

## ANOMALOUS REE PATTERNS IN UNEQUILIBRATED ENSTATITE CHONDRITES: EVIDENCE AND IMPLICATIONS.

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We present here a study of REE microdistributions in unequilibrated enstatite chondrites (EOCs). Although the whole rock REE contents are similar in both unequilibrated and equilibrated chondrites, the host minerals of these refractory elements are different. In the least equilibrated ordinary chondrites (UOCs), the REE reside mainly in glass whereas, in their more equilibrated counterparts, the bulk of the REE is in calcium phosphate, a metamorphic mineral that formed by oxidation of phosphorous originally contained in metal. In the smaller group of enstatite (E) chondrites, calcium phosphate is absent and the phase that contains the highest REE concentrations is a minor mineral, CaS (oldhamite) [1,2], which contains approximately 50% of the total Ca present. In E chondrites, elements typically considered to be lithophiles (such as Ca and Mn) occur in sulfides rather than silicates. This indicates formation under extremely reducing conditions, thus in a region of the solar nebula distinct from those that supplied the more abundant ordinary and carbonaceous chondrites. Previously, we observed [2] a variety of REE patterns in the oldhamite of UECs; they range from almost flat to some with pronounced positive Eu and Yb anomalies. Here, we searched for complementary REE patterns in other minerals from E chondrites and found them in the major mineral, enstatite. Whenever Eu and Yb anomalies are present in this mineral, they are always negative.

In oldhamite, most of the REE patterns belong to one of the following types. Pattern A is almost flat. Pattern B is relatively flat but with a small positive Yb anomaly; the LREE are somewhat enriched ( $\sim 60$ - $100 \times C1$ ) over the HREE ( $\sim 40$ - $70 \times C1$ ). Pattern C is characterized by both positive Eu and Yb anomalies. The Yb anomaly is more pronounced and the REE abundances are lower in C than in B. Pattern D is characterized by still larger positive Eu and Yb anomalies and much lower abundances of the remaining REE [3]. The variety of REE patterns observed in oldhamite is reminiscent, but not as extensive, of that observed in hibonite [4], a refractory mineral present in Ca-Al-rich inclusions (CAIs) of carbonaceous chondrites and which is among the first to form when a gas of solar composition condenses. In reducing environments, oldhamite may be the high temperature counterpart of refractory minerals such as hibonite (and perovskite). In oldhamite, the presence of Eu and Yb anomalies is most likely due to the relatively higher volatility of these two elements, when compared to that of the remaining REE [5]. The smaller diversity of REE patterns, when compared to that seen in hibonite, results from the more limited range of condensation temperatures of the REE in oldhamite than in hibonite [5].

The measurement of REE concentrations in other minerals of E chondrites presents more difficulties as they are typically 100 to 1,000 times lower than in oldhamite. Therefore, much larger primary ion beams are required and special attention has to be paid to the possibility of contamination by CaS. This was done by monitoring the S signal throughout the course of every single measurement. Data are most extensive for Qingzhen (EH3) but we have also obtained preliminary data for Y 691(EH3), MAC 88136 (EL3), ALHA 77156 (EH3-4) and Indarch (EH4).

In addition to oldhamite, REE are present above the detection limits of the ion microprobe in only three minerals: in enstatite, the major constituent of E chondrites, and in ningingerite and alabandite, minor minerals present respectively in EH and EL chondrites. In the last two of these minerals, the HREE are always strongly enriched over the LREE. Typically, there is an increase, by a factor of 10 of the chondrite-normalized abundance from Gd to Lu (from  $\sim 0.1$  to  $0.5 \times C1$  for Gd to  $\sim 1$  to  $5 \times C1$  for Lu), and sometimes there is also a hint of a positive Yb anomaly. Ningingerite and alabandite are not major sources of REE. In enstatite, the steep pattern (with HREE enrichment) usually observed in low-Ca pyroxenes is rarely encountered; instead REE patterns tend to be mirror images of those in oldhamite, either relatively flat or with modest (and almost constant) HREE enrichments. Eu and Yb anomalies, when present, are always negative. Although not usually as depleted as Eu, Sm is often present in lower abundances than expected

## REE in E CHONDRITES: Crozaz G. and Hsu W.

by extrapolating the REE pattern from La to Nd. This may suggest that Sm, to a lesser extent than Eu and Gd, is also a relatively volatile element under reducing conditions. Examples of complementary REE patterns in oldhamite and enstatite are shown in Figs. 1 and 2.

The negative Yb anomalies present in some enstatite grains are consistent with INAA data from mineral separates of Y-691 obtained by Ebihara[6]. According to [6], an acid residue of this unequilibrated chondrite (which included the major mineral enstatite) had low REE concentrations (less than  $0.5 \times C_1$ ) and its REE pattern was characterized by a pronounced negative Yb anomaly, the remaining REE in this meteorite being located in the leachate (i.e., in oldhamite). The present study not only shows that REE patterns in oldhamite and enstatite can be complementary (e.g., positive Eu and Yb anomalies in oldhamite and negative in enstatite) but also that there is a diversity of REE patterns represented in individual grains of the same mineral. As in the case of hibonite, this reflects the variety of conditions that prevailed where these grains formed. Many of these observations have no simple explanation. In particular, the complementary REE patterns in oldhamite and enstatite cannot be the result of simple sequential condensation as one would expect the most refractory mineral (i.e., oldhamite) to be depleted (rather than enriched) in the volatile REE, Eu and Yb.

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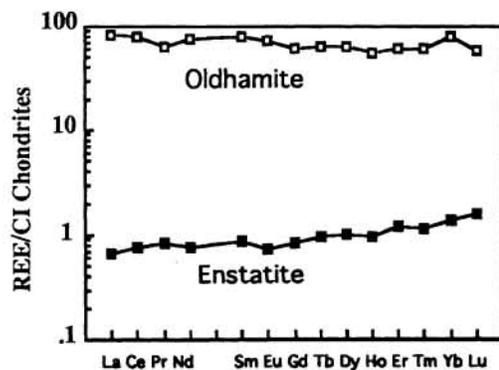


Fig. 1 CI normalized REE patterns without anomalies for oldhamite and enstatite

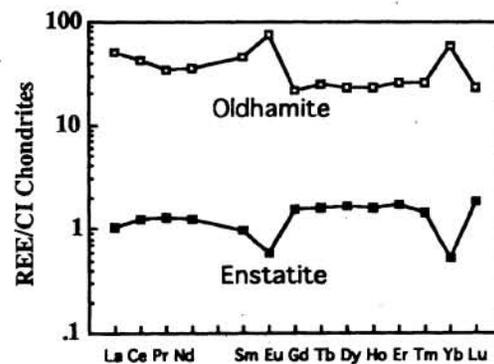


Fig. 2 Complementary CI normalized REE patterns with Eu and Yb anomalies for oldhamite and enstatite