Geochemical and petrographic studies of oldhamite, diopside, and roedderite in enstatite meteorites

WEIBIAO HSU*

Department of Earth and Planetary Sciences, McDonnell Center for the Space Sciences, Washington University, St. Louis, Missouri 63130, USA
*Present address: Division of Geological and Planetary Sciences, Mail Code 170-25, California Institute of Technology, Pasadena, California 91125, USA
Author's e-mail address: whsu@gps.caltech.edu

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(Part of a series of papers dedicated to the memory of Paul Barringer)

Abstract—In Qingzhen (EH3), oldhamite contains numerous types of inclusions and intergrows with other phases; but in equilibrated enstatite chondrites and aubrites, it usually occurs as individual grains. I suggest that oldhamite in unequilibrated enstatite chondrites (UECs) crystallized from a melt, probably during chondrule formation. Subsequent thermal metamorphism on the parent bodies further modified the oldhamite occurrences in enstatite chondrites. This suggestion is consistent with the results of melting experiments on UECs and aubrites and with the volatile element enrichments in this mineral.

I analyzed minor and trace element abundances in diopside from two aubrites. These data and petrographic observations suggest that diopside formed by igneous crystallization.

I report the first known occurrence of roedderite in an aubrite and its major, minor, and trace element concentrations. This mineral is rich in alkalis but is depleted in siderophile and refractory lithophile elements.

A negative Sm anomaly was noted in olivine from equilibrated enstatite chondrites and aubrites.

INTRODUCTION

The enstatite meteorites, which include the enstatite chondrites (EH and EL groups), the enstatite achondrites (aubrites) and some clasts in the polymict brecciated Kaidun meteorite, are unusual extra-terrestrial materials that contain a group of reduced minerals (Keil, 1989). The major phase is enstatite (MgSiO₃), which is essentially Fe-free. Minor and trace phases present in these meteorites include metallic Fe,Ni and a variety of rare sulfides and silicates, some of which are not known to terrestrial rocks or even other meteorites (Keil, 1968; Watters and Prinz, 1979).

Much information about enstatite meteorites has been gained over the past decades. It is now clear that these meteorites formed in a highly reducing environment distinctly different from those of other meteorites, indicating heterogeneity in the early solar nebula. Keil (1989) summarized their properties, relationships, and the nature of their parent bodies. In this paper, I report on the occurrences and compositions of some of the unusual minerals found in these meteorites. Several of these minerals have controversial origins. For example, attention has focused recently on whether oldhamite (CaS) in these meteorites formed as a nebular condensate (Larimer and Bartholomay, 1979; Larimer and Gaanapathy, 1987; Lodders and Fegley, 1993) or whether it has an igneous origin (Dickinson et al., 1991; Wheelock et al., 1994; Crozzaz and Lundberg, 1995; Dickinson and McCoy, 1996, 1997). In this work, I present mineralogical and petrographic studies of this mineral and seek to gain additional constraints on its origin.

It has been suggested that diopside [(Ca,Mg,Fe)SiO₃] in aubrites formed by oxidation of oldhamite (Fogle et al., 1988). If this were the case, one would expect that this mineral would inherit oldhamite rare-earth-element (REE) patterns. But it does not. Floss and Crozzaz (1993) found that aubritic diopside has different REE patterns, ranging from light-rare-earth-element (LREE) depleted to relatively flat. The LREE-depleted pattern with a negative Eu anomaly is consistent with REE partitioning between diopside and a melt. However, its relatively flat REE pattern is difficult to explain in terms of igneous fractionation. Coupled with petrographic observation, I measured minor and trace element concentrations of diopside in two aubrites, Bustee and Mayo Belwa, with the hope to shed new light on the formation of aubritic diopside.

Roedderite [(Na,K)₂[(Mg,Fe)₆(Si,Al)₅]O₂O₆], a rare alkaline silicate, was found to be present in unequilibrated EH chondrites (Fuchs et al., 1966; Kimura and El Goresy, 1988). In this study, I report the first known occurrence of roedderite in the Bustee aubrite. I compare its major, minor, and trace element abundances with those of roedderite in the EH chondrites.

EXPERIMENTAL METHODS

All samples studied are one inch diameter polished thin sections. They include the enstatite chondrites: Qingzhen 2,1, WU#1 (EH3); Yamato 691,79-3 (EH3); Indarch USNM4382-2, 551a.5a&b (EH4); Abeb UNM19a, UNM541, USNM2096-2 (EH4,5); St. Mark's USNM483-2 (EH5); MAC 88136,11 (EL3); EET 90299,7 (EL3); and Jahl deh Kot Lalu USNM1260-1 (EL6); and the two aubrites: Bustee BM2100 and Mayo Belwa BM1976,M,11.

The thin sections were studied first with an ELM-3R NUCLIDE luminoscope that also has transmitted light capability. An electron beam of ~0.5 mA at ~12 keV acceleration was focused to the microscope viewing area at 100x magnification. Oldhamite displays the orange color of cathodoluminescence under electron bombardment (Keil, 1968). Selected areas of the samples were photographed with a standard 35 mm camera using Kodak Ektrachrome ASA400 color film and an exposure time of 15 to 30 s. The localized oldhamite grains were studied further with an optical microscope and a JSM-840 A scanning electron microscope (SEM), equipped with an energy dispersive x-ray (EDX) spectrometer.

Major element compositions were obtained with an automated electron microprobe (ARL-SEMQ 9) at the Smithsonian Institution, Washington D.C., using the correction procedure of Bence and Albee (1968). The operating conditions were an accelerating voltage of 15
KeV and a beam current of 150 nA. Both natural and synthetic mineral standards were used. The approximate detection limits (3σ, based on counting statistics only) for the electron microprobe are SiO₂, 0.07 wt%; Al₂O₃, 0.06 wt%; FeO, 0.04 wt%; MgO, 0.03 wt%; CaO, 0.02 wt%; K₂O, 0.02 wt%; Na₂O, 0.02 wt%; MnO, 0.03 wt%; TiO₂, 0.03 wt%.

Rare earth elements and other selected trace- and minor element concentrations were determined with the Washington University ion microprobe (CAMECA IMS-3f), according to the methods described by Zimmer and Croazz (1986). The data were reduced with a modified analysis program to eliminate simple molecular interferences in the mass ranges of K-Ca-Sc-Ti, Rb-Sr-Y-Zr, and Ba-REEs (Hsu, 1995). The errors reported are 1σ, based on counting statistics only.

MINERALOGY AND PETROGRAPHY

Oldhamite

Oldhamite is typically a minor mineral phase in enstatite meteorites, except in the dark inclusions of Abeek (Rubin and Keil, 1983) and in the oldhamite-dominated lithic clasts of the Norton County aubrite (Wheelock et al., 1994). In unequilibrated enstatite chondrites (UECs), the oldhamite grains are usually small (rarely up to 200 μm) and are irregular in shape. El Goresy et al. (1988) reported that oldhamite in UECs usually occurs as individual grains in the matrix, as inclusions in chondrules, and also as multiphase metal-sulfide assemblages. My observations are generally in agreement with theirs. I found no systematic difference in the size of oldhamite grains as well as in their mode of occurrences between chondrules and matrix. In addition, this mineral sometimes contains inclusions or is intergrown with other phases.

The best examples are present in the UEC, Qingzhen, which is an observed fall. Most oldhamite inclusions or intergrow with other phases, such as roederite (Fig. 1a,b,c), enstatite (Fig. 1a,f), albite (Fig. 1d), silica (Fig. 1c,d,f), schreibersite (Fig. 1a,b), melt glass (Fig. 1e), and a sulfur vein (Fig. 1h). Figure 1c shows that an oldhamite inclusion in an enstatite grain of Qingzhen contains inclusions of roederite and silica. The textures of the inclusions within oldhamite are typically igneous but vary with the mineral phases. Roederite inclusions are usually euhedral; whereas enstatite inclusions vary from euhedral to irregular; schreibersite often occurs as spherules. The oldhamite grains shown in Fig. 1 were found in matrix. However, oldhamite grains were also found in the Qingzhen chondrules, and they are petrographically similar to those in matrix. For example, a porphyritic pyroxene chondrule of Qingzhen has a round oldhamite grain (~1 μm in diameter). It contains numerous schreibersite spherules (~5 μm) and a sulfur vein. In addition, this grain is partially intergrown with troilite (see Fig. 3.19 of Hsu, 1995). Oldhamite is highly hygroscopic. Most grains have weathered cracks or rims composed of fine-grained oldhamite (Fig. 1e). The other three type 3 UECs studied are Antarctic meteorites in which most oldhamite grains have been weathered. In MAC 88136, only a few oldhamite grains in Fe-metal spherules have been well preserved. They do not contain any inclusions and are not intergrown with other phases. Non-Antarctic EL3 chondrites have not been observed so far, but it would be interesting to see whether oldhamite grains have similar petrographic occurrences in other unweathered non-Antarctic EH3 chondrites. Further studies are clearly needed.

No inclusions were found in oldhamite grains of Indarch and the equilibrated enstatite chondrites Abeek, St. Mark's, and Jajh deh Kot Lal. Oldhamite in the Bustee and Mayo Belwa aubrites usually occurs as individual grains in the matrix; only one grain in Mayo Belwa has a melt glass inclusion (Fig. 1g).

Oldhamite also intergrows with other phases. In Qingzhen, an oldhamite grain is intruded by a troilite grain (Fig. 1h). They are in intimate contact. An oldhamite grain in Indarch clearly shows intergrowth with silica despite weathering effects (Fig. 1i). Oldhamite also intergrows with enstatite (Fig. 1j).

Thus, it appears that oldhamite textures and mineral associations vary systematically among enstatite chondrites of different petrological types. While oldhamite in Qingzhen (EH3) contains various inclusions, intergrowths with sulfides and silicates, and occurs as individual grains in chondrules and matrix, oldhamite from the more equilibrated Indarch and Abeek enstatite chondrites does not contain any inclusions but rather occurs primarily as individual grains or intergrowths with other phases. Oldhamite from the still more equilibrated enstatite chondrites St. Mark's and Jajh deh Kot Lal typically occurs as individual grains.

Electron microprobe analyses of oldhamite are given in Table 1. The measurements of oldhamite in Jajh deh Kot Lal consistently give low totals (~95 wt%). This is most likely due to rapid surface oxidation of oldhamite as I observed that this mineral is partly weathered in the thin section studied. Besides the major elements Ca and S, oldhamite usually contains minor amounts of Fe (~1 wt%), Mg (<1.5 wt%), and Mn (<1.6 wt%). Oldhamite from EH chondrites has lower Mn but higher Mg contents than that from EL chondrites, which is consistent with the results of Keil (1968). It is noteworthy that oldhamite in Bustee is essentially free of Fe (~0.02 wt%). Most oldhamite grains studied are quite homogeneous. However, Fe content varies considerably in oldhamite grains of Qingzhen (by a factor of 13), and some grains show chemical zoning (Fig. 2); the Fe content increases towards the rim, but Mg and Mn are relatively invariant. El Goresy et al. (1988) also noted large variation of Fe (more than a factor of 20) between oldhamite grains in Qingzhen. It is not clear whether Fe zoning in oldhamite is of primary origin or due to secondary alteration.

| Table 1. Averages and ranges of oldhamite compositions (wt%). |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                             | Qingzhen                   | MAC 88136                   | Indarch                     | Abeek                       |
| Fe                          | 0.32 (0.07–0.95)            | 0.59 (0.41–1.07)             | 0.62 (0.22–1.03)             | 0.74 (0.67–0.77)             |
| Mg                          | 0.51 (0.36–0.71)            | 0.10 (0.06–0.17)             | 1.08 (0.55–1.30)             | 1.40 (1.32–1.53)             |
| Ca                          | 55.5 (53.6–56.3)            | 55.4 (54.6–56.4)             | 54.7 (54.0–55.7)             | 52.8 (52.4–53.2)             |
| Ti                          | 0.01 (0.00–0.06)            | 0.01 (0.00–0.05)             | 0.02 (0.01–0.05)             | 0.02 (0.01–0.04)             |
| Cr                          | 0.03 (0.00–0.08)            | 0.03 (0.01–0.08)             | 0.04 (0.01–0.08)             | 0.06 (0.05–0.07)             |
| Mn                          | 0.15 (0.07–0.24)            | 0.47 (0.37–0.59)             | 0.20 (0.13–0.29)             | 0.33 (0.30–0.36)             |
| S                            | 43.3 (41.8–44.2)            | 42.5 (41.8–43.0)             | 43.6 (42.9–44.5)             | 43.1 (42.5–43.4)             |
| Zn                          | 0.10 (0.00–0.25)            | 0.08 (0.00–0.18)             | 0.10 (0.00–0.27)             | 0.05 (0.00–0.09)             |
| Total                       | 99.95                      | 99.24                       | 100.34                      | 98.52                       |
|                             |                             |                             |                             | 94.97                       |
|                             |                             |                             |                             | 99.35                       |

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Fig. 1. Oldhamite mineral associations in enstatite meteorites. All photos are backscattered electron images. (a) Roedderite (Roe), enstatite (En), and schreibersite (Sc) inclusions in an oldhamite (Old) grain of Qingzhen; (b) schreibersite spherules and a euhedral roedderite crystal in an oldhamite of Qingzhen; (c) an oldhamite inclusion in an enstatite grain of Qingzhen. The oldhamite itself contains roedderite and silica (Si) inclusions; (d) albite (Ab) and silica inclusions in an oldhamite grain of Qingzhen; (e) oldhamite of Qingzhen contains a melt (Mt) inclusion. This oldhamite grain is surrounded by a fine-grained oldhamite rim (FGOR); (f) oldhamite of Qingzhen contains enstatite and silica inclusions and is intergrown with another enstatite grain; (g) An oldhamite grain of Mayo Belwa has a melt inclusion; (h) Oldhamite intergrows with troilite (Tr) in Qingzhen. A sulfur (S) vein is present in the oldhamite grain; (i) oldhamite intergrows with silica in Indarch; (j) oldhamite intergrows with enstatite in Abee. Figure 1 is continued on the next page.
Diopside

Diopside occurs as a trace phase in enstatite chondrites (Grossman et al., 1985) but can be more abundant in aubrites (0.2–8.1%; Watters and Prinz, 1979). Some lithologies in the Norton County aubrite contain up to 20% of this mineral (Okada et al., 1988). Diopside occurs as large (1 mm) individual grains in Bustee and Mayo Belwa. In Bustee, this mineral is well crystallized and exhibits exsolution lamellae of enstatite (Fig. 3a); whereas in Mayo Belwa, it does not have any exsolution lamellae (Fig. 3b) but contains numerous micrometer-sized inclusions of enstatite, albite, and melt glasses (Fig. 3c). Diopside (En$_{53.9}$Wo$_{46.1}$) in Bustee is essentially Fe-free (FeO < 0.02 wt%), and that in Mayo Belwa has a composition of En$_{57.5}$Wo$_{42.4}$Fe$_{0.1}$ (Watters and Prinz, 1979).

Roedderite

Euhedral crystals of roedderite were found enclosed in olivine grains of Qingzhen (Fig. 1a,b). In some cases, roedderite intergrows with Fe,Ni metal and sphalerite. This mineral also occurs as individual grains in the matrix of UECs. One characteristic feature of roedderite in UECs is that it usually occurs in the form of euhedral crystals.
Roederite has not been observed previously in EL chondrites and aubrites. In this study, I report the first occurrence of a roederite grain in the Bustee aubrite (Fig. 4). It appears as an irregularly shaped grain, ~500 × 200 μm in dimension, and is surrounded by an olivine grain and enstatite grains.

I analyzed roederite in Qingzhen, Indarch, and Bustee (Table 2). This mineral is rich in Mg and the alkalis Na and K. Aluminum and Fe are minor components. The Ca content of roederite in Qingzhen reported here is considerably higher than previously reported (Fuchs et al., 1966; Krot and Wasson, 1994). This is probably due to interference from oldhamite in my analyses as I measured only roederite inclusions in oldhamite. The Bustee roederite has an atomic Na/(Na + K) ratio of 0.50, which is similar to roederite from Qingzhen (0.52) and Indarch (0.62). However, roederite in Bustee has an extremely low Fe content (FeO ~ 0.04 wt%), just as oldhamite and diopside from this meteorite do.

TRACE ELEMENT GEOCHEMISTRY

Diopside

Rare earth elements were measured in three diopside grains from Bustee and six from Mayo Belwa (Table 3). The abundances and patterns vary considerably from analysis to analysis, even in the same grain. Light-rare-earth-element abundances range from 0.1 to 5 × C1, and heavy-rare-earth-element (HREE) abundances from 0.5 to 10 × C1. In general, two REE patterns are observed: one LREE-depleted pattern with a negative Eu anomaly and the other with an enrichment of the REEs from light to heavy that may or may not

FIG. 3. Backscattered electron images of diopside in (a) Bustee and (b) in Mayo Belwa. (c) A closeup view of the diopside grain in (b) which contains inclusions of albite (Ab), enstatite (En), and melt glasses (Mt).

FIG. 4. Backscattered electron image of a roederite grain in Bustee. This grain is in contact with enstatite (En) and forsterite (Ol).
TABLE 2  Averages and ranges of roederite compositions (wt%).

<table>
<thead>
<tr>
<th></th>
<th>Qingzhen</th>
<th>Indarch</th>
<th>Bustee</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>71.5 (66.1–73.3)</td>
<td>72.2 (70.6–73.8)</td>
<td>71.9 ± 0.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.49 (0.31–0.86)</td>
<td>0.48 (0.18–3.59)</td>
<td>0.90 ± 0.12</td>
</tr>
<tr>
<td>FeO</td>
<td>0.51 (0.20–0.91)</td>
<td>0.97 (0.37–2.72)</td>
<td>0.04 ± 0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>19.4 (17.7–20.3)</td>
<td>19.2 (15.7–20.3)</td>
<td>19.1 ± 0.2</td>
</tr>
<tr>
<td>CaO</td>
<td>1.08 (0.27–4.68)</td>
<td>0.05 (0.00–0.41)</td>
<td>0.06 ± 0.06</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.29 (3.80–4.60)</td>
<td>3.44 (2.87–3.73)</td>
<td>4.78 ± 0.12</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01 (0.00–0.05)</td>
<td>0.01 (0.00–0.04)</td>
<td>0.03 ± 0.02</td>
</tr>
<tr>
<td>MnO</td>
<td>0.01 (0.00–0.05)</td>
<td>0.01 (0.00–0.06)</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.05 (2.43–3.63)</td>
<td>3.71 (2.93–4.46)</td>
<td>3.03 ± 0.11</td>
</tr>
<tr>
<td>Totals</td>
<td>100.34</td>
<td>100.07</td>
<td>99.81 ± 0.52</td>
</tr>
</tbody>
</table>

The errors quoted are 1σ standard deviation between individual measurements.

have a negative Eu anomaly (Fig. 5). This is consistent with the results of Floss and Croaz (1993). In addition, I found that this mineral in the two aubrites occasionally has a positive Eu anomaly and an upturn on the LREE side (Fig. 5).

For comparison, data for Na, Al, and K are also listed in Table 3 along with the REE abundances. The diopside of Mayo Belwa gen-

![REE/CI Chondrites](image1)

**Fig. 5.** Representative REE patterns observed in diopside from (a) Bustee and (b) Mayo Belwa.

![REE/CI Chondrites](image2)

**Table 3.** Sodium, Al, K, and REE concentrations (ppm) in diopside of aubrites.

<table>
<thead>
<tr>
<th>Grain</th>
<th>Bustee</th>
<th>Mayo Belwa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>51.5 ± 0.2</td>
<td>49.9 ± 0.2</td>
</tr>
<tr>
<td>K</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>REE</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Errors quoted are 1σ standard deviation from counting statistics only.*
eral has higher Na, Al, and K contents than that of Bustee. While there are differences in minor element abundances in diopside of Bustee and Mayo Belwa, their REE abundances and patterns show the same range of variations.

Roedderite

Two roedderite grains were studied, one from Indarch and the other from Bustee. Roedderite grains in UECs are usually very small (<20 μm) and a small primary ion beam (1 nA) was used to measure the Indarch roedderite. Results are reported in Table 4. The minor and trace elemental abundances of the two grains are very similar. Both are enriched in the alkali elements (5–100 × C1) and depleted in the siderophiles (~0.1 × C1) and refractory lithophiles (~0.1 × C1). The REE concentrations of the Indarch roedderite are below detection. The C1-normalized REE abundances of the Bustee roedderite decrease steadily from the LREEs (0.1 × C1) to the HREEs (0.02 × C1); a negative Eu anomaly is present (Fig. 6). It is not clear why the Lu abundance is exceptionally high (0.5 × C1).

Albite

Albite is a trace mineral phase in the UECs and its grain size is so small (micrometer-sized) that ion probe measurements are not possible. However, the size and abundance of albite in enstatite chondrites increase with petrological type and, thus, it was possible to make measurements in albite from equilibrated enstatite chondrites and subrites. Rare-earth-element abundances are very low in this mineral (Table 5) and, as expected, its REE pattern is LREE-enriched and has a pronounced positive Eu anomaly (Fig. 7). In addition, some albites show a negative Sm anomaly. MacPherson et al. (1996) also reported large negative Sm anomalies in plagioclase of the ungrouped E3 chondrite LEW 87234. Negative Sm and Yb anomalies were previously found in enstatite of UECs (Hsu and Crozaz, 1994). These anomalies may be due to the highly reducing conditions under which enstatite chondrites formed. 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 (Yb2+) 4f sub-shell. The presence of Sm2+ in minerals has been suggested also by Goldschmidt (1954). During melt crystallization, divalent REEs will be more incompatible in crystals, because of their larger ionic radii, than trivalent REEs.

![REE/C1 Chondrites](image)

**Fig. 6.** Rare-earth-element pattern in the Bustee roedderite. The C1-normalized abundances decrease steadily from the LREEs to HREEs, indicating igneous fractionation. Note that the Lu abundance is exceptionally high.

<table>
<thead>
<tr>
<th>REE/C1 Chondrites</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
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<tbody>
<tr>
<td>1.00</td>
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<td>0.01</td>
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</tbody>
</table>

**Table 4.** Trace-element abundances in roedderite from Indarch and Bustee.

For Bustee, the average of two measurements is reported.
TABLE 5 Rare-earth-element concentrations (ppm) in albite of equilibrated enstatite chondrites and the auhrite Bustee.

<table>
<thead>
<tr>
<th></th>
<th>Abee</th>
<th>Jah dKot LaLu</th>
<th>Bustee</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.091 ± 0.024</td>
<td>0.008 ± 0.002</td>
<td>0.021 ± 0.003</td>
</tr>
<tr>
<td>Ce</td>
<td>0.316 ± 0.040</td>
<td>0.020 ± 0.004</td>
<td>0.063 ± 0.006</td>
</tr>
<tr>
<td>Pr</td>
<td>0.025 ± 0.006</td>
<td>0.002 ± 0.001</td>
<td>0.007 ± 0.001</td>
</tr>
<tr>
<td>Nd</td>
<td>0.107 ± 0.012</td>
<td>0.011 ± 0.002</td>
<td>0.038 ± 0.004</td>
</tr>
<tr>
<td>Sm</td>
<td>0.005 ± 0.005</td>
<td>n.d.</td>
<td>0.013 ± 0.004</td>
</tr>
<tr>
<td>Eu</td>
<td>0.088 ± 0.015</td>
<td>0.059 ± 0.008</td>
<td>0.023 ± 0.006</td>
</tr>
<tr>
<td>Gd</td>
<td>0.017 ± 0.009</td>
<td>0.003 ± 0.002</td>
<td>0.010 ± 0.004</td>
</tr>
<tr>
<td>Tb</td>
<td>0.019 ± 0.007</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Dy</td>
<td>0.008 ± 0.004</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Er</td>
<td>0.019 ± 0.007</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td></td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.001 ± 0.000</td>
</tr>
</tbody>
</table>

n. d. = not detected. Each measurement was made in different albitic grains.

DISCUSSION

Oldhamite—Nebular Condensate or Igneous Product?

Oldhamite has been shown to be the major REE carrier in enstatite meteorites (Larimer and Ganapathy, 1987; Lundberg et al., 1989, 1991; Floss et al., 1990; Floss and Crozaz, 1993; Crozaz and Lundberg, 1995). In a study of oldhamite of UECs, Lundberg et al. (1991) observed five distinct REE patterns with both positive and negative Eu anomalies and positive Yb anomalies. Besides the highly refractory trace elements (e.g., REEs), oldhamite is also enriched in chalcophile and lithophile elements, such as Zn, Se, Sb, and Cs, which are generally considered to be volatile (Larimer and Ganapathy, 1987; Chen et al., 1989, 1993; Crozaz and Lundberg, 1995). Larimer and Ganapathy (1987) reported that oldhamite has high C1-normalized concentrations of Sb (~20 to 100 × C1), Cs (~5 to 50 × C1) and Zn (~2 to 10 × C1). Chen et al. (1993) found that the enrichments of these trace elements decrease with increasing petrologic type.

Oldhamite was suggested as an interstellar dust to have formed in stars with high C/O ratios (Gilman, 1969). If this circumstellar grain was injected into the solar nebula, it could survive the early solar nebular events and be preserved in primitive chondritic meteorites because pure oldhamite is a very refractory mineral. Lundberg et al. (1994) made in situ isotopic measurements of oldhamite from UECs and found that this mineral has normal S isotopic compositions and suggestive δ^{18}Ca anomalies. If these δ^{18}Ca anomalies are real, they are less common and much smaller (δ^{18}Ca < 7‰) than those found in hibonite (~56‰ to 104‰, Ireland, 1990). Therefore, it is unlikely that oldhamite in UECs has an interstellar origin.

Oldhamite in UECs has been thought to have condensed from a solar gas with an enhanced C/O ratio (>1) (Larimer and Bartholomay, 1979; Lodders and Fegley, 1993). Basically, two arguments seem to suggest that this mineral has a nebular origin. (1) The pure CaS has a melting point of 2450–2525 °C (Vogel and Heumann, 1941). It is probably that the UEC system never reached this temperature; therefore, oldhamite could not be a product of igneous crystallization. (2) Thermodynamic calculations under highly reducing conditions show that oldhamite is REE-enriched and that the predicted REE patterns are similar to those observed (Larimer et al., 1984; Lodders and Fegley, 1993). As for the enrichments of what are generally considered as volatile elements, Larimer and Ganapathy (1987) and Chen et al. (1993) argued that these enrichments were due to the interaction between oldhamite and the nebular gas at low temperature (800–500 K). On the other hand, Crozaz and Lundberg (1995) pointed out that oldhamite becomes unstable and reacts with C-rich nebular gas to form diopside or anorthite at ~100 K below that required for full condensation of the REEs (1200 K at 10^{-3} bar total pressure) (Lodders and Fegley, 1993). One reviewer of this paper (J. Larimer) pointed out that oldhamite could remain stable at all temperatures below its condensation temperature if the enhanced C/O ratio was raised by removing O or the gas-water reaction (H_2 + CO = CH_4 + H_2O) is significantly slow. It thus seems that nebular condensation could generally account for the chemistry and formation of oldhamite in UECs.

In a comprehensive study of REE abundances in oldhamite of UECs, Crozaz and Lundberg (1995) made a detailed comparison between observed and predicted REE patterns in this mineral. They found that while the condensation calculation explains the first order effects of differential volatility (i.e., Yb and Eu anomalies), it is difficult to account for the decrease of C1-normalized abundances from La to Pr in some oldhamite grains. They suggested that oldhamite in UECs may have formed from melts whose trace element compositions were determined by high-temperature transient events in the solar nebula. My petrographic observations of oldhamite in UECs are basically in agreement with this suggestion. Below I will show that nebular origin for oldhamite is not a necessity and that igneous crystallization is an equally plausible scenario for oldhamite formation.

Although it is not clear what a condensate should look like, the inclusions I observed within oldhamite grains are not consistent with the predictions from equilibrium condensation. For example, some
inclusions, such as roedderite, are low-temperature minerals. I considered whether such inclusions migrated into vesicles of early condensed olivine grains through cracks that were later sealed by metamorphism. However, it is difficult to explain the euhedral crystals and the absence of inclusions in olivine grains from equilibrated enstatite chondrites. Instead of euhedral crystals, irregular crystals are expected if material migrated into preexisting vesicles within olivine grains. In addition, various types of inclusions are present in olivine from UECs (e.g., Qingzhen); whereas in equilibrated enstatite chondrites, olivine is devoid of any inclusions. This suggests that the inclusions within olivine grains are not due to metamorphism. The diversity of olivine occurrences in UECs also poses a problem for the condensation model. Oldhamite intergrows with various mineral phases and the contacts between oldhamite and the other minerals are typical of igneous textures.

Oldhamite grains in the Norton County aureole contain abundant, droplet-like Mn-Fe-Mg-Cr-Na sulfide inclusions. Wheelock et al. (1994) argued that these phases formed as immiscible sulfides in oldhamite during its crystallization from a melt. In the case of the UECs, I cannot make the same argument because most inclusions are silicates or phosphate.

The textural relationships between oldhamite and other phases (such as schreibersite and roedderite) suggest that oldhamite is not the first phase to have formed during crystallization. It is noted that the pure oldhamite has a melting temperature of 2798 K (Vogel and Heumann, 1941) that is much higher than those of the silicate inclusions (e.g., 1440 K for roedderite; Roedder, 1951). However, oldhamite in UECs contains up to 2 wt% minor elements and is commonly in contact with other sulfides and metal, which probably depress its melting temperature. A CaS·FeS eutectic of 1120°C was reported (Vogel and Heumann, 1941). Indeed, during a melting experiment, Dickinson and McCoy (1996) observed that oldhamite crystallized from an olivine melt at temperatures down to 1200°C and that silicate crystallized before oldhamite. Melting experiments on UECs (e.g., Indarch) also showed that oldhamite could melt completely at temperatures 1200–1400°C (Fogel et al., 1996; McCoy et al., 1997). Therefore, the petrologic observations and experimental results suggest that oldhamite in UECs could have formed by igneous crystallization.

Oldhamite of UECs is enriched in the REEs (10–100 × CI) with distinct patterns, ranging from relatively flat with a negative Eu anomaly to LREE-enriched with positive Eu and Yb anomalies (Lundberg et al., 1991). The experimentally determined REE partition coefficients (DCaS/silicate melt) for oldhamite (<25) are much lower than inferred Ds (100–1000) in natural systems (Dickinson et al., 1991; Dickinson and McCoy, 1996). It seems that REE abundances of oldhamite cannot be determined solely by partitioning between crystallizing oldhamite and a melt. Dickinson and McCoy (1996) also found that the Ds vary with a number of parameters, such as oldhamite composition, temperature, and subsolidus annealing. In an attempt to explain the various REE patterns observed in aubrite oldhamite, Dickinson and McCoy (1997) suggest that this mineral may have had a complex igneous origin and that its REE abundances may be affected by a variety of processes, including partial melting, melt removal, fractional crystallization, and sub-solidus annealing and exsolution. In the case of UECs, it is somewhat different from enstatite chondrites did not experience large degrees of partial melting. At this point, it is not clear why oldhamite of UECs is enriched in REEs with distinct patterns if this mineral crystallized from a melt. It is possible, as suggested by Crozaz and Lundberg (1995), that the precursors of the melts had complex histories in the solar nebula and their trace element compositions were determined by high-temperature transient events.

**Origin of Diopside in Aubrites**

In an attempt to link aubrites to enstatite chondrites, Vogel et al. (1988) suggested that diopside of aubrites formed by oxidation of olivine according to the reaction:

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CaS + 3MgSiO_3 + 1/2O_2 = CaMgSi_2O_6 + Mg_2SiO_4 + 1/2S_2
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They argued that both diopside and forsterite occur in aubrites but not in enstatite chondrites. Keil (1989) pointed out two major objections. First, there is insufficient oldhamite in enstatite chondrites to form the abundant diopside observed in aubrites. In addition, aubrites contain nearly as much oldhamite as enstatite chondrites. He also noted that the O fugacity of the enstatite meteorite environment is too low for the reaction to proceed.

Floss and Crozaz (1993) found that diopside in aubrites (Bustee and Khor Temiki) display one of two REE patterns: one is LREE-depleted with a negative Eu anomaly and the other is relatively flat with no anomaly. The same results were obtained for the Mayo Belwa and Bustee aubrites in this work (Fig. 5). The LREE-depleted pattern is consistent with what we know about REE partitioning between diopside and a melt. However, the relatively flat pattern is not easily understood.

Diopside in Mayo Belwa contains inclusions of enstatite, albite, and melt glasses (Fig. 3c). These inclusions are very fine (micrometer-sized) and ubiquitous. The typical ion beam spots are ~30 μm. It is almost certain that all REE analyses of the Mayo Belwa diopside are the combination results of this mineral and its trapped inclusions. This is reflected by the data in Table 3 that diopside of Mayo Belwa has higher minor element (Na, K, and Al) concentrations than in Bustee. Enstatite has a HREE-enriched pattern with a negative Eu anomaly (Hsu and Crozaz, 1994) and albite is LREE-enriched with a positive Eu anomaly (Fig. 7). Both minerals have low REE concentrations. Melt glass inclusions are too fine (micrometer-sized) to make direct ion probe measurement. An ion probe study of albite glasses from IIE iron showed that these glasses have various REE patterns with highly variable abundances, ranging from LREE-enriched to HREE-enriched with or without a positive Eu anomaly and the abundances varying from 0.1 to 10 × CI (Hsu et al., 1997).

If aubrite diopside originally crystallized from a melt and trapped various amounts of inclusions, the overall REE pattern of diopside may vary from grain to grain. If diopside contains inclusions that are essentially free of REEs, it will have the LREE-depleted pattern with a negative Eu anomaly when crystallizing from a melt. The REE pattern changes when diopside contains inclusions with variable REE contents. The Eu depletion and the slope of REE pattern of diopside will decrease if the trapped inclusions have a LREE-enriched pattern with a positive Eu anomaly (Fig. 5). In this scenario, the relatively flat REE pattern observed in some aubritic diopsides is also compatible with REE partitioning between diopside and a melt.

In Bustee, the story is quite different. Diopside does not contain inclusions except for enstatite lamellae. The minor element concentrations (e.g., Na, Al, K) are much lower in the Bustee diopside than in Mayo Belwa (Table 3). However, diopsides in Bustee also exhibit different REE patterns (Floss, 1991, and this work). I suggest that, because the REEs have much lower diffusion rates than minor elements Na, Al, and K, after crystallization from a melt, minor elements migrated out of the Bustee diopside; whereas the REEs re-
mained during cooling. Petrographic observation seems to support this suggestion. The mineral crystals of enstatite and diopside in Bustee are well crystallized and rarely have any inclusions.

The Occurrence of Roederite in Enstatite Meteorites

Roederite is a rare silicate and belongs to the milarite group of minerals (roederite, merrihueite, osamulite, and yagiiite), which have hexagonal crystal structures (Khan et al., 1971). Roederite and merrihueite form a complete solid solution of Na₂K₃(Mg,Fe)₃Si₂O₅ with the former having Na > K and Mg > Fe (Fuchs et al., 1966).

Roederite was first discovered in the Indarch enstatite chondrite (Fuchs et al., 1966). It has been found also in other unequilibrated EH chondrites (Keil, 1968; Kimura and El Goresy, 1988; El Goresy and Ehlers, 1989), in silicate inclusions in IAB irons (Olsen, 1967) and in some unequilibrated ordinary chondrites (Krot and Wasson, 1994). El Goresy and Ehlers (1989) noted that roederite is associated with spialerite in Indarch. Kimura and El Goresy (1988) found that the abundance of roederite is anticorrelated to that of djéffisherite in UECs. Both minerals are alkali (Na and K)-bearing phases. In this study, roederite in UECs is found to be associated with enstatite, Fe-metal, and sulfides, such as oldhamite, trolite, and spialerite.

Formation of roederite by metamorphism on a UEC parent body can be easily eliminated. This mineral is enriched in alkalis, which have a great affinity for Al (Wood and Holmberg, 1994). In an equilibrated system, the alkalis tend to incorporate with Al to form feldspar. Therefore, metamorphism would decompose this mineral; it would not create it. Petrographic evidence is consistent with this conclusion. While roederite has been found in unequilibrated EH chondrites, it is absent from unequilibrated EH chondrites (Keil, 1968). Besides, the size and abundance of feldspar in EH chondrites increase with petrologic types.

Krot and Wasson (1994) suggested that merrihueite and roederite they found in some ordinary chondrites formed by reaction of alkali-rich gas with silica on a parent body during impact events. Basically, they found that these minerals occur in Si-rich and Al-poor chondrules and clasts and are commonly associated with silica. Furthermore, these minerals are in reactional relationships with silica as they corrode silica and occur as veins in silica. In the case of UECs, the mineral associations are different. Roederite is not commonly associated with silica but with enstatite, Fe-metal and sulfides. And roederite often occurs as euhedral crystals, implying an igneous origin. Reaction of alkali-rich gas with silica to form roederite either in the solar nebula or on a parent body seems unlikely.

In his experimental work in the system K₂O-MgO-SiO₂, Roeder (1951) found that roederite-like compound K₂Mg₂Si₂O₇ is stable at the liquidus in the system and forms by reaction between enstatite and the liquid. The reaction also simultaneously produces forsterite. The roederite grain found in the Bustee aubrite is in contact with enstatite and forsterite (Fig. 4). Therefore, this mineral association is consistent with roederite crystallizing from a melt. The REE pattern observed in this mineral further supports this conclusion. The C1-normalized abundances decrease steadily from the LREEs to HREEs, indicating igneous fractionation (Fig. 6). Roederite can only crystallize from a melt with an atomic ratio of (Na + K)/Al > 1. Otherwise, feldspar will form instead of roederite because of the affinity of alkalis for Al (Wood and Holmberg, 1994). The bulk composition of Bustee has a ratio of (Na + K)/Al < 1 (Watters and Prinz, 1979). Therefore, roederite in the Bustee aubrite may have formed after crystallization of feldspar that fractionated alkali and Al compositions in a melt.

CONCLUSIONS

Petrological studies show that oldhamite in UECs exhibits various occurrences and that this mineral contains numerous types of inclusions and intergrowths with other phases. In contrast, oldhamite in equilibrated enstatite chondrites occurs only as individual grains without any inclusions. This indicates that the diversity of petrological occurrences of oldhamite in UECs is primitive in origin and is not due to metamorphism. My observations do not support the suggestion that oldhamite is a nebular condensate but strongly suggest that this mineral has an igneous origin.

The petrological and elemental studies of diopside in aubrites suggest that its REE abundances were affected by the amount of trapped inclusions and that this mineral was crystallized from a melt.

The first known occurrence of roederite in the Bustee aubrite was reported. This mineral is enriched in alkalis and depleted in siderophile and refractory lithophile elements. The C1-normalized REE abundances in roederite are low (0.01–0.1×C1) and decrease with increasing atomic number.

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REFERENCES


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