RARE EARTH ELEMENT FRACTIONATION IN CHONDRULES.

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Introduction: Large and discontinuous fractionations of rare earth elements (REEs) are well known from highly refractory Ca- and Al-rich inclusions (CAIs) in primitive meteorites. REE patterns are used as one classification scheme for CAIs [1,2]. Discontinuous C1-normalized REE distributions can be explained in terms of high-temperature gas/solid fractionation [3]. In chondrules, mesostasis is the dominant REE carrier and largely controls their REE budget. Chondrules usually have unfractionated REE patterns with only Eu showing some variability [4]. Only a few chondrules from carbonaceous chondrites were reported to show highly fractionated REEs with discontinuous patterns resembling those of CAIs, but with lower abundances [5–8]. Chondrules with CAI like fractionated REEs may have acquired their REE patterns due to formation processes similar to those of CAIs or due to incorporation of CAI material into their precursors.

We have conducted a LA-ICPMS study of olivine rich chondrules and chondrule mesostases from ordinary (OCs: Chainpur LL3.4, DaG369 L/H3, DaG378 H/L3) and carbonaceous chondrites (CCs: Allende CV3, Vigarano CV3). The results for 12 chondrules are reported here (Figs. 1, 2). The laser spot diameter of 40–60 µm did not, in all cases, allow uncontaminated mesostasis analyses. Analyses of barred olivine chondrules (DaG378/RF10, Vig1/RF14) overlapped with olivine and rather represent the REEs of the bulk chondrules. The analyses of cryptocrystalline chondrules Cha1/GC, DaG369/A and B represent the bulk composition of these chondrules.

Results: Most analyzed chondrules from OC and one from Allende have unfractionated REEs, but variable Eu (Fig. 1) [4]. A slight LREE > HREE fractionation may be due to fractional crystallization of minerals that preferably incorporate HREEs (e.g. pyroxene) [4].

Four chondrules show peculiar REE fractionations with varibilities in Sm, Eu, Tm and Yb (Fig. 2), two with strong negative and two with slightly positive Sm anomalies. Porphyritic olivine chondrules DaG369/-RF02 and DaG378/RF03 have very Na-rich and Ca-poor mesostases and exhibit strong negative anomalies in Sm, Eu and Yb along with HREE > LREE fractionations. Barred olivine chondrule Vig1/RF14 from Vigarano has a nearly complementary pattern with positive anomalies in Eu, Tm and Yb and a slight LREE > HREE fractionation. Sm apparently exhibits a very small positive anomaly in this chondrule. The different REE abundances of three analyzed spots reflect variable amounts of olivine sampled by the laser (Fig. 2). Chondrule DaG378/RF05 is a porphyritic olivine chondrule and contains also Na-rich and Ca-poor mesostasis. The REE pattern of the mesostasis shows distinct positive anomalies in Sm and Yb and a slight LREE > HREE fractionation, but no anomalous Eu (Fig. 2).

Discussion: Variations of Eu in chondrules could either be controlled by the volatility of Eu relative to the other REEs or by the amount of feldspar with fractionated Eu in the precursor. Olivine crystallization is not expected to change the REE pattern of the mesostasis very much, since REEs are highly incompatible with respect to olivine. Although we have not representatively sampled chondrules, Eu anomalies seem to be not unusual in OC and Allende chondrules [4].

Negative anomalies in Eu and Yb and HREE > LREE fractionation as present in DaG369/RF02 and DaG378/RF03 are typical of ultra refractory condensates [3,9]. In a gas of solar composition, however, Sm is not expected to show any anomalous behavior. If CAI material has condensed from a gas of solar composition, the absence of Sm anomalies in them indicates that Sm is similarly volatile as the other LREEs in a gas of solar C/O (0.5). Thermodynamic calculations suggest that Sm, along with Eu, Yb and minor Tm becomes considerably more volatile in a gas much more reduced than solar (C/O = 1.2 [10]). Hence, the data from chondrules DaG369/RF02 and DaG378/RF03 indicate that either the whole chondrule or some of its precursor components have acquired their reduced, ultra refractory REE patterns by equilibration with a gas at a high C/O ratio. Since both chondrules have rather normal bulk REE abundances (estimated <5×C1) and are non-refractory in composition (no plagioclase, spinel or Al-,Ti-rich pyroxene), formation of the bulk chondrule material by fractional condensation at high C/O seems unlikely. The silicate mineralogy of these chondrules is another argument against formation of the whole chondrule material in an environment with high C/O [11]. One alternative is that the anomalous REE fraction is indicative of small amounts of an ultra refractory high-REE phase with a distinct negative Sm-anomaly that had been incorporated into chondrule precursors. Addition of ultra refractory oldhamite (CaS) condensates [10] to the precursor may explain the peculiar REE pattern in the two OC chondrules (Fig. 2). Oldhamite, the reduced counterpart of ultra refractory CAI assemblages, is expected to have negative Sm, Eu and Yb anomalies and is amongst the first phases to condense from a gas with C/O > 0.95 [10,11]. It is the major REE carrier phase in enstatite chondrites (ECs), but, so far, no ultra refractory oldhamite has been identified in them [12].

The REE pattern in chondrule Vig1/RF14 indicates that the precursor material formed from a nebular reservoir depleted in ultra refractory condensates. The small Sm anomaly may indicate that the ultra refractory component was also depleted in Sm and hence may have formed under reducing conditions. The same is true for the mesostasis of chondrule DaG378/RF05. However, the C1-normalized Sm/Nd ratio of 1.4 clearly exceeds the analytical uncertainty. This chondrule also exhibits a LREE > HREE fractionation with a distinct positive anomaly in Yb. Eu is not anomalous, although anomalies in Sm and Yb are expected to be accompanied by anomalies in Eu [10].

Summary: Although we have not sampled a representative set of chondrules from OCs and CCs, we have shown that many chondrules have large variations in Eu. Furthermore, this is the first report on material that exhibits highly fractionated REE patterns resembling those suggested for ultra refractory oldhamite [10]. We suggest that oldhamite (or a reduced equivalent) was sampled by the chondrule precursor material as high REE carrier phase, but has been disintegrated during the chondrule forming event. This scenario implies (a) condensation of oldhamite at high C/O, (b) effective isolation and (c) transport to and incorporation into OC chondrule precursors. Two chondrules, including one from Vigarano, show complementary patterns with positive Sm anomalies, indicating removal of a highly reduced, ultra refractory component. The data suggest that high temperature condensation occurred at high C/O and that OC [13] and possibly also Vigarano chondrules have samples highly reduced materials.

Note: Parts of these data will be published in [14].

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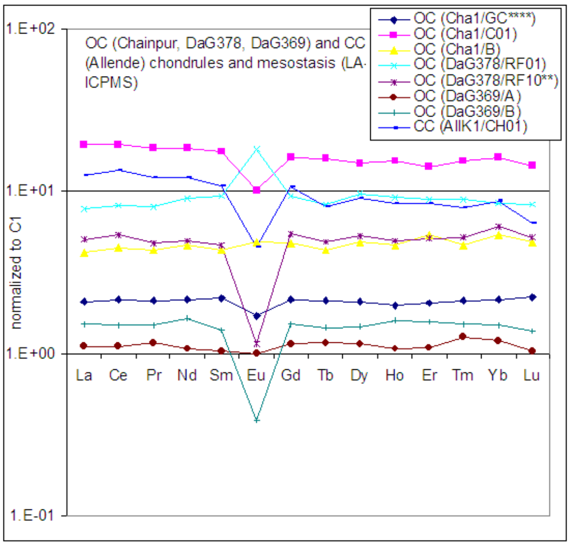

Fig. 1: C1-normalized REE abundances of chondrules and mesostases (**** average of 4 and ** average of 2 analyses).

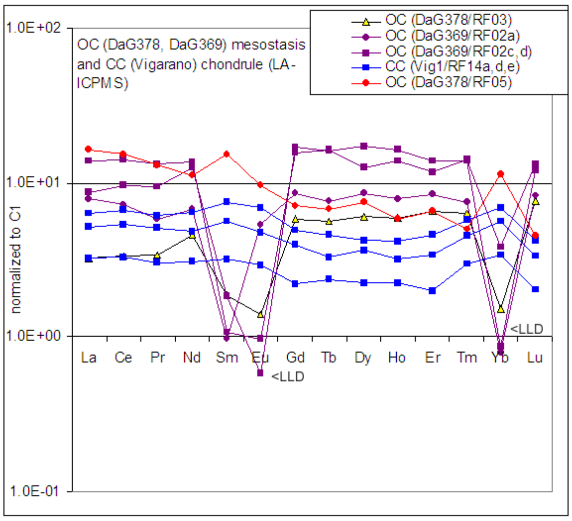

Fig. 2: C1-normalized REE abundances with anomalous patterns in chondrules and mesostases.