includes samples which are known on the basis of petrographic data to have been heavily shocked (facies d-f) and heated to ~1100°C. (See SEARS, 1980, for the identification of individual meteorites.)

Several of the meteorites in the low TL tail ( $<0.15$ ) are thought to have experienced a temperature of at least  $1100^{\circ}\text{C}$  as a result of the shock event. The shocked meteorite with the lowest TL sensitivity plotted in Fig. 6 is Lubbock, for which SMITH and GOLDSTEIN (1977) and HEYMANN (1967) estimate  $1100\text{--}1150^{\circ}\text{C}$  and  $900\text{--}1000^{\circ}\text{C}$ , respectively. Also in the low TL tail is Farmington, for which SMITH and GOLDSTEIN (1977) estimate  $1050\text{--}1100^{\circ}\text{C}$ , and Kingfisher for which TAYLOR and HEYMANN (1970) estimated a reheating temperature of  $>600^{\circ}\text{C}$ . Metallographic studies indicate that Wickenburg has not been heated above  $1000^{\circ}\text{C}$ ; SMITH and GOLDSTEIN (1977) estimate a maximum reheating temperature of  $950\text{--}1000^{\circ}\text{C}$ , while HEYMANN (1967) estimated  $600\text{--}1000^{\circ}\text{C}$ . Wickenburg plots near the beginning of the low TL tail with a TL sensitivity of 0.14.

We have also indicated across the top of the histogram in Fig. 6 the TL values we observed in the present study in samples of Kernouve which had been annealed for 10 hours (Fig. 1). Meteorites with TL sensitivity  $> 0.15$  (facies a–c) display values similar to our samples which had been annealed to temperatures less than about  $1000^{\circ}\text{C}$ , while meteorites with TL sensitivity  $<0.15$  have values similar to our samples which have been annealed at temperatures between  $1000$  and  $1100^{\circ}\text{C}$ . There is slightly greater spread in the observed TL sensitivities of the relatively less severely shocked meteorites than one would expect on the basis of this comparison between our annealing data and the histogram. Three factors responsible for this are: first, that our annealing data are for only 10 hours and we know that for the  $500\text{--}1000^{\circ}\text{C}$  drop in TL there is a time dependence (Fig. 2); second, there is some spread in the TL data due to the use of powders rather than disks (SEARS, 1980); third, shock effects are highly heterogeneous and the best comparisons are those where the TL and other studies are made on the same material. On occasion, an individual meteorite can display bewildering heterogeneity of apparent shock intensity on a 1–10 cm scale; perhaps even on larger scales. Orvinio is such a meteorite. However, such heterogeneity is the exception rather than the rule, and it does not normally prevent an unambiguous shock class assignment (D. HEYMANN, pers. commun.).

The similarity in the TL sensitivity of samples which have been annealed at  $1100^{\circ}\text{C}$  and the meteorites which are thought to have been heated to  $1100^{\circ}\text{C}$  on the basis of metallographic data suggests that either our experiments matched rather closely the conditions under which the natural shock reheating occurred, or that for annealing as severe as this the duration of annealing, and the post-shock cooling rate, have minor influence on the TL decrease.

#### SUMMARY AND CONCLUSIONS

The effect of annealing for times between 1 and 10 h at temperatures between  $500$  and  $1200^{\circ}\text{C}$  on

the Kernouve H chondrite has been investigated. A decrease in TL sensitivity of the samples occurred in two steps:  $<1000^{\circ}\text{C}$  there was 40% decrease with a small time-dependence; between  $1000$  and  $1200^{\circ}\text{C}$  there was a 100-fold decrease, the change occurring mainly near  $1100^{\circ}\text{C}$ . The first decrease has an activation energy  $\sim 8$  kcal/mole and the pattern of TL decrease resembles the pattern of Cs loss in the annealing experiments of Lipschutz and co-workers. We observed no loss of Na but a very small loss of K over this temperature range. The sharp decrease in TL sensitivity at  $1100^{\circ}\text{C}$  may be associated with the fusion of the TL phosphor (feldspar, MP  $1120^{\circ}\text{C}$ ), but the highly approximate activation energy we estimate ( $85\text{--}145$  kcal/mole) seems to suggest concurrent decomposition of the phosphor; consistent with this we observed a 30–50% loss of Na and K in our samples annealed  $> 1000^{\circ}\text{C}$ . Meteorites for which there is petrographic evidence for heating above  $1100^{\circ}\text{C}$  by natural shock processes, have TL sensitivities 0.1 to 0.01 times those of unshocked and similar to our samples which had been annealed at  $1100^{\circ}\text{C}$  for 1 or 10 h.

**Acknowledgements**—We are grateful to R. Hutchison, British Museum (Natural History), for donating the material used in this work, to P. Baedeker, U.S.G.S., Reston for making his computer program SPECTRA available to us, and to J. Carney (University of Missouri Research Reactor), J. McKimney and K. Curtis (Arkansas) for technical assistance, and D. Heymann and M. E. Lipschutz for constructive reviews. We are also grateful to the Research Corporation and NASA (NAGW 296) for funding, and the US Dept. of Energy (grant DEFG-0280-ER-110725 to the UMRR facility) for partially covering the costs of the INAA irradiation.

#### REFERENCES

- BAEDECKER P. A. (1976) SPECTRA: A computer code for the evaluation of high resolution gamma-ray spectra from instrumental activation analysis. In *Advances in Obsidian Glass Studies: Archaeological and Geochemical Perspectives* (ed. R. E. TAYLOR) p. 334–339. Noyes Press, Park Ridge, NJ.
- BART G., IKRAMUDDIN M. and LIPSCHUTZ M. E. (1980) Thermal metamorphism of primitive meteorites—IX. On the mechanism of trace element loss from Allende heated up to  $1400^{\circ}\text{C}$ . *Geochim. Cosmochim. Acta* **44**, 719–730.
- BOGARD D. D. and HIRSCH W. C. (1980)  $^{40}\text{Ar}/^{39}\text{Ar}$  dating, Ar diffusion properties, and cooling rate determinations of severely shocked chondrites. *Geochim. Cosmochim. Acta* **44**, 1667–1682.
- BOGARD D. D., HUSAIN L. and WRIGHT R. J. (1976)  $^{40}\text{Ar}/^{39}\text{Ar}$  dating of collisional events in chondrite parent bodies. *J. Geophys. Res.* **81**, 5664–5678.
- DODD R. T. and JAROSEWICH E. (1979) Incipient melting in and shock classification of L-group chondrites. *Earth Planet. Sci. Lett.* **44**, 335–340.
- HEYMANN D. (1967) On the origin of hypersthene chondrites: ages and shock effects of black chondrites. *Icarus* **6**, 189–221.
- IKRAMUDDIN M., BINZ C. M. and LIPSCHUTZ M. E. (1977a) Thermal metamorphism of primitive meteorites—V. Ten trace elements in Tieschitz H3 chondrites heated at  $400\text{--}1000^{\circ}\text{C}$ . *Geochim. Cosmochim. Acta* **46**, 1247–1256.
- IKRAMUDDIN M., BINZ C. M. and LIPSCHUTZ M. E. (1977b) Thermal metamorphism of primitive meteorites—III. Ten

- trace elements in Krymka L3 chondrite heated at 400–1000°C. *Geochim. Cosmochim. Acta* **41**, 393–401.
- IKRAMUDDIN M., LIPSCHUTZ M. E. and GIBSON E. K., JR. (1979) On mobile element transport in heated Abee. *Meteoritics* **14**, 69–80.
- KEIL K. (1962) On the phase composition of meteorites. *J. Geophys. Res.* **67**, 4055–4061.
- KOMOVSKY G. F. (1961) Thermoluminescence of stony meteorites (in Russian). *Meteoritika* **21**, 64–69.
- LALOU C., NORDEMAN D. and LABYRIE J. (1970) Etude preliminaire de la thermoluminescence de la meteorite Saint Severin. *C.r. hebdomadaire Seances Acad. Sci. (Paris) Series D* **270**, 2104–2401.
- LIENER A. and GEISS J. (1968) Thermoluminescence measurements on chondritic meteorites. In *Thermoluminescence of Geological Materials* (ed. D. J. MCDUGALL) 559–582. Academic Press.
- MASON B. (1979) Data of Geochemistry, Sixth Edition, Chapter B. *Cosmochemistry Part I. Meteorites*. Geol. Surv. Prof. Paper 440, B-1.
- NGO H. T. and LIPSCHUTZ M. E. (1980) Thermal metamorphism of primitive meteorites—X. Additional trace elements in Allende (C3V) heated to 1400°C. *Geochim. Cosmochim. Acta* **44**, 731–739.
- SEARS D. W. (1980) Thermoluminescence of meteorites: Relationships with their K-Ar age and their shock and reheating history. *Icarus* **44**, 190–206.
- SEARS D. W. G. and WEEKS K. S. (1983) Chemical and physical studies of type 3 chondrites: 2. Thermoluminescence sensitivity of sixteen type 3 ordinary chondrites and relationships with oxygen isotopes. *J. Geophys. Res.* **88**, Supplement, B301–B311.
- SEARS D. W., GROSSMAN J. N., MELCHER C. L., ROSS L. M. and MILLS A. A. (1980) Measuring the metamorphic history of chondritic meteorites. *Nature* **287**, 791–795.
- SEARS D. W., ASHWORTH J. R., BROADBENT C. P. and BEVAN A. (1984) Studies of an artificially shock-loaded H group chondrite. *Geochim. Cosmochim. Acta* **48**, 343–360.
- SMITH B. A. and GOLDSTEIN J. I. (1977) The metallic micro-structures and thermal histories of severely reheated chondrites. *Geochim. Cosmochim. Acta* **41**, 1061–1072.
- SMITH J. V. (1972) Critical review of synthesis and occurrence of plagioclase feldspars and a possible phase diagram. *J. Geol.* **80**, 505–525.
- TAYLOR G. J. and HEYMANN D. (1969) Shock, reheating and the gas retention ages of chondrites. *Earth Planet Sci. Lett.* **7**, 151–161.
- TAYLOR G. J. and HEYMANN D. (1970) Electron microprobe study of metal particles in the Kingfisher meteorite. *Geochim. Cosmochim. Acta* **34**, 677–687.
- TAYLOR G. J. and HEYMANN D. (1971) Postshock thermal histories of reheated chondrites. *J. Geophys. Res.* **76**, 1879–1893.
- TURNER G. (1969) Thermal histories of meteorites by the <sup>39</sup>Ar-<sup>40</sup>Ar method. In *Meteorite Research* (ed. P. M. MILLMAN), 407–417. D. Reidel, Dordrecht, Netherlands.
- TURNER G., ENRIGHT M. C. and CADOGAN P. H. (1978) The early history of chondrite parent bodies inferred from <sup>40</sup>Ar-<sup>39</sup>Ar ages. *Proc. Lunar Planet Sci. Conf. 9th* **1**, 989–1025.
- VAN SCHMUS W. R. and RIBBE P. H. (1968) The compositional and structural state of feldspar from chondritic meteorites. *Geochim. Cosmochim. Acta* **32**, 1327–1342.
- WALSH T. M. and LIPSCHUTZ M. E. (1982) Chemical studies of L chondrites—II. Shock induced trace element mobilization. *Geochim. Cosmochim. Acta* **46**, 2491–2500.