Meteoritics & Planetary Science 31, 87–96 (1996)

NASA-CR-201813

Pyroxene structures, cathodoluminescence and the thermal history of the enstatite chondrites

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(Received 1995 May 30; accepted in revised form 1995 October 17)

Abstract–In order to explore the thermal history of enstatite chondrites, we examined the cathodoluminescence (CL) and thermoluminescence (TL) properties of 15 EH chondrites and 21 EL chondrites, including all available petrographic types, both textural types 3–6 and mineralogical types α–δ. The CL properties of EL3α and EH3α chondrites are similar. Enstatite grains high in Mn and other transition metals display red CL, while enstatite with low concentrations of these elements show blue CL. A few enstatite grains with >5 wt% FeO display no CL. In contrast, the luminescent properties of the metamorphosed EH chondrites are very different from those of metamorphosed EL chondrites. While the enstatites in metamorphosed EH chondrites display predominantly blue CL, the enstatites in metamorphosed EL chondrites display a distinctive magenta CL with blue and red peaks of approximately equal intensity in their spectra. The TL sensitivities of the enstatite chondrites correlate with the intensity of the blue CL and, unlike other meteorite classes, are not simply related to metamorphism. The different luminescent properties of metamorphosed EH and EL chondrites cannot readily be attributed to compositional differences. But x-ray diffraction data suggests that the enstatite in EH5γ,δ chondrites is predominantly disordered orthopyroxene, while enstatite in EL6β chondrites is predominantly ordered orthopyroxene. The difference in thermal history of metamorphosed EL and EH chondrites is so marked that the use of single "petrographic" types is misleading, and separate textural and mineralogical types are preferable. Our data confirm earlier suggestions that metamorphosed EH chondrites underwent relatively rapid cooling, and the metamorphosed EL chondrites cooled more slowly and experienced prolonged heating in the orthopyroxene field.

INTRODUCTION

Enstatite chondrites were formed in a very reducing environment and contain essentially FeO-free enstatite, high-Si metal and the cubic monosulfides, such as niningerite and alabandite (Keil, 1968; Mason 1966). While essentially chondritic in bulk composition, variations in Fe/Si, Mg/Si and similar ratios enable the definition of discrete EH (high-Fe, high-siderophile) and EL (low-Fe, low-siderophile) classes (Sears *et al.*, 1982). The enstatite chondrites also have especially interesting thermal histories. Several authors have used equilibria for enstatite, metal and other phases to estimate equilibration temperatures, which seem reasonable in terms of the observed textures and the petrographic types (Larimer and Buseck, 1968; Fogel *et al.*, 1989; Zhang *et al.*, 1992). However, equilibration temperatures (more precisely, closure temperatures) based on minor mineral systems are very different from those based on the major phases and are higher for the EH chondrites than for the EL chondrites. For the cubic sulfides, equilibration temperatures are <400 °C for the EL and ~600 °C for the EH chondrites (Skinner and Luce, 1971; Zhang *et al.*, 1992). The usual interpretation is that EH chondrites cooled more rapidly than EL chondrites. The dichotomy between texture and equilibration temperatures determined from the sulfide and phosphide systems led Zhang *et al.* (1995) to argue that the Van Schmus and Wood (1967) scheme, which works well for ordinary chondrites, is not well-suited to enstatite chondrites. They proposed separate mineralogical and petrographic "types" for these classes. Thus, while the textural types 3–6 reflect peak metamorphic temperatures and are similar for H and L chondrites, mineralogical types α–δ reflect mineralogical closure temperatures and are quite different for H and L chondrites.

There has always been a high degree of interest in the cathodoluminescence (CL) properties of the enstatite chondrites and the related igneous class, the aubrites. This interest is partly because the CL intensity is so high but also because variations in trace-element compositions cause major differences in CL properties (Derham and Geake, 1964; Derham *et al.*, 1964; Geake and Walker, 1966, 1967; Reid and Cohen, 1967; Grögler and Liener, 1968; Keil, 1968; Leitch and Smith, 1982; McKinley *et al.*, 1984; Steele, 1989; Lofgren and DeHart, 1992a,b, 1993; DeHart and Lofgren, 1994, 1995; Weisberg *et al.*, 1994). The luminescent properties of enstatite have been reviewed several times (*e.g.*, Marshall, 1988; Steele, 1989). Enstatite grains with red CL (~700 nm) have high concentrations of transition metal activators, such as Cr and Mn, while enstatite with blue CL (~450 nm) is relatively pure $MgSiO_3$. While the dependence of CL on composition is well established, an important proposal by Reid and Cohen (1967) that has not been discussed very much in the literature is that the degree of stacking disorder of the enstatite also affects its CL.

While it is recognized that CL offers particular insights into the origin and history of the host rocks, most of the studies of enstatite chondrites to date have concerned only single or small groups of meteorites with attention focused on individual grains and their compositional profiles. The discovery of a great many enstatite chondrites among the Antarctic collection in the last decade or so (Cassidy *et al.*, 1992), including many in previously unoccupied positions in the chemical-petrologic grid (*e.g.*, the EL3 chondrites described by Lin *et al.*, 1991, and Chang *et al.*, 1992), means that this is an opportune time to examine the luminescent properties of enstatite meteorites as a class. We obtained a suite of EH and EL chondrites, covering the available spectrum of textural and mineralogical types, and made photographic mosaics of the CL of entire thin sections. We discovered trends not previously recognized that we suggest are the result of differences in the thermal history of the EH and EL classes. To help interpret these trends, we performed x-ray diffraction measurements.

The thermoluminescence (TL) process usually involves the same luminescent centers as CL, and the two techniques are closely related, although our TL apparatus is equipped with filters to restrict black-body radiation that results in a bias towards blue light. Because metamorphic history is a particularly important aspect of enstatite chondrite history and since induced TL measurements have proved useful in exploring the metamorphic history of ordinary and carbonaceous chondrites (Sears *et al.*, 1980, 1991a,b; Guimon *et al.*, 1995), we included induced TL measurements in the present study.

EXPERIMENTAL

Samples Studied

The samples that were obtained are listed in Table 1. Descriptions can be found in Keil (1968) and Zhang *et al.* (1995). The samples included representative EH and EL chondrites of all available textural types 3–6 and mineralogical types α–δ. LEW88180 was classified as an EH6 by Mason (1990) while Zhang *et al.* (1995) described it as EH5δ. TIL91714 is the second known EL5; RKPA80259 was the first. Both meteorites have the CL properties of EL6 chondrites, which are quite unlike those of EH5 chondrites (Zhang *et al.*, 1994a). There can no longer be any uncertainty as to the classification of RKPA80259 (Weeks and Sears, 1985; Kallemeyn and Wasson, 1986); it is clearly an EL5 chondrite.

Cathodoluminescence

Cathodoluminescence mosaics were prepared from 10–20 photographs using polished thin sections, typically 1 cm × 1.5 cm, of 23 enstatite chondrites. A commercial Nuclide Instruments "Luminoscope" attached to a low-magnification optical microscope was operated at 13 ± 1 kV and 8 ± 1 mA and the images photographed with Kodak "Gold" 400 film, exposed for 20 s to 40 s. Equilibrated EH chondrites typically required ~10 s longer

TABLE 1. Cathodoluminescence and related properties of enstatite chondrites.*

Meteorite**	Class	Wtg‡	CL	B/R§	B/R@	B/R$	Mn# (ppm)	XRD‡‡	Pyroxene structure†	References for Mn and pyroxene structure††
ALH84170	EH3α	B	Red + Blue	0.20	–	0.06	–	–	twinned cpx	1
ALH84206	EH3α	A/B	Red + Blue	0.20	0.23	–	1500	0.9	twinned cpx	1
Qingzhen	EH3α	Fall	Red + Blue	0.15	–	0.08	2000	0.47	twinned cpx	2
Abee	EH4γ	Fall	Blue	1.42	1.82	–	<77	0.37	cpx and disordered opx	3
Indarch	EH4β,γ	Fall	Red + Blue	0.19	–	0.04	1630	0.80	cpx and disordered opx	3
PCA82518	EH4α,β	B	Red + Blue	0.28	–	0.38	400	0.73	twinned opx	1
PCA91085	EH4α	B/C	Red + Blue	0.36	0.33	0.07	390	0.89	twinned opx	1
St. Mark	EH5β	Fall	Blue + Yellow	1.9	0.94	–	1300	0.88	disordered opx	3
Saint-Sauveur	EH5γ	Fall	Blue	5.0	3.0	–	<77	0.83	cpx and disordered opx	3
LEW88180	EH5δ	B/C	Blue	1.9	2.3	2.7	<77	0.74	highly cleaved opx, unlike the EL6s	1
ALH85119	EL3α	B	Red + Blue	0.26	0.25	0.54	770	0.53	twinned cpx	1
MAC88136	EL3α	A	Red + Blue	0.29	–	0.78	700	0.97	twinned cpx	1
MAC88184	EL3α	C	Red + Blue	0.33	0.62	–	380	0.76	twinned cpx	1
TIL91714	EL5β	C	Magenta	n.a.	0.38	–	100	3.04	euhedral opx	1
RKPA80259	EL5γ	B/C	Magenta	n.a.	–	–	600		euhedral opx	4
ALH81021	EL6β	A	Magenta	n.a.	0.10	–	70	1.17	euhedral px, 1% ol and 1% twinned cpx	1
Atlanta	EL6β	Find	Magenta	n.a.	0.64	–	<77	1.14	well-cryst, ordered opx	3
Hvittis	EL6β	Fall	Magenta	n.a.	0.50	–	<77	1.4	well-cryst, ordered opx	3
Khaipur	EL6β	Fall	Magenta	n.a.	0.51	–	<77	0.78	well-cryst, ordered opx	3
LEW87119	EL6γ	C	Red	n.a.	0.31	–	<77	1.36	some euhedral px	1
LEW88135	EL6β,γ	B/C	Magenta	n.a.	0.60	–	80	1.13	euhedral opx	1
Yilmia	EL6β	Find	Magenta	n.a.	0.33	–	70	0.63	opx	5
Happy Canyon	An EL	Find	Red	n.a.	0.22	–	70	0.65	disordered opx	6
Bishopville	Aub	Fall	Bluish red	–	0.23	–	150	1.15	disordered and ordered opx	7, 8
Bustee	Aub	Fall	Bluish red	–	0.10	–	850	–	disordered and ordered opx	7, 8
Khor Temiki	Aub	Fall	Bluish red	–	0.05	–	310	–	disordered and ordered opx	7, 8
Norton County	Aub	Fall	Bluish red	–	0.12	–	150	–	disordered and ordered opx	7, 8
Pena Blanca Spring	Aub	Fall	Red	–	0.03	–	460	–	disordered and ordered opx	7, 8

* Meteorites listed alphabetically within class, mineralogical (α–δ) and textural (3–6) type. See Zhang *et al.* (1995) for details. – = data not available.
** Cathodoluminescence data for meteorites in italics were obtained by JMD at the Johnson Space Center; Aubrite data from Geake and Walker (1966).
‡ Weathering category as defined by Score and Lindstrom (1990).
§ Ratio of the blue CL to red CL as determined by point-counting the cathodoluminescence images. n.a. indicates that this parameter is not applicable to these samples.
@ The intensity of the 450 nm to 700 nm CL (aubrite data from Geake and Walker, 1966).
$ Data from DeHart and Lofgren (1995).
\# Mn contents of the enstatite were obtained without regard to CL and are thus weighted averages of grains with blue and red CL. Typically, in unmetamorphosed (type 3α) enstatite chondrites, red grains contain ~2000 ppm Mn while in blue CL grains the Mn is below detection limits.
‡‡ The ratio of the intensity of the (420), (221) doublet and (610) peak in the X-ray diffraction pattern, see Pollack and Ruble (1964).
† "cpx," "opx" and "ol" refer to clinopyroxene, orthopyroxene and olivine, respectively.
†† References as follows: 1. Zhang *et al.* (1995); 2. Wang and Xie (1981); 3. Keil (1968); 4. Sears and Weeks (1984); 5. Buseck and Holdsworth (1972); 6. Olsen *et al.* (1977); 7. Watters and Prinz (1979); 8. Pollack (1966).

than equilibrated EL chondrites. The film was developed with the C-41 process. Some of the present mosaics were obtained at the Johnson Space Center using the same techniques. Aubrite data were taken from the literature.

Spectra were obtained from the CL negatives using a UV-visible spectrometer (HP8452). Three areas each of ~0.2 cm × 1 cm were scanned; backgrounds measured using blank portions of the same negatives were subtracted; and the spectra were averaged. The data were then converted from absorbancies to reflectivities for comparison with the CL prints. Repeated measurements on blank portions of film processed over a two-year period showed remarkable constancy in film response. The spectra obtained agree very well with those of individual grains obtained by direct spectrometry by Geake and Walker (1966). We tried to determine a quantitative relative estimate of the blue and red grains by point-counting the CL mosaics and by taking the ratios of the heights of the red (~700 nm) and blue (~450 nm) peaks in the CL spectra. On occasion, the blue peak did not reach a maximum before the instrumental cut-off and the value at 450 nm was taken. These two methods of data reduction are insensitive to exposure times because they are both essentially "internally calibrated."

Optical Microscopy, Electron-Microprobe Analysis and X-ray Diffraction

The thin sections were examined under the optical microscope and observations on the nature of the pyroxene are reported in Table 1. Enstatite compositions for 12 samples were determined using the Cameca electron microprobe at the Johnson Space Center, Houston. The accelerating voltage was 15 kV with a beam diameter of 1 μm and beam current of 17 nA. Data for five to ten grains were normally averaged for each meteorite. kaersutite $[Ca_2(Na,K)(Mg,Fe)_4TiSi_6Al_2O_{22}F_2]$ was used as a standard for Ca, Ti, Fe, Si and Mg and garnet for Mn. Complete analyses are reported in Zhang *et al.* (1995).

The x-ray diffraction patterns over the 26° to 38° 2θ range were obtained for 20 mg nonmagnetic powder using a Philips diffractometer with a scanning rate of 2°/min and Cu Kα radiation. The relative heights of the (420), (221) doublet and the (610) peak were used as an order/disorder parameter in the way described by Pollack and Ruble (1964). These authors pointed out that for ordered orthopyroxene the doublet was usually more intense than the singlet, while the reverse was true for disordered orthopyroxene. To test our methods and evaluate precision, we prepared four samples each of Qingzhen (EH3α) and Hvittis (EL6β) and ran each sample three times, making sure that different parts of the powder were scanned each time. The ratios of the peak heights of the doublet to that of the singlet are shown in Fig. 1. The precision obtained in this experiment is comparable to the standard deviation of the mean peak height ratios for EH and EL chondrites (Table 1) and is ~30% of the value measured.

Induced Thermoluminescence

We performed TL measurements on 14 EH chondrites and 20 EL chondrites of textural types 3–6 and mineralogical type α–δ (Table 2), the samples were those used in the recent study of bulk and mineral compositions by Zhang *et al.* (1993, 1995). The apparatus and procedures were those of Sears *et al.* (1991a). Dhajala was used as a normalization standard and long-term stability check for the apparatus. All operations were performed in temperature- and humidity-controlled laboratories and under red light; the TL measurements were made with Daybreak Nuclear and Medical apparatus fitted with thermal and blue filters and a heating rate of 7.5 °C/s. After draining the natural TL by heating to 500 °C, the samples were exposed to a 250 mCi ^{90}Sr beta-ray source and the induced TL measured. Three 4 mg aliquots of nonmagnetic, homogenized 100-mesh powder were used for the TL measurements, and three aliquots were analyzed for each sample. Some variation in TL sensitivity is possibly the result of weathering, but acid-washing experiments as described by Benoit *et al.* (1991) indicate that this is of minor importance for the present samples.

RESULTS

Cathodoluminescence

The CL Images of EH Chondrites–Photographs of representative CL mosaics are shown in Plate 1a–d. Enstatite grains with red or blue CL, and rare areas of chondrule mesostasis with yellow CL, are observed in both EH3α and EH4α chondrites. Very occasionally, we observed isolated grains with yellow CL that might be CaS, but weathering would have destroyed this mineral in most of our samples. A few grains displaying no CL are rare enstatites with >5 wt% FeO (Lusby *et al.*, 1987; Weisberg *et al.*, 1994). Enstatite with almost pure blue CL was the major luminescent phase in the Saint-Sauveur (EH5γ) chondrite. However, in the LEW88180 (EH5δ) and Abee (EH4γ) chondrites, ~90% of the enstatite displays blue CL and the remainder shows magenta CL. While in St. Marks (EH5β), ~90% of the enstatite displays blue CL, and the remainder is yellow CL, which is characteristic of chondrule mesostasis.

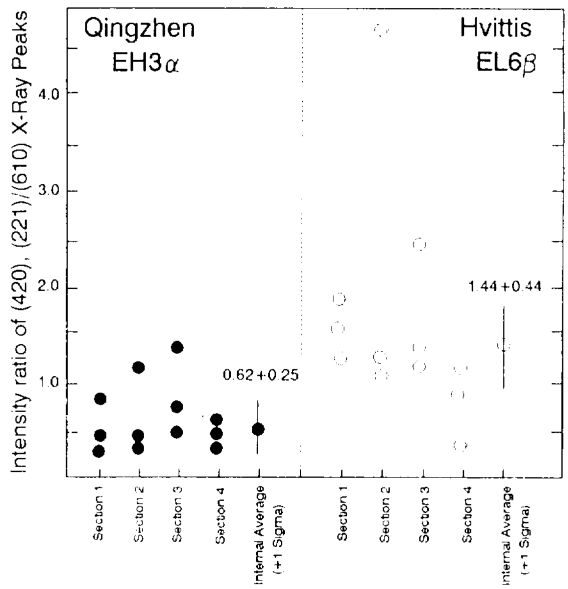

FIG. 1. Plots of the ratio of the 420, 221 doublet to the 610 singlet in the x-ray diffraction pattern of two enstatite chondrites. Four sections of each sample were prepared, and each was scanned three times. According to Pollack and Ruble (1964), the doublet is more intense than the singlet for ordered enstatites while the reverse is true of disordered enstatite. The internal average (average ignoring the highest and lowest points) is shown for the peak height ratios of each meteorite.

The CL Images of EL Chondrites–The EL3α chondrites resemble the EH3α chondrites in their CL properties, containing mostly enstatite with red CL but occasionally grains with blue CL or no CL are found (Plate 1a–h). There are very rare chondrules whose mesostases produce yellow CL (Plate 1e–h). The enstatite grains in the EL5β and EL6β chondrites display a magenta CL with irregular and interdigitated regions whose CL appears to be brown. The RKPA80259 (EL5β), TIL91714 (EL5β), LEW87119 (EL6γ) and anomalous Happy Canyon EL-related chondrite also display magenta CL.

The CL Spectra–Some representative spectra are shown in Fig. 2. The spectra for a given meteorite are highly reproducible, especially for the higher petrographic types, with peaks at ~450 nm and ~700 nm. Quantitative data, extracted from the spectra, are shown in Fig. 3. The relative abundance of red and blue grains, determined by point counting the CL photographs, agrees well with peak height ratios determined from spectra (Table 1). In general, EL chondrites have stronger blue and red CL intensity than EH chondrites. The metamorphosed EH chondrites are noteworthy for their high blue-to-red CL ratios. For the EH series, the intensity of the blue CL increases with textural and mineralogical types. For the EL chondrites, the CL intensity and blue-to-red ratio are independent of types.

The X-ray Diffraction, Optical Microscopy and Electron Microprobe Data

Observations based on optical microscopy, x-ray diffraction and electron microprobe analysis are listed in Table 1 and shown in Fig. 4. The intensity of the (420), (221) doublet in the x-ray diffraction patterns is less than the intensity of the (610) peak for the EH chondrites and the EL3α chondrites analyzed, which is indicative of disordered orthopyroxene. The x-ray diffraction data for the EL6β chondrites are fairly heterogeneous, but for eight of twelve samples the doublet is stronger than the singlet, indicating the presence of ordered orthopyroxene. Only for Khairpur and Yilmia is the doublet weaker than the singlet. Both EH3α and EL3α chondrites contain mainly twinned-clinopyroxene, in a variety of grain sizes, while Saint-Sauveur (EH5γ), Abee (EH4γ), St. Mark (EH5β) and LEW 88180 (EH6δ) contain disordered orthopyroxene (Table 1). The EL6β chondrites contain euhedral pyroxene without cleavage planes, which is generally ordered orthopyroxene. The Mn content of the enstatite generally decreases with increasing textural type for both EH and EL chondrites and is below the detection limit in textural types 5 and 6.

Thermoluminescence

The EH and EL chondrites display TL peaks at ~140 °C and ~300 °C. However, the ~140 °C peak can sometimes be resolved into separate peaks at 125 °C and 175 °C and the ~300 °C peak may show peaks at 280 °C and 330 °C (Fig. 5). The EH3α chondrites are missing the higher temperature peak. Figure 6 shows the TL sensitivities. The high temperature peak for the EL6β chondrites shows considerable scatter, which might be related to the scatter in the x-ray diffraction data. The EL chondrites show a much larger range than the EH chondrites and extend to higher TL sensitivities by factors of ~4. Both TL peaks show a small increase in TL sensitivity with petrographic type within the EH chondrites with values going from <0.01 to 0.2 (Dhajala = 1). However, there is no systematic trend in TL sensitivity with petrographic type among the EL chondrites. Instead, both TL peaks range from <0.05 to 0.6 for the EL3α chondrites and from <0.01 to 0.9 for the EL6β chondrites (Zhang *et al.*, 1994b).

TABLE 2. Induced thermoluminescence and related properties of enstatite chondrites.*

Meteorite	Class	Wtg†	Peak 1 T_p (°C)	Peak 1 TL sens (Dhajala = 1)	Peak 2 T_p (°C)	Peak 2 TL sens (Dhajala = 1)
ALH84170	EH3α	B	145 ± 3	0.061 ± 0.004	–	–
ALH84206	EH3α	A/B	150 ± 7	0.046 ± 0.005	–	–
EET83322	EH3α	A/B	138 ± 15	0.042 ± 0.005	–	–
EET87746	EH4α,β	C	135 ± 7	0.071 ± 0.007	–	–
Qingzhen	EH3α	Fall	134 ± 8	0.183 ± 0.008	–	–
Kota-Kota	EH3α	Find	140 ± 11	0.040 ± 0.005	312 ± 3	0.017 ± 0.003
Abee+	EH4γ	Fall	121 ± 5	0.122 ± 0.010	313 ± 21	0.073 ± 0.007
Adhi-Kot	EH4γ	Fall	114 ± 5	0.069 ± 0.017	293 ± 5	0.115 ± 0.021
Indarch	EH4β, γ	Fall	142 ± 11	0.042 ± 0.004	313 ± 6	0.024 ± 0.003
PCA82518	EH4α,β	B	174 ± 4	0.069 ± 0.014	309 ± 1	0.141 ± 0.029
PCA91085	EH4α	B/C	122 ± 9	0.163 ± 0.020	291 ± 8	0.050 ± 0.006
PCA91238	EH4α	B	169 ± 26	0.046 ± 0.006	315 ±1 7	0.137 ± 0.040
St. Marks+	EH5β	Fall	121 ± 3	0.230 ± 0.030	311 ± 3	0.150 ± 0.020
LEW88180+	EH5δ	B/C	111 ± 5	0.086 ± 0.006	294 ± 9	0.052 ± 0.008
ALH85119	EL3α	B	126 ± 6	0.285 ± 0.022	304 ± 4	0.145 ± 0.023
EET90299	EL3α	C	119 ± 6	0.223 ± 0.020	311 ± 10	0.190 ± 0.015
MAC88136	EL3α	A	146 ± 6	0.142 ± 0.020	300 ± 8	0.126 ± 0.016
MAC88180	EL3α	C	147 ± 10	0.540 ± 0.046	302 ± 2	0.460 ± 0.040
MAC88184	EL3α	C	124 ± 7	0.087 ± 0.008	288 ± 7	0.080 ± 0.010
PCA91020+	EL3β	C	115 ± 8	0.434 ± 0.028	310 ± 16	0.523 ± 0.060
TIL91714	EL5β	C	145 ± 10	0.307 ± 0.013	263 ± 13	0.171 ± 0.012
ALH81021	EL6β	A	116 ± 2	0.480 ± 0.050	340 ± 0	0.280 ± 0.030
Atlanta	EL6β	Find	131 ± 17	0.300 ± 0.060	282 ± 20	0.130 ± 0.020
Daniel's Kuil	EL6β	Fall	119 ± 3	0.899 ± 0.178	317 ± 11	0.485 ± 0.100
Eagle	EL6β,γ	Fall	130 ± 10	0.330 ± 0.030	281 ± 10	0.140 ± 0.010
EET90102	EL6	B/C	147 ± 14	0.220 ± 0.024	–	–
Hvittis	EL6β	Fall	136 ± 9	0.604 ± 0.027	236 ±1 2	0.460 ± 0.009
Khairpur	EL6β	Fall	134 ± 5	0.420 ± 0.070	324 ± 14	0.250 ± 0.040
LEW87119	EL6γ	C	124 ± 6	0.108 ± 0.013	268 ± 6	0.041 ± 0.007
LEW88135	EL6β,γ	B/C	141 ± 6	0.069 ± 0004	347 ± 7	0.024 ± 0.004
LEW88714	EL6γ	C	130 ± 8	0.142 ± 0.010	280 ± 12	0.047 ± 0.004
Pillistfer	EL6β	Fall	122 ± 14	0.430 ± 0.049	331 ± 2	0.250 ± 0.028
Yilmia	EL6β	Find	134 ± 5	0.088 ± 0.009	333 ± 6	0.043 ± 0.003
Happy Canyon	ELAn‡	Find	175 ± 4	0.200 ± 0.030	287 ± 3	0.140 ± 0.020

* Meteorites listed alphabetically within class, mineralogical (α–δ) and textural (3–6) type. See Zhang *et al.* (1995) for details. Uncertainties are standard deviations based on triplicate measurements of aliquots from a single homogenized powder. – = peak absent.
† Weathering category as defined by Score and Lindstrom (1990).
\+ These meteorites have resolvable peaks at intermediate temperatures. The temperatures and TL sensitivities of these peaks are: Abee = 196 ± 5, 0.085 ± 0.010; St. Marks = 181 ± 2, 0.200 ± 0.030; LEW88180 = 170 ± 5, 0.074 ± 0.008; PCA91020 = 176 ± 14, 0.385 ± 0.030, respectively.
‡ An = anomalous; see Zhang *et al.* (1995) for details.

DISCUSSION

Composition, Structure and CL of the Pyroxene in Enstatite Chondrites

Compositional Factors–Iron and several minor and trace elements in enstatite underwent reduction or diffusive equilibration with other phases during metamorphism and fell to values near or below their detection limits (Keil, 1968; Table 1). A great many studies of the CL and composition of enstatite and profiles within individual grains have shown that high transition element abundances favor red CL while grains low in these elements have blue CL (Reid and Cohen, 1967; Leitch and Smith, 1982; McKinley *et al.*, 1984; Steele, 1989; Lofgren and DeHart, 1992a,b, 1993; DeHart and Lofgren, 1994; Weisberg *et al.*, 1994). It, therefore, seems reasonable to predict that the CL properties of enstatite chondrites would become progressively dominated by blue CL grains with increasing metamorphism. While blue CL is associated with low trace-element content, the mechanism producing the CL is unclear. The blue CL of α quartz (450 nm) is thought to be an intrinsic property of the SiO_4 tetrahedron and not due to activation by impurity ions (Waychunas, 1988). The ubiquitousness of the blue CL in silicates is consistent with this idea although not proof (Steele, 1989). As expected, the EH chondrites show a trend of decreasing Mn with increasing blue/red ratio (Fig. 7). However, the equilibrated EL chondrites, while containing enstatite with low Mn and other trace and minor elements that are similar to those of the equilibrated EH

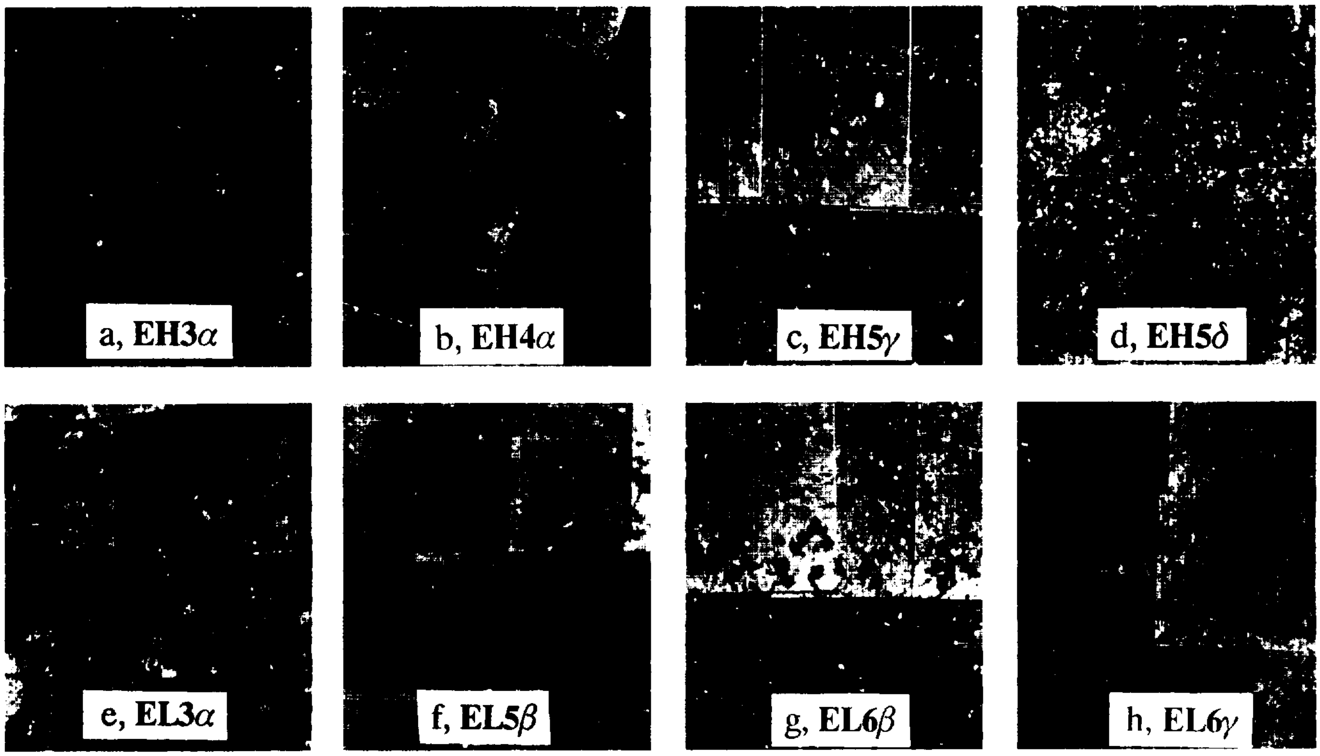

PLATE 1. Mosaics of the cathodoluminescence of EH chondrites (upper series) and EL chondrites (lower series) in order of increasing petrographic type. (a) ALH84206, (b) PCA91085 (paired with PCA82518), (c) Saint Sauveur, (d) LEW88180, (e) ALH85119, (f) TIL91714, (g) ALHA81021 and (h) LEW87119. The EH3α, EL3α and EH4α chondrites (there are no known EL4 chondrites) display predominantly red CL with occasional grains of blue or no CL. For the EH chondrites of higher petrologic type, the CL is predominantly blue with relatively few grains exhibiting magenta CL. The equilibrated EL chondrites have enstatite with almost entirely magenta CL and a few obscure well-integrated regions of brownish CL. The horizontal field of view in all images is ~0.5 cm.

chondrites, display a large range in CL intensity and blue to red ratio, which is unrelated to the composition of the enstatite (Fig. 7). It should be mentioned that while we discuss Mn, which is widely associated with the red CL of enstatite, other transition metal impurity ions are strongly correlated with Mn in enstatite, and the same arguments apply if they are activators. Properties besides trace-element abundances determine the CL properties of the enstatite in these meteorites.

Structural Factors–Enstatite exists as orthoenstatite, low-clinoenstatite, high-clinoenstatite and protoenstatite, but the detailed phase relations are unclear (*e.g.*, Brown and Smith, 1963; Mason, 1968; Smyth, 1974; Pacalo and Gasparik, 1990; Kanzaki, 1991; Angel *et al.*, 1992). Clinopyroxene occurs in low textural types of enstatite chondrites, while orthopyroxene occurs in the high types (Mason, 1968; Keil, 1968). Isolated descriptions of ordered and disordered orthopyroxene in enstatite chondrites and aubrites have been reported by many authors (Keil, 1968; Reid *et al.*, 1964; Reid and Cohen, 1967), but no systematic variation with class or type has been reported. At low pressures, protoenstatite is the stable form of $MgSiO_3$ between 1000 °C and 1300 °C (Smyth 1974). Orthoenstatite and low-temperature clinoenstatite are the common forms in meteorites since high-clinoenstatite is stable only at pressures >7 GPa. The phase boundary between orthoenstatite and low-clinoenstatite is indistinct, largely because of the slow kinetics of the transformation, so that it is possible for enstatite to occur as a mixture of orthoenstatite and low-clinoenstatite (Buseck *et al.*, 1982).

The co-existence of two polymorphs in individual enstatite grains is sometimes referred to as stacking disorder and is distinct from cation disordering (*e.g.*, Skogby, 1992). Stacking disorder in orthopyroxene is readily detected by the single crystal Weissenberg method because it produces both sharp and diffuse spots (Pollack, 1968). It has been suggested that fast cooling of protopyroxene from 1000 °C to 700 °C produces disordered pyroxene sometimes with twinned clinopyroxene, while slow cooling (slower than a few degrees per hour) of protopyroxene between 1000 °C and 800 °C produces ordered orthopyroxene (Brown and Smith, 1963; Smyth, 1974).

Reid *et al.* (1964) noted that the luminescence of disordered orthoenstatite in enstatite achondrites was weaker and the ratio of the intensity of blue to red luminescence was higher than for ordered orthoenstatite. Reid and Cohen (1967) suggested that disordered grains produced blue CL, while ordered grains from the same meteorite produced red CL. The x-ray powder diffraction suggests that one EH4γ (Abee), one EH5β (St. Mark), one EH5γ (St. Sauveur) and one EH5δ (LEW88180) contains mixtures of disordered and ordered orthopyroxene with disordered orthopyroxene being dominant (Fig. 4). As noted above, these meteorites produce blue CL. On the other hand, the EL5β and EL6β chondrites are composed predominantly of ordered orthoenstatite, and their enstatite produces magenta CL. Thus, we suspect that Reid and Cohen's (1967) suggestion that ordered orthoenstatite luminesces red and disordered orthoenstatite luminesces blue in aubrites

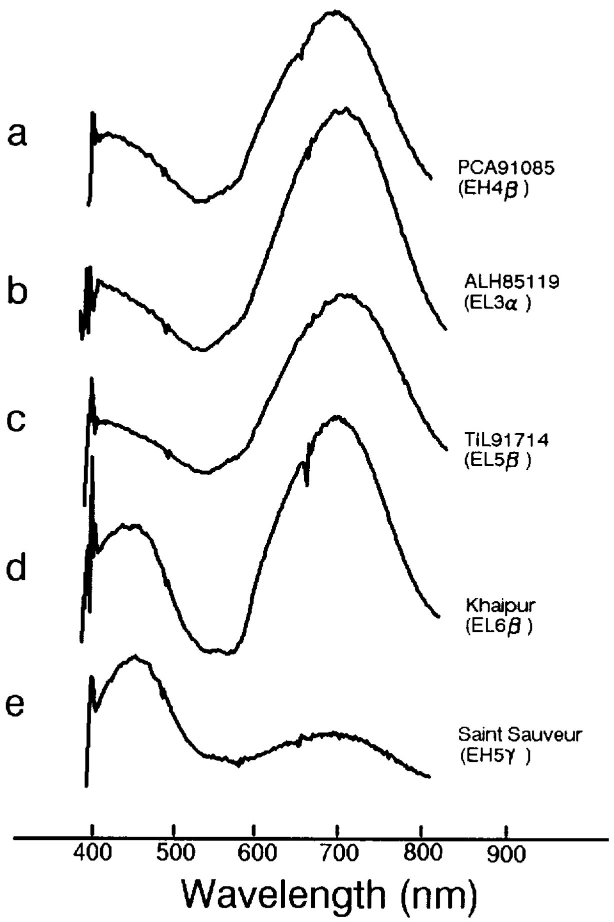

FIG. 2. Representative cathdoluminescence spectra of bulk samples of enstatite chondrite. Baselines have been displaced vertically for clarity. Little-metamorphosed chondrites of both the EH (a) and EL (b) classes have spectra with strong red (~700 nm) and weak blue (~450 nm) CL peaks. Metamorphosed EL chondrites (c and d) also have spectra with strong red peaks, but the blue CL peaks can be of almost comparable intensity to the red CL peak. Metamorphosed EH chondrites have strong blue and weak red CL peaks. These spectra are consistent with CL images in Plate 1.

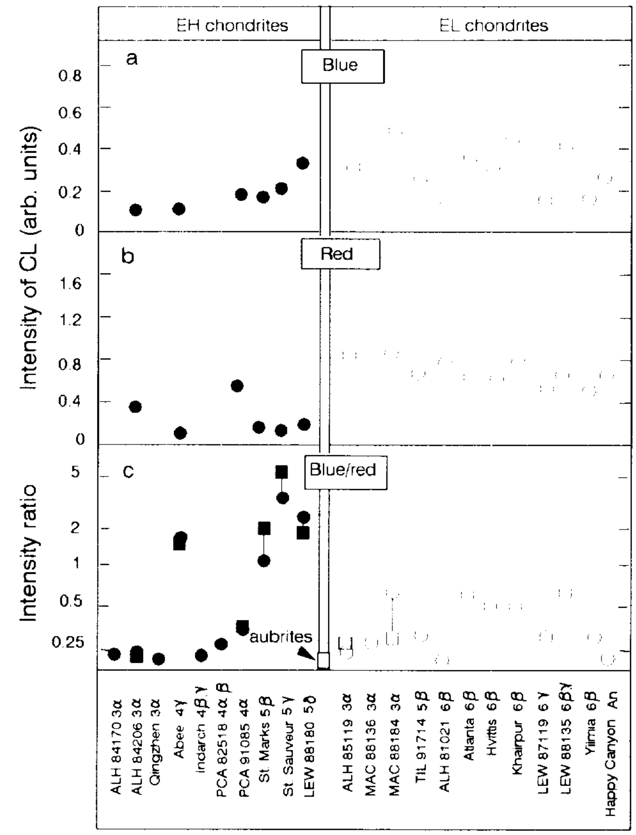

FIG. 3. Quantitative data for the bulk CL properties of enstatite chondrites determined from CL spectra similar to those of Fig. 2. (a) The intensity of the blue peak increases with textural and mineralogical type in the EH chondrites, but the EL chondrites display no systematic trends. (b) The intensity of the red peak does not appear to vary systematically with textural and mineralogical type in either class but is a factor of ~2 higher in the EL chondrites. (c) The ratio of the intensity of blue and red peaks increases with type for the EH chondrites and is independent of type in the EL chondrites. It is higher for equilibrated EH chondrites than the other enstatite meteorites. Blue/red ratios obtained by point counting the CL images are also shown as squares and connected to the spectral data by tie lines. Unless otherwise indicated, on all our figures 1σ experimental precisions are approximately twice the size of the symbols. Also shown is the range of blue to red spectral peak ratios measured for aubrites by Geake and Walker (1966).

is also true for the enstatite in the EL and EH chondrites. The present x-ray diffraction data suggest that a major factor governing the CL of metamorphosed enstatite chondrites is the structural state of the pyroxene.

We have begun a series of experiments in which we heat enstatite from meteorites in furnaces and observe the changes to their CL and structure. To date, we have not been able to disorder enstatite from ALHA81021 (EL6β), nor change the color from magenta to blue, but we did observe a change in the color of the CL from magenta to yellow-green, suggesting that the structure of the enstatite can affect its CL (Schneider *et al.*, 1995). The technique best suited to exploring the structural dependence of the CL of pyroxenes is arguably transmission electron microscopy (TEM). Unfortunately, such studies are very few. Buseck *et al.* (1982) summarized the major properties of enstatite with emphasis on TEM, and McCoy *et al.* (1995) reported data for Ilafegh 009. Ilafegh 009 is an unusual impact melt whose CL we have not examined. It contains a disordered mixture of ortho- and clinopyroxene. Another promising method is single crystal XRD coupled with CL spectra (I. Steele, pers. comm.).

Induced Thermoluminescence Properties of Enstatite Chondrites

Since the mineral producing the TL signal is undergoing structural and compositional changes as a result of metamorphism, it is worth considering whether the enstatite chondrites display major changes in TL sensitivity as a function of textural and mineralogical type like the ordinary chondrites. Variations in TL sensitivity resemble those of blue CL as determined from the spectra, including an increase in the TL sensitivity of the EH chondrites with increasing petrologic type. However, the increase is fairly modest (about a factor of four), partly because the blue TL is coming from both the "primary" blue enstatite of the sort observed in EH3α chondrites (Weisberg *et al.*, 1994) and the "metamorphic" blue enstatite of the sort observed in EH6δ chondrites (McKinley *et al.*, 1984). The EH chondrites plot at the lower end of the TL sensitivity range for EL chondrites, which is consistent with their difference in CL intensity. The mosaics of CL from EH chondrites require longer photographic exposure times than those of the EL chondrites.

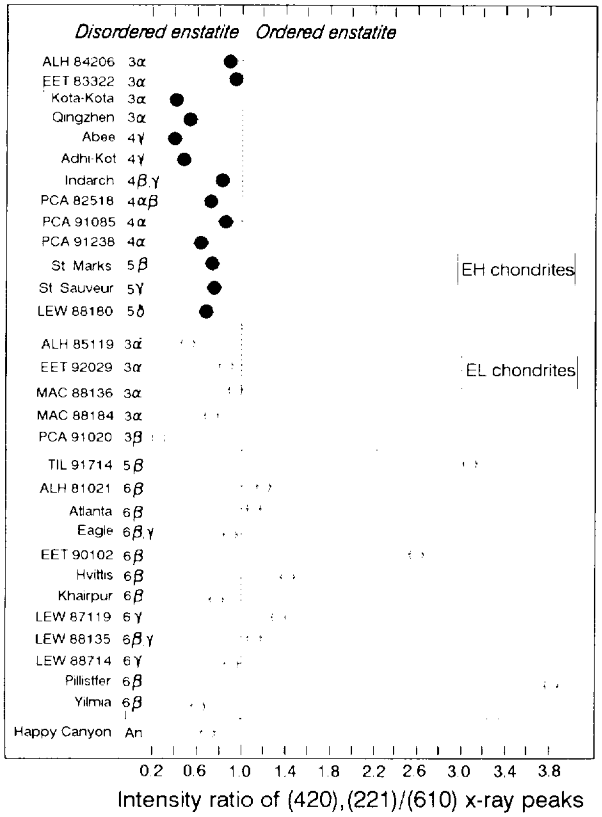

FIG. 4. The x-ray diffraction data for enstatite chondrites. According to Pollack and Ruble (1964), the relative intensity of the (420), (221) doublet and the (610) peak is a measure of the stacking order in the enstatite; the doublet peak is stronger than the singlet in ordered orthopyroxene but weaker for disordered orthopyroxene. All of the EH chondrites and the EL3α chondrite appear to contain disordered enstatite, while eight of twelve EL6 chondrites contain ordered enstatite.

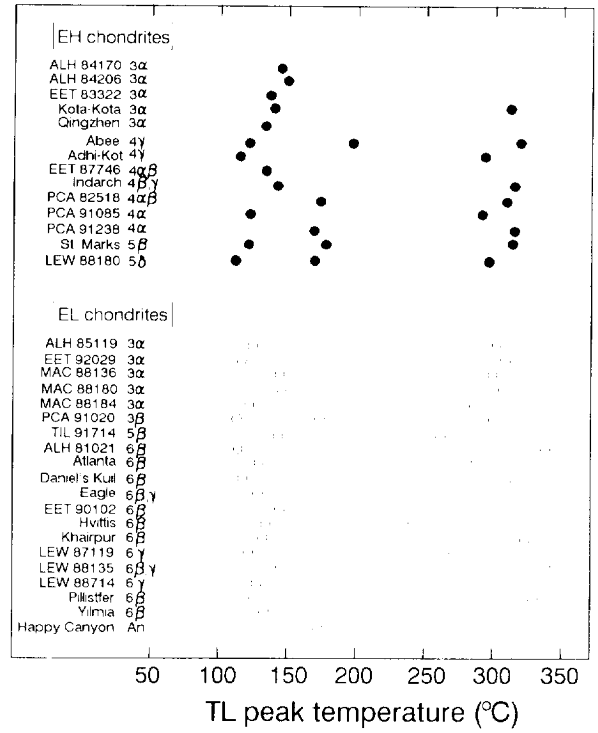

FIG. 5. Plot to compare the induced thermoluminescence peak temperatures of enstatite chondrites. Except for EH3α chondrites, enstatite chondrites show peaks at ~140 °C and ~300 °C in the glow curve. In a few instances, the ~140 °C peak can be resolved into two peaks (at ~120 °C and ~170 °C). The EL6β chondrites show considerable scatter in the position of the high temperature peak.

The EL chondrites span almost a factor of 10 in their TL sensitivity, and the spread in TL sensitivity values displayed by EL6β chondrites alone is comparable with the range shown by the EL chondrites as a whole. Peak metamorphism alone, at least as reflected by the textural type, is clearly not governing TL sensitivities. However, these EL6 meteorites are primarily mineralogical type β, which suggests that their high TL sensitivities are associated with ordered enstatite.

The Thermal History and Origin of Enstatite Chondrites

Probably the simplest explanation for the CL trends in Plate 1 is that while the enstatite is predominantly clinopyroxene in the EH3α and EL3α chondrites, it is disordered orthopyroxene in the metamorphosed EH chondrites and is ordered orthopyroxene in the metamorphosed EL chondrites. This is the situation that is suggested, at least to some extent, by the optical and x-ray diffraction data in Table 1 and Fig. 4. With this as a working hypothesis, we will now summarize the available data.

The EL5,6 Chondrites–The lack of chondrules in the EL6 chondrites, and the presence of only a few chondrule relics, indicates that they experienced very high peak metamorphic temperatures. Mason (1968) suggested a maximum equilibration temperature of 870 °C based on the presence of quartz. Peak metamorphic temperatures for EL5,6β chondrites lie between 600° C to 800 °C, which are bounded by the stability field of clinopyroxene (600 °C; Mason, 1968) and the ordered structure of their pyroxene. The Schneider *et al.* (1995) heating experiments indicate significant changes in CL after heating >800 °C. There are some exceptions to this generalization. Eagle, for instance, which was considered a post-metamorphism breccia with inclusions by Olsen *et al.* (1988), appears to contain disordered orthopyroxene and, therefore, equilibration temperatures >800 °C (Fig. 4). Happy Canyon, which was considered an impact melt of EL composition by McCoy *et al.* (1995), also contains disordered orthopyroxene. Despite this high-temperature episode, the low equilibration temperatures of the cubic sulfides for these two meteorites indicate that some systems closed at lower temperatures (Zhang *et al.*, 1992).

It seems that the transition between petrologic type 3 to 5,6 in EL chondrites is not continuous, either because we have not yet recovered an EL4 chondrite or because there was some mechanical process to separate these EL5,6 chondrites from original EL3 chondrites before they underwent high peak temperatures that destroyed chondrules. Experience shows that it is probably due to the lack of complete sampling of the enstatite meteorite classes.

The EH5,6 chondrites–The EH5,6 chondrites contain a mixture of clino, ordered and disordered orthopyroxene (Table 1). In fact, based on their textures, the homogeneity of their mineral chemistry and the presence of only ~10% enstatite grains with magenta color, it is clear that these meteorites underwent prolonged metamorphism at high temperatures with the equilibration temperatures for a number of mineral systems being ~900 °C (Zhang *et al.*, 1992). We suggest that their equilibration temperatures (as opposed to their peak-metamorphic temperatures) are higher than those of

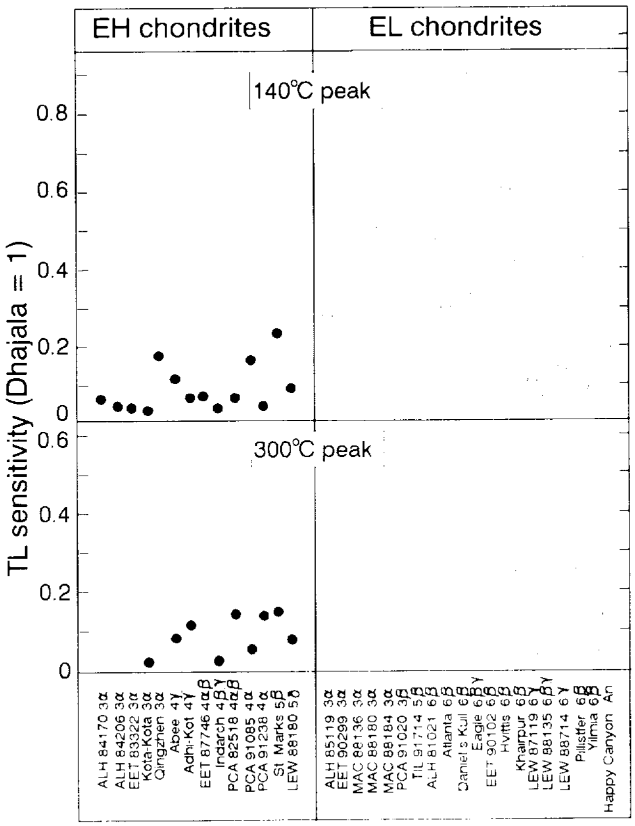

FIG. 6. Plot comparing the thermoluminescence sensitivities of enstatite chondrites. The ~140 °C and the ~300 °C peaks behave similarly, suggesting that they are caused by the same luminescent minerals and activators. Since our TL apparatus is biased towards blue wave lengths, the variations in TL sensitivity shown by enstatite chondrites resemble those of the blue CL intensity.

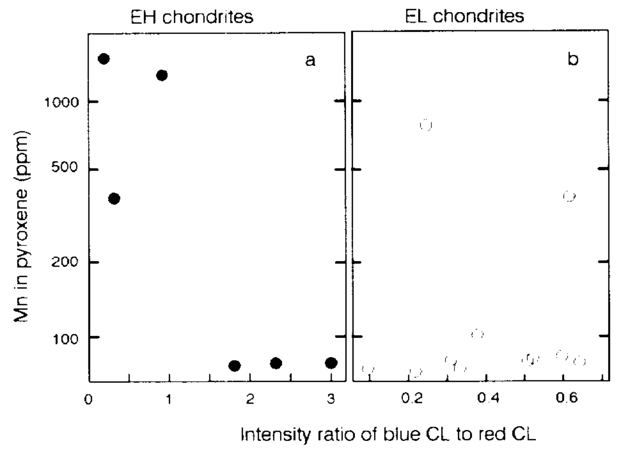

FIG. 7. Plot to compare the Mn content in pyroxene in enstatite chondrites with the intensity ratio of blue CL to red CL obtained from the spectra. (a) EH chondrites show a decrease in the Mn content of the enstatite with increasing blue CL to red CL ratio. (b) EL chondrites display no obvious trend.

EL5,6 chondrites (~800 °C) in order to produce the disordered structure. At the end of this metamorphic event or subsequent to it, most of these meteorites underwent rapid cooling (faster than a few degrees per hour) to produce the observed mixture of enstatite structural states and metal structures observed in Abee (Herndon and Rudee, 1978). This scenario is consistent with the proposed higher shock levels of EH5,6 chondrites compared with EL5,6 chondrites (Rubin and Scott, 1995) because rapid cooling following shock would favor disordered structures. However, interpretation of shock effects must be considered tentative until the effects of shock on the various pyroxene structures are considered.

The E3 Chondrites–In type 3 chondrites, the clinopyroxene has either blue or red CL depending on transition metal contents; apparently, CL color is not uniquely identified with this structure. Weisberg *et al.* (1994) proposed that chemical processes in the nebula resulted in the compositional diversity (and thereby CL colors) of the enstatite in type 3α chondrites and that red CL enstatite grains are solid-state reduction products while blue CL enstatite grains are condensates from the nebula. Hsu and Crozaz (1994) argued that both types of enstatite were produced from melts, based on their similar REE patterns.. Previous studies suggested that clinopyroxene produced by the fast cooling of protopyroxene is usually twinned while clinopyroxene produced by shearing stress from orthopyroxene is not usually twinned (Brown and Smith, 1963; Smyth, 1974). The higher abundances of twinned clinopyroxene in E3 chondrites compared to EH5,6 chondrites reflects the difference in metamorphic history.

Comparison Between EH and EL Parent Bodies–Several authors have suggested that the EH and EL chondrites represent different parent bodies with the arguments centering on differences in breccia types and abundances, bulk compositions (Keil, 1989) and cosmic-exposure age distributions (Crabb and Anders, 1981). The EL and EH chondrites also experienced different thermal histories, and there is, thus, a different distribution of enstatite chondrites over the textural and mineralogical types (Fig. 8). Most EH chondrites are low textural and low mineralogical types, whereas most EL chondrites are high mineralogical and high textural types, which suggests that the EL chondrites experienced a prolonged period of low-temperature metamorphism that the EH chondrites escaped. This different thermal history took place after peak metamorphism and possibly involved breakup of the EH and EL parent bodies. Virtually all the equilibrated EH chondrites and a few EL chondrites were involved in an event that resulted in rapid cooling. The fragmental breccias among the EH chondrites (*e.g.*, Abee and St. Sauveur) may be evidence of this event. The environment is a matter of speculation. Zhang *et al.* (1995) suggested that differences in thermal blanketing in a regolith might have been responsible.

Aubrites–The aubrites have thermal histories that are more like EH chondrites than the EL chondrites. The aubrites experienced a violent breakup, which resulted in heating and rapid cooling. Aubrites contain large enstatite crystals and a mixture of ordered and disordered orthoenstatite. It is possible that the impact and rapid cooling event was associated with the event(s) that produced the numerous breccias observed in this meteorite group (Keil, 1989).

CONCLUSIONS

The CL properties of enstatite in un- or little-metamorphosed EH and EL chondrites are similar; enstatites with high transition metal contents have red CL, while relatively pure enstatites have blue CL. Rare enstatites with >5 wt% FeO have no CL. Metamorphosed EH chondrites display predominantly blue CL, while metamorphosed EL chondrites display magenta CL whose spectra contain blue and red peaks of approximately equal intensity.

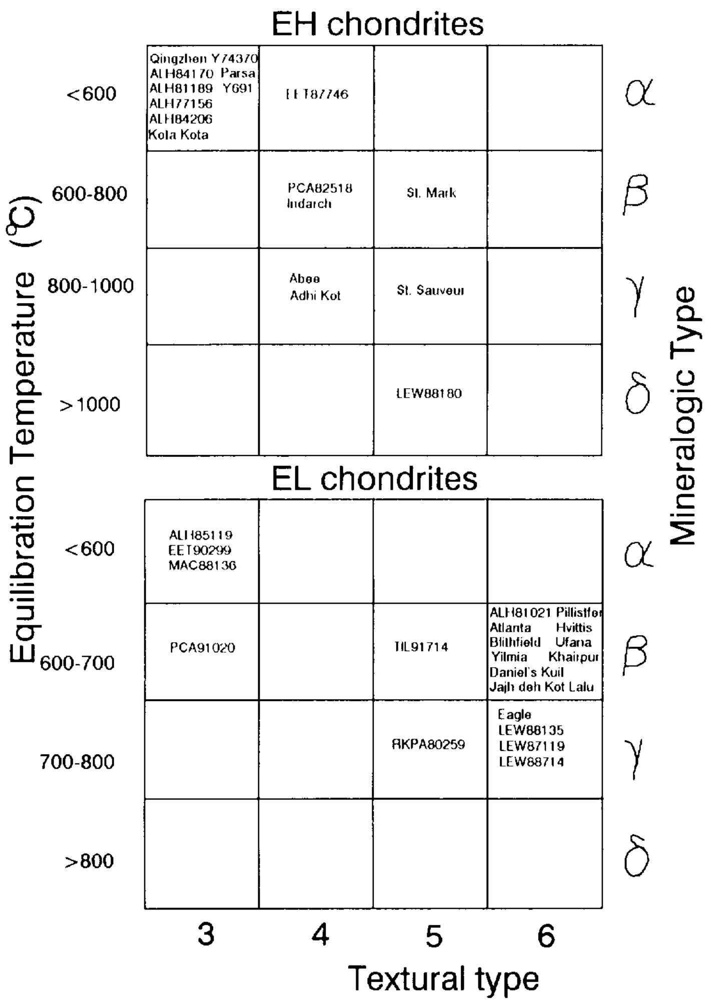

FIG. 8. Distribution of enstatite chondrites over mineralogic (α–δ) and textural (3–6) types with suggested equilibration temperatures that are based on the pyroxene structure.

The TL sensitivities of EH chondrites correlate with the intensity of the blue CL and correlate very weakly with textural type. The TL sensitivities of EL chondrites show a wide range, being generally higher than those of EH chondrites, and show no evidence of correlating with textural type.

The diverse CL properties of enstatite in unmetamorphosed enstatite chondrites are readily understood in terms of minor- and trace-element composition, but this is not the case for metamorphosed enstatite chondrites. The x-ray diffraction measurements and optical microscopy suggest that unmetamorphosed enstatite chondrites of both classes contain clinopyroxene (with small amounts of disordered orthopyroxene), but metamorphosed EH chondrites contain predominantly disordered orthopyroxene and metamorphosed EL chondrites contain predominantly ordered orthopyroxene. These conclusions are summarized in Table 3.

TABLE 3. Summary of cathodoluminescence color, composition and structure of enstatite in enstatite chondrites.

CL color	Mn (ppm)	Structure*
Red	>350	Cpx and opx
Magenta	<350	Ordered opx
Yellow-green	<350	Disordered opx with twinned cpx
Blue	<350	Disordered opx with untwinned cpx

* "cpx" and "opx" refers to clinopyroxene and orthopyroxene, respectively.

The differences in the structural form of the enstatite in metamorphosed EH and EL chondrites indicate major differences in the thermal history of the two classes following peak metamorphism. The EH chondrites cooled relatively quickly, but the EL chondrites were heated for a prolonged period in the stability field of orthopyroxene (600 °C–800 °C).

Acknowledgments–We are grateful to the Meteorite Working Group of NASA/NSF, I. Casanova (Field Museum of Natural History, Chicago, Illinois), R. Hutchison (The Natural History Museum, London), G. Kurat (Naturhistorisches Museum Wien, Vienna), M. Prinz (American Museum of Natural History, New York), L. S. Schramm (National Museum of Natural History, Smithsonian Institution, Washington, D.C.), L. Schultz (Max-Planck Institut für Chemie, Mainz) and B. Zanda (Muséum d'Histoire Naturelle, Paris) for supplying samples; especially to Walter Manger and Ronald Konig (University of Arkansas, Geology Department) for their continued generous loan of the cathodoluminescence and x-ray diffraction equipment; and to Gordon McKay and Vincent Yang for access to and help with the JSC electron microprobe analysis. We also especially appreciate useful reviews by Katherina Lodders and Ian Steele. This work was supported by a grant from NASA (NAGW 3519) while DS was supported by an NSF REU award.

Editorial handling: K. Keil

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