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

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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; Gröger 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 MgSiO3. 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 "Fir 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 black-body radiation that results in a bias towards blue light.

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-β). LEW88180 was classified as an EH6 by Mason (1990) while Zhang et al. (1995) described it as EH5. TIL91714 is the second known EL5; RKP80259 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 RKP80259 (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.

<table>
<thead>
<tr>
<th>Meteorite**</th>
<th>Class</th>
<th>Weight</th>
<th>CL.</th>
<th>B/R$</th>
<th>B/R@</th>
<th>Mn $ (ppm)</th>
<th>XRD↑++</th>
<th>Pyroxene structure$</th>
<th>References for Mn and pyroxene structure$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALH84170</td>
<td>EHαε</td>
<td>B</td>
<td>Red + Blue</td>
<td>0.20</td>
<td>-</td>
<td>0.06</td>
<td>-</td>
<td>twinned cpx</td>
<td>1</td>
</tr>
<tr>
<td>ALH84206</td>
<td>EHαε</td>
<td>A/B</td>
<td>Red + Blue</td>
<td>0.20</td>
<td>0.23</td>
<td>-</td>
<td>-0.6 mot.</td>
<td>twinned cpx</td>
<td>1</td>
</tr>
<tr>
<td>Qingchen</td>
<td>EHβε</td>
<td>Fall</td>
<td>Red + Blue</td>
<td>0.15</td>
<td>-</td>
<td>0.07</td>
<td>2000</td>
<td>twinned cpx</td>
<td>2</td>
</tr>
<tr>
<td>Abeec</td>
<td>EHγε</td>
<td>Fall</td>
<td>Blue</td>
<td>1.42</td>
<td>1.82</td>
<td>-</td>
<td>&lt;77</td>
<td>cpx and disordered opx</td>
<td>3</td>
</tr>
<tr>
<td>Indarch</td>
<td>EHαε/γ</td>
<td>Fall</td>
<td>Red + Blue</td>
<td>0.19</td>
<td>-</td>
<td>0.04</td>
<td>1630</td>
<td>cpx and disordered opx</td>
<td>3</td>
</tr>
<tr>
<td>PCA82518</td>
<td>EHαεβ</td>
<td>B</td>
<td>Red + Blue</td>
<td>0.28</td>
<td>-</td>
<td>0.38</td>
<td>400</td>
<td>twinned opx</td>
<td>1</td>
</tr>
<tr>
<td>PCA91085</td>
<td>EHβε</td>
<td>C</td>
<td>Red + Blue</td>
<td>0.36</td>
<td>0.33</td>
<td>0.07</td>
<td>390</td>
<td>twinned opx</td>
<td>1</td>
</tr>
<tr>
<td>St. Mark</td>
<td>EHβε</td>
<td>Fall</td>
<td>Blue + Yellow</td>
<td>1.9</td>
<td>0.94</td>
<td>-</td>
<td>1300</td>
<td>disordered opx</td>
<td>3</td>
</tr>
<tr>
<td>Saint-Sauveur</td>
<td>EHεγ</td>
<td>Fall</td>
<td>Blue</td>
<td>5.0</td>
<td>3.0</td>
<td>&lt;77</td>
<td>0.36</td>
<td>cpx and disordered opx</td>
<td>3</td>
</tr>
<tr>
<td>LEW88180</td>
<td>EHβε</td>
<td>B/C</td>
<td>Blue</td>
<td>1.9</td>
<td>2.3</td>
<td>2.7</td>
<td>&lt;77</td>
<td>highly cleaved opx,</td>
<td>unlike the EL6s</td>
</tr>
<tr>
<td>ALH85119</td>
<td>EHαε</td>
<td>B</td>
<td>Red + Blue</td>
<td>0.26</td>
<td>0.25</td>
<td>0.54</td>
<td>770</td>
<td>twinned cpx</td>
<td>1</td>
</tr>
<tr>
<td>MAC88136</td>
<td>EHαε</td>
<td>A</td>
<td>Red + Blue</td>
<td>0.29</td>
<td>-</td>
<td>0.78</td>
<td>700</td>
<td>twinned cpx</td>
<td>1</td>
</tr>
<tr>
<td>MAC88184</td>
<td>EHαε</td>
<td>C</td>
<td>Red + Blue</td>
<td>0.33</td>
<td>0.62</td>
<td>-</td>
<td>380</td>
<td>twinned cpx</td>
<td>4</td>
</tr>
<tr>
<td>TIL91714</td>
<td>ELβε</td>
<td>C</td>
<td>Magenta</td>
<td>0.38</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>euhedral opx</td>
<td>1</td>
</tr>
<tr>
<td>RKP80259</td>
<td>ELγε</td>
<td>B/C</td>
<td>Magenta</td>
<td>0.38</td>
<td>-</td>
<td>-</td>
<td>600</td>
<td>euhedral opx</td>
<td>4</td>
</tr>
<tr>
<td>ALH81021</td>
<td>ELβε</td>
<td>A</td>
<td>Magenta</td>
<td>0.10</td>
<td>-</td>
<td>-</td>
<td>70</td>
<td>euhedral px</td>
<td>1</td>
</tr>
<tr>
<td>Atlantic</td>
<td>ELβε</td>
<td>Find</td>
<td>Magenta</td>
<td>0.64</td>
<td>-</td>
<td>&lt;77</td>
<td>1.14</td>
<td>highly cleaved opx</td>
<td>1</td>
</tr>
<tr>
<td>Hwittis</td>
<td>ELβε</td>
<td>Fall</td>
<td>Magenta</td>
<td>0.50</td>
<td>-</td>
<td>&lt;77</td>
<td>1.4</td>
<td>highly cleaved opx</td>
<td>3</td>
</tr>
<tr>
<td>Khaipur</td>
<td>ELβε</td>
<td>Fall</td>
<td>Magenta</td>
<td>0.51</td>
<td>-</td>
<td>&lt;77</td>
<td>0.78</td>
<td>highly cleaved opx</td>
<td>3</td>
</tr>
<tr>
<td>LEW87119</td>
<td>ELεγ</td>
<td>C</td>
<td>Red</td>
<td>0.31</td>
<td>-</td>
<td>&lt;77</td>
<td>1.36</td>
<td>some euhedral px</td>
<td>1</td>
</tr>
<tr>
<td>LEW88135</td>
<td>ELβε/γ</td>
<td>B/C</td>
<td>Magenta</td>
<td>0.60</td>
<td>-</td>
<td>80</td>
<td>1.13</td>
<td>euhedral opx</td>
<td>1</td>
</tr>
<tr>
<td>Yilmia</td>
<td>ELβε</td>
<td>Find</td>
<td>Magenta</td>
<td>0.33</td>
<td>-</td>
<td>70</td>
<td>0.63</td>
<td>opx</td>
<td>5</td>
</tr>
<tr>
<td>Happy Canyon</td>
<td>An EL</td>
<td>Find</td>
<td>Red</td>
<td>0.22</td>
<td>-</td>
<td>70</td>
<td>0.65</td>
<td>disordered opx</td>
<td>6</td>
</tr>
<tr>
<td>Bishopville</td>
<td>Aub</td>
<td>Fall</td>
<td>Bluish red</td>
<td>0.23</td>
<td>-</td>
<td>150</td>
<td>1.15</td>
<td>disordered and ordered opx</td>
<td>7, 8</td>
</tr>
<tr>
<td>Bostee</td>
<td>Aub</td>
<td>Fall</td>
<td>Bluish red</td>
<td>0.10</td>
<td>-</td>
<td>850</td>
<td>-</td>
<td>disordered and ordered opx</td>
<td>7, 8</td>
</tr>
<tr>
<td>Khor TemiK</td>
<td>Aub</td>
<td>Fall</td>
<td>Bluish red</td>
<td>0.05</td>
<td>-</td>
<td>310</td>
<td>-</td>
<td>disordered and ordered opx</td>
<td>7, 8</td>
</tr>
<tr>
<td>Norton County</td>
<td>Aub</td>
<td>Fall</td>
<td>Bluish red</td>
<td>0.12</td>
<td>-</td>
<td>150</td>
<td>-</td>
<td>disordered and ordered opx</td>
<td>7, 8</td>
</tr>
<tr>
<td>Pen Blanca Spring</td>
<td>Aub</td>
<td>Fall</td>
<td>Red</td>
<td>0.03</td>
<td>-</td>
<td>460</td>
<td>-</td>
<td>disordered and ordered opx</td>
<td>7, 8</td>
</tr>
</tbody>
</table>

* Meteorites listed alphabetically within class, mineralogical (α-β) 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 3) 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.

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. Aurbite data were taken from the literature.

Spectra were obtained from the CL negatives using a 1.0-visible spectrometer (HP8452). Three areas each of 0.2 cm × 1 cm were scanned, background measured using blank portions of the same negatives were subtracted; and the spectra were averaged. The data were then corrected 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, mosas 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 [Ca2(Na,K)(Mg,Fe)4TiSi6Al2O22F2] 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 (EH3c) and Hvittis (EL6f) 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–ε (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). Daphgal 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 luminescence at 500 °C, the samples were exposed to a 250 mCi 90Sr 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 EH chondrites are shown in Plate la–d. Enstatite grains with red or blue CL, and rare areas of chondrule mesostasis with yellow CL, are observed in both EH3α and EH4ε 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 (Lushy et al., 1987; Weisberg et al., 1994). Enstatite with almost pure blue CL was the major luminescent phase in the Saint-Sauveur (EH15α) chondrite. However, in the LIEW88180 (EH15α) and Abe (EH4py) chondrites, ~90% of the enstatite displays blue CL and the remainder shows magenta CL. While in St. Marks (EH15β), ~90% of the enstatite displays blue CL, and the remainder is yellow CL, which is characteristic of chondrule mesostasis.

**The CL Images of El Chondrites—**The El3α chondrites resemble the EH3α chondrites in their CI properties, containing mostly enstatite with red CL but occasionally grains with blue CL or no CL are found (Plate la–h). There are very rare chondrules whose mesostases produce yellow CL (Plate 1e–h). The enstatite grains in the El5β and El6f chondrites display a magenta CL with irregular and interdigitated regions whose CL appears to be brown. The RKPA30259 (El5β), TIL91714 (El5β), L187119 (El6f) 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 EL3± chondrites analyzed, which is indicative of disordered orthopyroxene. The x-ray diffraction data for the EL6± 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 Khaipur and Yilmia is the doublet weaker than the singlet. Both EH3± and EL3± chondrites contain mainly twinned-clinoenstatite, in a variety of grain sizes, while Saint-Sauveur (EH5±), Abee (EH4±), St. Mark (EH5±) and LEW88180 (EH6±) contain disordered orthopyroxene (Table 1). The EL6± chondrites contain euhenoidal 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 EH3± chondrites are missing the higher temperature peak. Figure 6 shows the TL sensitivities. The high temperature peak for the EL6± 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 EL3± chondrites and from <0.01 to 0.5 for the EL6± chondrites (Zhang et al., 1994b).

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Class</th>
<th>Wgt</th>
<th>Peak 1</th>
<th>Peak 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALH84170</td>
<td>EH3±</td>
<td>B</td>
<td>145 ± 3</td>
<td>0.061 ± 0.004</td>
</tr>
<tr>
<td>ALH84206</td>
<td>EH3±</td>
<td>A/B</td>
<td>150 ± 7</td>
<td>0.046 ± 0.005</td>
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<tr>
<td>EET83322</td>
<td>EH3±</td>
<td>A/B</td>
<td>138 ± 15</td>
<td>0.042 ± 0.005</td>
</tr>
<tr>
<td>EET87746</td>
<td>EH4cβ</td>
<td>C</td>
<td>135 ± 7</td>
<td>0.071 ± 0.007</td>
</tr>
<tr>
<td>Qingzhen</td>
<td>EH3±</td>
<td>Fall</td>
<td>134 ± 8</td>
<td>0.183 ± 0.008</td>
</tr>
</tbody>
</table>

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; Loebregen and Delhart, 1992a, b, 1993; Delhart and Loebregen, 1994; Weiberg 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 SiO4 tetrahedron and not due to activation by impurity ions (Waychunas, 1988). The ubiquity of the blue CL in silicates is consistent with this idea although not proof (Steele, 1989). As expected, the EI1 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

* Meteorites listed alphabetically within class, mineralogical (c–d) 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, 0.204 ± 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.
Pyroxene structures, cathodoluminescence and the thermal history of enstatite chondrites

1. Mosaics of the cathodoluminescence of EH chondrites (upper series) and EL chondrites (lower series) in order of increasing petrographic type. (a) ALH84006, (b) PCA91085 (paired with PCA82518). (c) Saint Sauveur, (d) LEW88180, (e) ALH833119, (f) TIL91714, (g) ALH81021 and (h) LEW87119. The EH3α, EL3α and EH4α 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 uncertain (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 MgSiO₃ 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 EH4y (Abee), one EH5y (St. Mark), one EH5y (St. Sauveur) and one EH5y (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 cathodoluminescence 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 C. images in Plate 1.

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 ALHA1019 (EH4B), 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. Busack et al. (1982) summarized the major properties of enstatite with emphasis on TEM, and McCoy et al. (1995) reported data for Hafeg 009. Hafeg 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 (L. Steele, pers. comm.).

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 the 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).

**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 EH3 chondrites (Weisberg et al., 1994) and the "metamorphic" blue enstatite of the sort observed in EH6 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.
Morphic temperatures for E1,5.6 chondrites lie between 600 °C to temperature of 870 °C based on the presence of quartz. Peak metamorphic temperatures, Mason (1968) suggested a maximum equilibration that they experienced very high peak metamorphic chondrites, and the presence of only a few chondrule relics. Peak metamorphism alone, at least as 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 corrected by the textural type, is clearly not governing Ti, sensitivity, and the spread in Ti+ sensitivity values displayed by E1,6 chondrites contain ordered enstatite. The E1, chondrites span almost a factor of 10 in their TL sensitivitiy, and the spread in TL sensitivity values displayed by E1,6 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 CI trends in Plate 1 is that while the enstatite is predominantly clinopyroxene in the E13β and EL3α chondrites, it is disordered orthopyroxene in the metamorphosed EI3 chondrites and is ordered orthopyroxene in the metamorphosed E1 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 EL 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 EL5,6 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 CI 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 E15,6 chondrites—The E15,6 chondrites contain a mixture of chemo, 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...
Y. Zhang et al.

**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 3cl 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 clino-

**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 textual 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-β) 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 CI, and correlate very weakly with textural type. The TL sensitivities of EL chondrites show a wide range, being generally higher than those of EL chondrites, and show no evidence of correlating with textural type.

The diverse CI 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.

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).

**REFERENCES**


