Mineral chemistry and the origin of enstatite in unequilibrated enstatite chondrites

WEIBIAO HSU*† and GHISLAINE CROZAZ

McDonnell Center for the Space Sciences and Department of Earth and Planetary Sciences, Washington University, St. Louis, Missouri 63130, USA

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Abstract—A comprehensive study of the petrography, cathodoluminescence (CL), rare earth element (REE) abundances, and magnesium and silicon isotopic compositions of enstatite, the major mineral in unequilibrated enstatite chondrites (UECs), is reported. For comparison, observations were also made in equilibrated enstatite chondrites (ECCs) andaubrites. In UECs, there are no REE patterns or abundances that uniquely characterize the CL color and intensity, grain size, or occurrence of enstatite. Red enstatite is dominant in UECs and blue enstatite in ECCs. Three REE patterns represent the diversity observed in UEC enstatite; many grains are depleted in one or more of the three most volatile REEs under reducing conditions (i.e., Yb, Eu, and Sm). All REE patterns are compatible with the fractional crystallization (during chondrule formation) of melts whose precursors either had flat REE patterns or were depleted in the most volatile REEs. No evidence was found to suggest that enstatite grains require nebular condensation or multiple reservoirs, as suggested by others. Magnesium and silicon isotopic ratios are normal, therefore excluding the role of evaporation in separating the REEs. This fractionation was most likely accomplished during condensation of the chondrule precursors. Our data, combined with synthetic experiments, support the idea that coexisting red and blue CL enstatites formed by crystalization from a single melt. Most of the red enstatite was converted to blue by diffusion and recrystallization to form the more equilibrated E chondrites. It is not clear why enstatite is depleted in the most volatile REEs while oldhamite, a highly refractory mineral which is the major carrier of REE in E chondrites, commonly has enrichments of these elements. Copyright © 1998 Elsevier Science Ltd

1. INTRODUCTION

Although few in number (less than 1% of the meteorite population), enstatite chondrites are of great interest because of their extremely reduced nature. They consist mainly of nearly Fe-free enstatite (FeO < 1.0 wt%; Keil, 1968) with variable amounts of metallic nickel-iron and troilite and a series of rare minerals that reflect formation under highly reducing conditions. Elements that are typically lithophile in other chondrites tend to be siderophile (e.g., S) or chalcophile (e.g., Cu, Mg, Mn, Cr, Na, K) in enstatite chondrites. In particular, the metal in these meteorites has a high silicon content (1.1–3.6 wt%; Keil, 1968).

Because enstatite is the major component of enstatite chondrites, it is key to our understanding of the conditions and processes responsible for the formation of these meteorites. However, its origin is still largely controversial. It is not clear whether enstatite is the product of nebular condensation or igneous activity. While most work on enstatite has focused on its major and minor element chemistry, trace elements, especially the rare earth elements (REEs), have not been extensively studied.

A unique feature of this mineral is that it shows either a red or a blue cathodoluminescence (CL) color under electron bombardment. By studying the minor element abundances and cathodoluminescence of enstatite, Leitch and Smith (1982) proposed that the red and blue CL enstatites formed by mechanical aggregation of crystals and liquids of both color types which formed in separate regions of the solar nebula. On the other hand, Weisberg et al. (1994) suggested that some red enstatite is a reduction product of igneous FeO-rich pyroxene and that blue enstatite was formed directly by nebular condensation. Their conclusions were based on petrographic observations and REE patterns of enstatite in unequilibrated enstatite chondrites (UECs). However, Weisberg et al. (1994) analyzed only a few enstatite grains and acknowledged that more enstatite REE analyses were needed to better understand the origin of this mineral. Lundberg and Crozaz (1988) also studied a few enstatite grains and showed that their REE patterns can be very different, but they did not determine the CL color of the grains they analyzed.

In this work, we carried out an extensive study of the petrography, CL, and REE abundances of enstatite in UECs. A few analyses of enstatite from equilibrated enstatite chondrites andaubrites were also made. Lundberg and Crozaz (1988) had noted that enstatite is sometimes depleted in Yb, the most volatile REE under highly reducing conditions (Lodders and Fegley, 1993). We wondered whether enstatite formation may also have caused isotopic mass fractionation. Thus, we measured the magnesium and silicon isotopic compositions of individual enstatite grains in UECs to determine whether or not Yb depletions in enstatite are associated with isotopic mass fractionation. Preliminary trace element and isotopic data on enstatite from UECs were previously reported in four abstracts (Crozaz and Hsu, 1993; Hsu and Crozaz, 1994a, 1994b, 1995).

2. EXPERIMENTAL METHODS

We studied thin sections of two EH3 (Qingzhen 2.1, WU#1; Yamato-691.79-3), one EH4 (Indarch USNM348-2, 551a.5a&b), one EH4/5 (Abee UNM619a, UNM541), one EH5 (St. Mark’s USNM483-2), two EL3 (MAC8181.11, EET90299), and one EL6 (Jajh deh Kot Lala, USNM1260-1) chondrites, and twoaubrites (Bustee BM32100 and Mayo Belwa BM1976.11). Minerals were

*Author to whom correspondence should be addressed (whsu@gps.caltech.edu).
†Present address: Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, USA.
observed with the Washington University JEOL 840 A scanning electron microscope (SEM), equipped with an energy dispersive X-ray (EDX) spectrometer.

The cathodoluminescence of enstatite was induced with an ELM-3R NUCLIDE luminoscope which also has transmitted light capability. An electron beam of ~0.5 mA at ~12 keV acceleration was focused to the microscope viewing area at 100-times magnification. Selected areas of the samples were photographed with a standard 35 mm camera using Kodak Ektachrome ASA400 color film and an exposure time of 15~30 seconds.

Quantitative minor and trace element analyses of enstatite were obtained with the modified Cameca IMS-3F ion microprobe at Washington University, following the method described by Zinner and Crozaz (1986a). REE sensitivity factors were taken from Zinner and Crozaz (1986b) and those for other trace and minor elements from Hsu (1995). A deconvolution was performed in the mass ranges of K-Ca-Sr-Ti, Rb-Sr-Y-Zr, and Ba-REEs, to remove simple molecular interferences. REE concentrations in enstatite are usually very low. Consequently, relatively large primary ion beams (10~20 nA) were used. Two focused ion beam spots up to ~50 μm in size. A (Ca) is the major REE carrier (Crozaz and Lundberg, 1995), special attention was paid to potential contamination by this mineral by monitoring the Ca and S signals throughout the analysis. Fortunately, olivine is a trace mineral phase in UECs and only a few measurements were found to be affected by it; these were excluded from further consideration. In addition, any enstatite grains with unexpected REE patterns, such as a positive Eu anomaly and/or LREE enrichment, were reexamined by SEM to identify any inclusions.

Magnesium and silicon isotopic compositions in enstatite of UECs were measured with the ion microprobe at a mass resolution of about 3500 and with an O− beam of 0.5 nA. Enstatite from the Bushbee aubrite was used as a standard. The details of the isotopic measurements can be found in Fahey et al. (1987). The error in the isotopic composition was calculated by obtaining the total mass fractionation of the sample (Δ) with that of the standard. The total and intrinsic mass fractionations are taken to be (similar equations for 26Mg, 29Si, and 30Si):

\[ \Delta^{26}\text{Mg} = \left( \frac{^{12}M/^{12}\text{M}_{\text{sample}}}{^{12}M/^{12}\text{M}_{\text{standard}}} - 1 \right) \times 1000 \]

and

\[ \delta_{\text{Si}} = \Delta^{28}\text{Mg}_{\text{sample}} - \Delta^{28}\text{Mg}_{\text{standard}} \]

where the reference (REF) magnesium and silicon isotopic ratios are, respectively, from Catanazzo et al. (1996) and Barnes et al. (1975). The enstatite in UECs is essentially free of Al. Therefore, 26Mg excesses due to the decay of live 26Al in the early solar system are negligible.

3. PETROGRAPHY AND CATHODOLUMINESCENCE OF ENSTATITE

Most enstatite in UECs is irregularly-shaped and ranges in size up to several hundred μm. Euhedral crystals of enstatite are typically rare and small (about 10 μm), occurring only as inclusions in sulfide-metal assemblages, although larger euhedral enstatite grains (about 100 μm) were observed in MAC88136 (EL3). From petrologic type 3 to 6, euhedral enstatite becomes more abundant and larger in size and are either enclosed by or protruding into sulfide or Fe-Ni-metal. Euhedral crystals in aubrites are generally large (~cm) and well-crystallized. Usually, enstatite in UECs contains numerous tiny inclusions of Fe-Ni-metal, sulfides (mainly troilite), albitite, or albitic glass (Smith, 1983). In some cases, Fe-Ni-metal droplets are arranged in arrays parallel to structural features.

Under electron bombardment, enstatite in UECs shows either a red or a blue CL color, which may be associated with minor element concentrations or crystal defects (Keil, 1968; Leitch and Smith, 1982). UECs are dominated by red CL enstatite, but there are no systematic differences in the sizes of red and blue enstatite crystals nor in their modes of occurrence (Leitch and Smith, 1982). Both are found in chondrules (most often porphyritic) and in the matrix. Some individual blue CL enstatite crystals completely surrounded by red CL enstatite rims were found in this study, but red enstatites enclosed in blue rims, as reported by Weisberg et al. (1994), were not. A few enstatite crystals show no CL color (i.e., are black); this is due to their high FeO contents (Mckinley et al., 1984; Weisberg et al., 1994). Weisberg et al. (1994) also reported that some red enstatites occur along black pyroxene lamellae, fractures, and grain boundaries, and that almost all black pyroxenes are rimmed by blue enstatite. In this study, no blue enstatite rims were found on black pyroxene. In general, most enstatite luminesces in various shades and intensities of red or blue, from dull to bright. All types were included in the ion microprobe measurements.

UFCs contain abundant well-defined chondrules and chondrule fragments. Porphyrity, framboid, and radial chondrules were all observed. Leitch and Smith (1982) reported that porphyritic chondrules from UECs contain either only red or both red and blue CL enstatite crystals. In this study, porphyritic blue enstatite chondrules were also observed in Indarch and MAC88136. Some porphyritic blue CL enstatite chondrules (e.g., from Indarch) have a thin red enstatite rim. A glassy to microcrystalline mesostasis of Fe-Ni-metal, troilite and melt glass is present between enstatite crystals in porphyritic chondrules of Qingshen. Fine-grained chondrules of UECs consist of either red or blue CL enstatite peppered with tiny albitite, melt glass, sulfide, and Fe-Ni-metal droplets. This observation is not consistent with the Leitch and Smith assertion (1982) that all fine-grained chondrules contain only blue enstatite and that no inclusions of metal, sulfide, or other silicates are found in these chondrules. Some of the fine-grained chondrules have rims. One fine-grained, euhedral enstatite chondrule from Qingshen is completely surrounded by a thin sulfide rim. Leitch and Smith (1982) observed one fine-grained blue enstatite chondrule with a thin red enstatite rim. Radical chondrules of UECs are composed predominantly of red CL enstatite laths. Troilite and Fe-Ni-metal veins often occur between the laths. Blue enstatite only occurs as inclusions in radial chondrules of EET90929. No blue enstatite radial chondrules were found. One red enstatite radial chondrule fragment from Qingshen is surrounded by a thin blue enstatite rim. Both red and blue enstatite-burred chondrules were observed in UECs although Leitch and Smith (1982) reported only red ones. A barred blue enstatite chondrule from Qingshen contains barred red CL olivine and minute sulfide, Fe-Ni-metal, and melt glass inclusions between the enstatite blades.

Blue enstatite becomes dominant in EECs. In Abeec (EH4.5), red enstatite is rarely observed. This is consistent with the results of Keil (1968), McKinley et al. (1984), and Zhang et al. (1994) who reported that the abundance of blue enstatite in enstatite chondrites increases with petrologic type. Chondrules were not found in the three Abeec thin sections studied.

4. ANALYTICAL RESULTS

4.1. REE Concentrations and Patterns in Enstatites

The REE concentrations and patterns for all enstatites analyzed (~100) were documented by Hsu (1995). Here, we report the results of forty of the best analyses (Table 1). These include measurements of both red and blue enstatites, in the various types of chondrules as well as in the matrix.

4.1.1. Unequilibrated enstatite chondrules (UECs)

Absolute REE concentrations of enstatites vary significantly from measurement to measurement; the range of light rare earth (LREE) concentrations is larger (more than a factor of 1,000) than that of heavy rare earths (HREEs) (about a factor of 100). There are no REE patterns or abundances that uniquely characterize the CL color and intensity, the grain size, or the occurrence of enstatite. Enstatites with bright or dull CL colors are indistinguishable as far as REE abundances are concerned and, basically, there are three types of REE patterns that represent the diversity observed in UEC enstatite (Fig. 1).

Pattern I. Pattern I, observed in ~25% of the cases, is relatively flat, with a slight increase from LREEs to HREEs
Enstatite in unequilibrated enstatite chondrites

4.1.3. Aubrites

Floss (1991) measured REE concentrations in enstatite from the Bishopville and Bustee aubrites. She found that REE abundances were so low that only the HREEs (Lu up to 0.3 × C1) could be measured. Our measurements in Bustee and Mayo Belwa (Table 1) are consistent with hers but we were also able to measure LREE concentrations in some grains. All grains have a REE Pattern III without any Yb anomalies.

4.2. Other Selected Minor and Trace Elements

4.2.1. Unequilibrated enstatite chondrites (UECs)

Previous electron probe studies (Leitch and Smith, 1982; Smith, 1983) showed that red and blue enstatites from UECs have different concentrations of minor elements such as Ti, Al, Cr, Mn, Ca, and Na. Because inclusions in enstatite are common, the ion microprobe data for these elements are not useful to compare grains with distinct CL colors. In addition, data for chalcophiles and siderophiles in enstatite are largely contaminated by sulfide and Fe-Ni-metal inclusions and will not be reported here.

Nevertheless, a few interesting observations can be made. Like the REE, minor and trace element concentrations have large variations (Table 1), and some trends are apparent. Although there is much overlap, enstatites with REE Pattern III tend to have lower minor (Na, Al, K, Ca, and Ti) and trace (Sc, Y, and Zr) element concentrations than those with Patterns I and II. In addition, average abundances tend to decrease from EH3 to EL3 to EH4 (Table 2).

4.2.2. Equilibrated enstatite chondrites (EECs) and aubrites

The variations of most minor and trace element abundances in enstatite from equilibrated E chondrites and aubrites can also be large but their average abundances are significantly lower than in UECs (Table 2). Elemental abundances in enstatite from the more equilibrated enstatite chondrites (e.g., St. Mark's and Jahl deh Kot Lalu) are generally depleted relative to chondritic values, except for Sc (1.65 × C1 on the average) in Jahl deh Kot Lalu. This is also true for aubrite enstatite. Alkali abundances in Mayo Belwa enstatite are higher than in Bustee enstatite (Table 1).

4.3. Magnesium and Silicon Isotopic Compositions of Enstatite in UECs

We measured the isotopic ratios of major elements in enstatites to determine whether or not differences in REE patterns are associated with distinct isotopic compositions. Because aubritic (e.g., Bustee) enstatite is generally believed to have crystallized from a magma (Watters and Prinz, 1979; Keil, 1989), its Mg and Si mass fractionations were assumed to be insignificant.

In UECs, the magnesium and silicon isotopic compositions were measured in enstatites with and without negative REE anomalies. A total of 116 analyses were made (Hsu, 1995).
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W. Haue and G. Crozet
Table 1 (Continued)

| Occurrence | Matrix | MacB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) | MACB8136 (EL3) |
|------------|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| **CL**     | **Butte** | **Matrix** | **Butte** | **Butte** | **Butte** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** | **Mayo Belva** |
| **Pattern** | **Anomalies** | 0.30 | 0.53 | 0.56 | 0.35 | 0.68 | 0.30 | 0.72 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 |
| **Y** | **Sm/Sm*** | 0.20 | 0.12 | 0.55 | 0.20 | 0.12 | 0.55 | 0.20 | 0.12 | 0.55 | 0.20 | 0.12 | 0.55 | 0.20 | 0.12 | 0.55 | 0.20 | 0.12 | 0.55 | 0.20 | 0.12 | 0.55 | 0.20 | 0.12 | 0.55 | 0.20 | 0.12 | 0.55 | 0.20 | 0.12 | 0.55 | 0.20 | 0.12 |
| **Y/Yb** | **Eu/Eu*** | 0.30 | 0.72 | 0.64 | 0.30 | 0.72 | 0.64 | 0.30 | 0.72 | 0.64 | 0.30 | 0.72 | 0.64 | 0.30 | 0.72 | 0.64 | 0.30 | 0.72 | 0.64 | 0.30 | 0.72 | 0.64 | 0.30 | 0.72 | 0.64 | 0.30 | 0.72 | 0.64 | 0.30 | 0.72 | 0.64 | 0.30 | 0.72 |

Errors quoted here are 1σ standard deviation from counting statistics only. JdKL = Jdah deh Kot Lani. Rp = Radial pyroxene chondrule. BP = Barred pyroxene chondrule. PPr = Porphyritic pyroxene chondrule. FGP = Fine grained pyroxene chondrule. n.d. = not detected. n.m. = not measured.

* Interpolated REE abundances

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Estates in unequalitarian statistic chords.
These include forty eight measurements in enstatite with negative Eu, Yb, and Sm anomalies, sixteen in enstatite with negative Eu and Yb anomalies, twenty-one in enstatite with a negative Eu anomaly, eight in enstatite with negative Yb and Sm anomalies, and seven in enstatite without REE anomalies, plus a few measurements in enstatite with undetermined REE patterns. Magnesium and silicon isotopic measurements for enstatites from UECs representing the various types just listed are reported in Table 3 where they are compared with data for four different spots of Bustee enstatite. Magnesium and silicon isotopic compositions of all enstatites measured are unfractionated, within 2σ errors, relative to aubrite enstatite. Thus, there is no correlation between magnesium and silicon isotopic compositions and REE anomalies.

5. DISCUSSION

5.1. Correlations between Minor and Trace Element Abundances in Enstatite of UECs: The Importance of Melt Glass Inclusions

We have shown in Fig. 1 and Table 1 that REE concentrations in enstatite of UECs vary widely, with larger variations for the LREEs than for the HREEs. Of the three REE patterns observed, only Pattern III is consistent with what would be expected for a low-Ca pyroxene crystallizing from a melt. For this reason, Weisberg et al. (1994) invoked nebular condensation to explain the relatively flat REE pattern I they observed in blue enstatite of UECs. As shown below, there is a more likely explanation that involves melt inclusions.

The work of Kennedy et al. (1993), who experimentally determined the mineral/melt partition coefficients of enstatite representative of the radial pyroxene chondrules in unequilibrated ordinary chondrites, is consistent with this explanation. Although richer in Fe, the enstatite they produced under equilibrium conditions has a REE pattern that resembles our Pattern III. However, as the cooling rate is increased, the enstatite REE abundances tend to be higher and the patterns flatter, similar to our REE Patterns I and II. These authors suggested that melt inclusions (which they observed in their products) accounted for the increased REE concentrations they measured at high cooling rates. Lofgren (pers. commun.) further suggested that
rapid crystal growth can cause departures from equilibrium in the partitioning behavior.

As mentioned earlier, enstatite in UECs contains numerous kinds of tiny inclusions, including Fe,Ni-metal, sulfides (mainly troilite), albite, and melt glass. For the ion microprobe measurements, a relative large ion beam (20–50 μm) had to be used because of the low REE concentrations in enstatite and, thus, it is very likely that the enstatite analyses were contaminated by these inclusions. We took steps, as discussed previously, to assure that any measurement affected by either old-hamite (the main REE carrier in enstatite meteorites) or albite inclusions would not be further considered. Fe,Ni-metal and troilite are essentially free of REEs and, thus, we wondered whether or not melt glass inclusions, which are expected to be enriched in REEs relative to enstatite if this mineralized from a melt, could be responsible for Patterns I and II. Although too small (μm-sized) for direct analysis, the melt glass inclusions, which are albite in composition (Smith, 1983; Grossman et al., 1985), can be monitored by using elements that are characteristic of these inclusions but not normally found in enstatite.

To determine whether REE concentrations in enstatite are correlated with melt inclusions, we compared a number of elemental concentrations. Rather than using the LREEs whose concentrations in enstatite are so low that they often cannot be accurately determined, we selected Y, the analog of the HREEs. It is a more abundant and, therefore, easier element to measure. Positive correlations are observed between the abundances of a number of elements in UEC enstatites (with both blue and red CL; Figs. 3 and 4). Enstatite grains with high Ti, Y, and Zr abundances also have higher Na, Al, Ca, and K concentrations and those with the lowest REE abundances (e.g., Pattern III) usually have the lowest Na, Al, Ca, and K contents. The scatter in some of the diagrams is attributed to the distinct compositions of melt glasses (Grossman et al., 1985).

Because Na, Al, Ca, and K are also the major components of albite, one must consider whether or not what we attribute here to melt glass inclusions may in fact be due to albite, the only other type of inclusion that is rich in these elements. However, we have already excluded from the reported analyses those with the LREE enrichments and positive Eu anomalies characteristic of albite. Furthermore, we note that Y will not correlate as steeply with Na.

### Table 2: The averages and ranges of minor and trace element abundances (ppm) in enstatite from enstatite chondrites and aubrites

<table>
<thead>
<tr>
<th>Element</th>
<th>EH3</th>
<th>EL3</th>
<th>EH4</th>
<th>EH4,5</th>
<th>EH5</th>
<th>EL5</th>
<th>Aubrites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>8200 (120 - 37500)</td>
<td>5250 (56 - 13600)</td>
<td>4200 (530 - 17040)</td>
<td>2600 (1190 - 8540)</td>
<td>200 (150 - 320)</td>
<td>50 (16 - 175)</td>
<td>400 (75 - 940)</td>
</tr>
<tr>
<td>Al</td>
<td>21500 (290 - 85000)</td>
<td>15100 (2150 - 9870)</td>
<td>6600 (376 - 73165)</td>
<td>1650 (1160 - 5510)</td>
<td>1200 (1090 - 1830)</td>
<td>1145 (1140 - 1150)</td>
<td>950 (580 - 1590)</td>
</tr>
<tr>
<td>Ti</td>
<td>10700 (150 - 5115)</td>
<td>78 (16 - 450)</td>
<td>220 (135 - 615)</td>
<td>140 (43 - 335)</td>
<td>25 (15 - 34)</td>
<td>145 (2 - 290)</td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>12 (0.6 - 65)</td>
<td>9 (0.8 - 25)</td>
<td>4.3 (1.3 - 78)</td>
<td>3 (2 - 10)</td>
<td>1.3 (1.3 - 1.3)</td>
<td>9.3 (0.2 - 9.5)</td>
<td>4 (2.3 - 5.8)</td>
</tr>
<tr>
<td>Y</td>
<td>3.3 (0.3 - 28)</td>
<td>1.4 (3 - 25)</td>
<td>25 (7.5 - 2370)</td>
<td>6600 (14 - 2765)</td>
<td>25 (10 - 50)</td>
<td>9.5 (0.4 - 9.6)</td>
<td>120 (50 - 233)</td>
</tr>
<tr>
<td>Zr</td>
<td>0.7 (0.7 - 6)</td>
<td>0.6 (0.3 - 0.8)</td>
<td>0.15 (0.13 - 0.3)</td>
<td>0.15 (0.05 - 0.02)</td>
<td>0.53 (0.52 - 0.54)</td>
<td>0.25 (0.06 - 0.32)</td>
<td></td>
</tr>
</tbody>
</table>

n=Number of analyses. JdKL=Jahal deh Kot Lalu.

### Table 3: Mg and Si isotopic measurements of enstatites (in %)

<table>
<thead>
<tr>
<th>REE Anomalies</th>
<th>$\Delta^{26}$Mg ($\Delta_{\text{mean}}$)</th>
<th>$\Delta^{28}$Si ($\Delta_{\text{mean}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BUSTEE</td>
<td>- 4.89 ± 3.54</td>
<td>- 10.85 ± 5.06</td>
</tr>
<tr>
<td></td>
<td>- 4.80 ± 2.40</td>
<td>- 10.60 ± 2.68</td>
</tr>
<tr>
<td></td>
<td>- 5.97 ± 2.50</td>
<td>- 11.79 ± 3.84</td>
</tr>
<tr>
<td></td>
<td>- 5.46 ± 2.46</td>
<td>- 11.41 ± 4.00</td>
</tr>
<tr>
<td>QINGZHOU</td>
<td>- 5.94 ± 2.47</td>
<td>- 10.38 ± 3.46</td>
</tr>
<tr>
<td></td>
<td>- 5.28 ± 3.82</td>
<td>- 10.53 ± 4.62</td>
</tr>
<tr>
<td></td>
<td>- 5.02 ± 1.56</td>
<td>- 10.04 ± 3.26</td>
</tr>
<tr>
<td></td>
<td>- 5.72 ± 2.40</td>
<td>- 9.45 ± 4.80</td>
</tr>
<tr>
<td></td>
<td>- 6.50 ± 2.96</td>
<td>- 12.91 ± 4.92</td>
</tr>
<tr>
<td></td>
<td>- 4.24 ± 1.84</td>
<td>- 9.54 ± 1.70</td>
</tr>
<tr>
<td></td>
<td>- 5.94 ± 3.50</td>
<td>- 11.19 ± 4.46</td>
</tr>
<tr>
<td></td>
<td>- 5.81 ± 1.52</td>
<td>- 10.79 ± 3.22</td>
</tr>
<tr>
<td></td>
<td>- 4.54 ± 3.32</td>
<td>- 9.67 ± 3.48</td>
</tr>
<tr>
<td>MAC08136</td>
<td>- 5.04 ± 2.94</td>
<td>- 10.37 ± 2.82</td>
</tr>
<tr>
<td></td>
<td>- 6.17 ± 2.90</td>
<td>- 11.02 ± 5.56</td>
</tr>
<tr>
<td></td>
<td>- 4.67 ± 2.30</td>
<td>- 10.55 ± 3.68</td>
</tr>
<tr>
<td></td>
<td>- 5.72 ± 2.28</td>
<td>- 12.70 ± 2.60</td>
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<tr>
<td>FET90299</td>
<td>- 4.80 ± 1.80</td>
<td>- 9.74 ± 2.68</td>
</tr>
<tr>
<td></td>
<td>- 5.90 ± 1.72</td>
<td>- 10.86 ± 3.24</td>
</tr>
<tr>
<td></td>
<td>- 5.19 ± 2.26</td>
<td>- 9.71 ± 2.80</td>
</tr>
</tbody>
</table>

NO=No REE anomalies; UD=Undetermined REE pattern.
Al, Ca, and K if the REE budget of enstatite is controlled by albite inclusions. Therefore, we believe that REE abundances in enstatite are strongly controlled by the amount of trapped melt.

Assuming an initial melt with chondritic REE abundances, one can estimate its REE concentrations after a certain degree of fractional crystallization of enstatite. The REE partition coefficients for this mineral are calculated from the equation given by McKay et al. (1986) for Wo = 0.03. The D value for Eu is expected to be very low because of the extremely low oxygen fugacity in the enstatite chondrite environment. The results (for 50% enstatite crystallization) show that REE abundances in the melt are essentially unfractionated relative to initial REE abundances but enriched relative to chondritic values (Fig. 5a), as noted by Alexander (1994) who analyzed melt glasses from unequilibrated ordinary chondrites. The crystallized enstatite has very low REE abundances with a fractionated REE pattern similar to Pattern III. Similar results are obtained for different degrees of enstatite crystallization.

In Fig. 5b, we show that the REE pattern of pure enstatite can be modified to Pattern I or II by the inclusion of variable amounts of trapped melt, thus supporting the role of melt inclusions in our analyses.

A further indication that all three REE patterns (i.e., Pattern I, II, and III) are the result of REE partitioning during igneous processes is provided by the fact that all can be found in fine-grained, radiating, and barred chondrules, which have crystallized from liquids. Enstatite from the same chondrule can either have the same REE pattern (e.g., four analyses of enstatite from a barred blue enstatite chondrule of Qingzhen yielded REE Pattern II), or different REE patterns (e.g., REE Patterns II and III for two analyses of enstatite from a barred red enstatite chondrule fragment of MAC88136). The three types of REE patterns were also observed in enstatite (with both red and blue CL) from porphyritic chondrules and the matrix, suggesting that all enstatites may have more in common than previously assumed.

5.2. REE Anomalies in Enstatite

5.2.1. Cerium anomalies

Cerium anomalies have previously been observed in pyroxenes from Antarctic eucrites and shergottites (e.g., Floss and Crozaz, 1991; Harvey et al., 1993; Hsu and Crozaz, 1996) and, in this work, both positive and negative Ce anomalies are present in enstatite from Antarctic UECs (Fig. 2a). This is yet another example of REE mobilization caused by terrestrial weathering. In the terrestrial environment, Ce (III) is partially
oxidized to Ce (IV), which is less soluble than trivalent REEs. This results in the separation of Ce from the other REEs when these elements are leached from or deposited on pyroxene. The details of this process are complex; Floss and Crozaz (1991) and Harvey et al. (1993) reported that the nature (positive or negative) and size of Ce anomalies in a single pyroxene grain can vary on the scale of a few microns. In the case of UECs, mobilization of REEs is potentially more extensive due to the hygroscopic nature of olivine, the major REE carrier in these meteorites. Indeed, most olivine grains in Antarctic UECs have been weathered. We suspect that REE mobilization following olivine weathering may be responsible for the high REE abundances (up to 10 × C1) (Fig. 2a) in some analyses of Antarctic UEC enstatite.

5.2.2. Samarium, europium, and ytterbium anomalies

The negative Eu anomalies in most UEC enstatite are consistent with partitioning between low-Ca pyroxene and melt during igneous fractionation under reduced conditions. Some enstatites, however, have negative Sm and Yb anomalies, which are not usually associated with solid-liquid partitioning. In nature, REEs tend to occur in the trivalent state. In extreme cases (e.g., highly reducing conditions), Eu and Yb can be divalent because of the enhanced stability of the half-filled (Eu²⁺) and completely-filled (Yb³⁺) 4f subshell. The presence of Sm²⁺ in minerals has also been suggested by Goldschmidt (1954). During melt crystallization, divalent REEs will be more incompatible in pyroxene than trivalent REEs, because of their larger ionic radii. If some Eu, Yb, and Sm were in the divalent state under the highly reducing conditions that are believed to have prevailed during the formation of enstatite chondrites, it would be possible to account for the observed negative anomalies in enstatite. However, this interpretation does not take into account the observation that not all enstatite grains in UECs have negative Yb and Sm anomalies despite the likelihood that they were formed under similar conditions. Furthermore, enstatite grains from the equilibrated E chondrite Jäg deh Kot Lulu and the aubrites rarely have negative REE anomalies (except for Eu).

Thermodynamic calculations (Lodders and Fegley, 1993) indicate that, under highly reducing conditions, Yb, Eu, and, to a lesser extent, Sm, are relatively volatile compared to the other REEs. Therefore, the anomalies could be the products of processes that involved either condensation or evaporation in the early solar nebula.

The fact that evaporation not only enriches refractories, by preferentially vaporizing volatile constituents, but also increases the ratios of heavy to light isotopes in residues provided the rationale for magnesium and silicon isotopic measurements in enstatite. However, we showed here that Magnesium and silicon isotopic ratios in UEC enstatites are normal (i.e., unfractonated) whether REE depletions are present or not. We thus conclude that REE depletions in enstatites of UECs cannot be attributed to evaporative loss during chondrule formation. On the other hand, fractionation of the rare earths according to volatility, during gas condensation in the early solar nebula, is a likely mechanism for the production of these REE anomalies. Indeed, there is convincing evidence in the more oxidized carbonaceous chondrites, that some REE anomalies can only be attributed to condensation (e.g., Boynton, 1984) and, in addition, it is becoming clear from evaporation experiments that condensation is a much more efficient process than evaporation for generating the largest REE fractionations observed in many refractory inclusions in these meteorites (Davis and Hashimoto, 1995; Floss et al., 1997). Although no evaporation experiments have attempted to reproduce the reducing conditions experi-
enced by the enstatite chondrites, it is also likely that condensation played a more important role than evaporation in determining the compositions of the enstatite chondrule precursors.

5.3. The Formation of UEC Enstatite

5.3.1. Reevaluation of previous models

When Leitch and Smith (1982) observed red and blue CL enstatites (as well as orange and blue forsterites) in E chondrites, they suggested that two different processes, acting in different regions of the solar nebula, were responsible for the formation of these two types of pyroxene and olivine. The red pyroxene and the orange olivine would be the result of near-equilibrium crystallization in which the early reduced condensates continued to react with the ambient gas whereas the blue minerals, with their lower concentrations of many elements, would have been produced by fractional condensation after physical removal of the early condensates. A complex sequence of events, including mechanical aggregation of solid and liquid materials of both blue and red/orange types, were then required to produce the various textures observed. Leitch and Smith (1982) also argued that red and blue CL silicates in the same porphyritic chondrule could not have been produced by crystallization from a single liquid because of their distinct mineral chemistries. According to their model, some enstatite crystals in porphyritic chondrules are pre-existing nebular condensates which survived the melting events that formed chondrules; mechanical processes resulted in the subsequent incorporation of these relict crystals into chondrules.

However, our petrological observations do not support their conclusions. The presence of blue enstatite intermixed with thin orange CL forsterite lamellae in a barred chondrule from Qingzhen strongly suggests that these two minerals crystallized from the same liquid droplet. A similar observation was made in a barred chondrule fragment from MAC88136 consisting of red CL enstatite bars and Bluish enstatite lamellae. These observations are remarkably similar to results of dynamic crystallization experiments reported by Lofgren et al. (1991) who studied the CL characteristics of enstatite crystallized from a melt with average enstatite chondrule composition. They found...
that olivine is in peritectic relationship with enstatite and barred olivine can be produced at melt temperatures above the liquidus. The fastest cooling rates result in dendritic and/or barred enstatite. While predominantly red in CL color, the enstatite crystallized in these experiments is mixed with blue CL enstatite lamellae. The CL colors of these experimental products correlates with Mn and Cr abundances, as previously reported for naturally occurring red and blue CL enstatites (Leitch and Smith, 1982). Thus, petrological observations and synthetic experiments indicate that red, bluish red, and blue CL silicates can crystallize from the same liquid. Although the average concentrations of Mn and Cr in enstatite chondrites are too high to grow enstatite with a blue CL (Leitch and Smith, 1982; Lofgren and DeHart, 1992), local heterogeneities (i.e., low concentrations of Mn and Cr) in the parent melt may provide an environment suitable for the crystallization of this type of enstatite.

As we have shown here, REE patterns in red and blue enstatites are similar and they too can be explained by the simple crystallization of liquids (the chondrule melts). If red and blue enstatites or their precursors were formed by different processes, they should not be so much alike. In particular, we would expect to find some blue enstatite (supposedly formed by fractional condensation after the removal of high temperature condensates) enriched in the most volatile REEs (i.e., blue enstatite with positive Eu and/or Yb anomalies). In fact, no enstatite of any color was found to be enriched in either of these elements.

Thus, our petrological and trace element studies do not support the conclusions of Leitch and Smith (1982), but strongly suggest that associated red and blue CL enstatites formed by igneous crystallization. This is entirely consistent with the conclusions of McKinley et al. (1984) who first emphasized the role of fractionation during chondrule crystallization in establishing compositional differences between enstatite crystals.

Weisberg et al. (1994) also advocated nebular condensation for the formation of some blue enstatite, on the basis of the relative flat REE pattern found in this mineral. According to their model, the rims of blue CL enstatite on black and red CL enstatite fragments and chondrules are relics of condensed enstatite, as are the blue CL enstatite crystals embedded in red CL enstatite chondrules or included within red CL enstatite crystals. However, we found that the latter have igneous-fractionated REE patterns (e.g., Patterns II and III). And we have shown that the relatively flat REE pattern (i.e., Pattern I) is also compatible with crystal/melt partitioning of REEs in enstatite. In addition, we note that their conclusions were based on only four ion microprobe analyses of two thin (∼30 microns) blue enstatite rims around FeO-rich black pyroxene. Considering that the beam itself had a size of ∼30 microns and that, in the words of Weisberg et al. (1984), they had to eliminate much of the REE data obtained, we feel that their conclusions are not based on sufficiently strong evidence. In our opinion, there is no need to invoke independent modes of formation for red and blue CL enstatites in UECs. Instead, we feel that the suggestion by McKinley et al. (1984) and Losby et al. (1987), that blue enstatite rims formed by elemental diffusion during planetary metamorphism, is the most appealing.

5.3.2. Metamorphism and its effects

Metamorphism affects the CL characteristics of enstatite. With increasing petrological type, the abundance of blue enstatite increases while that of red enstatite decreases. Thus, most blue enstatite in equilibrated enstatite chondrites may have derived from red enstatite by metamorphic processes such as diffusion and recrystallization. Diffusion of minor elements out of red CL enstatite was invoked by McKinley et al. (1984) to account for the presence of blue enstatite in enstatite chondrites and our ion microprobe data for enstatite support their suggestion. Indeed, the average minor element concentrations in enstatites decrease from UECs to equilibrated enstatite chondrites (Table 2). Our observations are consistent with those of McKinley et al. (1984) who found that euhedral enstatite crystals have a bright blue CL color and much lower minor element concentrations than any other enstatite, and that the size and abundance of these crystals increase from UECs to equilibrated enstatite chondrites. Euhedral enstatites in the Jajh deh Kot Lalu equilibrated enstatite chondrite indeed have the lowest average Na (30 ppm) contents.

Leitch and Smith (1982) reported higher Na concentrations in blue than in red enstatite and took this as an argument against metamorphism. However, their Na data for red and blue enstatites show a great deal of overlap (see their Fig. 7) and the Na concentrations in bright blue enstatite reported by McKinley et al. (1984) are not higher than those in red enstatite. Similarly, our ion probe data in blue enstatites from Jajh deh Kot Lalu are also inconsistent with the results of Leitch and Smith (1982). Seven analyses in blue enstatites yield an average Na concentrations of 50 ppm, ranging from 16 to 175 ppm, well below the average Na concentration (∼370 ppm) reported by Leitch and Smith (1982) for red enstatite in EH4 chondrites.

In summary, we concur with McKinley et al. (1984) in acknowledging the role of metamorphism in modifying enstatite compositions.

5.3.3. The Puzzling complementarity of enstatite and oldhamite REE patterns

There is still another observation relevant to the formation of enstatite for which, unfortunately, there is no obvious explanation. The major REE carrier in enstatite meteorites is a minor and highly refractory mineral, oldhamite (CaS). In UEC oldhamite, the chondrite-normalized concentrations of each REE vary from ∼10 to ∼100 and positive Yb anomalies (accompanied or not by positive Eu anomalies and small positive Sm anomalies) are present in about half of the grains (Crozaz and Lundberg, 1995). Negative Yb anomalies were not observed in any of the sixty-four oldhamites analyzed by these authors, just as no positive Yb anomalies were detected in any of our 100 enstatite analyses. Thus, oldhamite can have an excess, and enstatite a deficit, of Yb, the most volatile REE under reducing conditions, which is the reason we refer to their REE patterns as complementary.

In the case of oldhamite, Crozaz and Lundberg (1995) argued that the precursors of the oldhamite we now observe in UECs formed in distinct reservoirs (as little as two), one in which nebular condensation proceeded to a temperature low enough to condense all the REEs and the other one in which
early condensation and isolation of oldhamite produced a reservoir depleted in the most refractory REEs from which more oldhamite formed. Mixing (in various proportions) of these late oldhamites with those from the first reservoir produced, after homogenization (i.e., melting), the continuum of spectra (from unfraccionated to severely depleted in Yb) observed in UEC oldhamites. Similarly, for enstatite, we can argue here that there were two types of precursors to the chondrule melts, one in which the REEs were all present in relative chondritic proportions and the other in which REEs were fractionated according to volatility. The processes proposed to form both minerals are reassuringly similar but how can enstatite, apparently the less refractory of the two minerals, be commonly depleted in volatiles and oldhamite be enriched? Although a connection must exist between these two facts, we fail to see what it is.

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REFERENCES


Hsu W. and Crozaz G. (1994b) REE concentrations and anomalies in the enstatite of unequilibrated enstatite chondrites. Meteoritics 29, 475 (abstr.).


