

Ca AND S ISOTOPIC COMPOSITIONS AND REE CONCENTRATIONS IN OLDHAMITE OF FIVE UNEQUILIBRATED ENSTATITE CHONDRITES; Laura

L. Lundberg^{1,3}, Ghislaine Crozaz^{1,3} and Ernst Zinner^{2,3}, (1) Department of Earth and Planetary Sciences, (2) Department of Physics, (3) McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130.

Enstatite chondrites are among the most reduced objects known in the solar system. They contain an accessory mineral, oldhamite (CaS), which may be the reduced analogue of hibonite and perovskite in the more oxidized carbonaceous chondrites and, therefore, a carrier of isotopic anomalies. We report the results of a correlated study of Ca isotopic compositions, rare earth element (REE) abundances and mineral associations of CaS in five of the least equilibrated enstatite chondrites, Qingzhen (E3), Yamato-691 (E3), MAC88136 (E3), Indarch (E4) and ALHA77156 (E3-4). Sulfur isotopes were also measured in three sulfides, CaS, niningerite (MgS) and troilite (FeS).

CaS is easily dissolved by water. Consequently, in the Antarctic meteorites (Yamato-691, MAC88136 and ALHA77156), most of the oldhamite grains were weathered and Ca isotopic determinations were possible only for seven MAC88136 oldhamite grains that were sufficiently preserved to present smooth surfaces of greater than 15µm diameter for analysis. In Qingzhen and Indarch (both falls) we measured Ca in, respectively, 10 and 15 oldhamite grains. CaS from Norton County, an enstatite achondrite, was used as a Ca isotopic standard. A power fractionation law was found to be more appropriate for instrumental mass fractionation correction than the exponential law used earlier [1]. Thus, previous data are re-evaluated here and additional data are reported. No Ca anomalies were found in 10 CaS grains from Indarch. However, 4 out of 15 grains from Qingzhen ($\delta^{48}\text{Ca} = -7.1 \pm 2.5, -4.6 \pm 2.3, -5.0 \pm 2.4, -3.4 \pm 2.0\text{‰}$, 2σ errors) and 2 out of 7 grains from MAC88136 ($\delta^{48}\text{Ca} = -5.2 \pm 2.5, -3.1 \pm 1.5\text{‰}$) show depletions in ^{48}Ca . The other grains have normal Ca isotopic compositions. Ca isotopic anomalies are observed only in E3 chondrites.

Small negative $\delta^{34}\text{S}$ effects ($-0.26 \pm 0.07\text{‰}$) were reported in whole rock samples of 7 enstatites [2]. Although sulfur cannot be measured with that precision by ion microprobe mass spectrometry, effects might be larger in a given sulfide phase. We analyzed the S isotopic compositions (^{32}S , ^{33}S , ^{34}S , and ^{36}S) of 6 CaS, 2 MgS and 5 FeS grains from Qingzhen and 2 CaS grains from MAC88136. All these grains are normal within the uncertainty of our method (1σ errors of 2-4‰). Four out of the 6 grains with ^{48}Ca depletions are included in this data set. In view of the larger errors associated with these measurements, a lack of a S isotopic effect is not inconsistent with the results of Thiemens and his co-workers.

The REE abundances were measured in 43 oldhamite grains and 17 weathered oldhamite areas. It has been shown previously that terrestrial weathering does not alter oldhamite REE patterns [3]. Five REE patterns, designated A,B,C,D and E could be distinguished and are displayed in figure 1. Patterns A through D have been described [1]. Pattern E is relatively flat but, unlike the others, has a slight to pronounced negative Eu anomaly and sometimes a positive

Ca, S AND REE IN OLDHAMITE OF E-CHONDRITES: Lundberg L. L. et al.

Yb anomaly. The example shown is from a weathered CaS crystal from MAC88136 and the elevated REE abundances may be an artifact due to the normalization to Ca (it was assumed that the same fractions of Ca and REE were lost). Table 1 summarizes the types of REE patterns observed for each meteorite, with the number of analyses given in parentheses. In Yamato-691 and ALHA77156 only weathered grains were found. The REE patterns for the 6 grains with anomalous Ca are A(1), B(1), C(3) and E(1). The mineral associations of the 6 anomalous grains also vary. Two grains occur with niningerite and/or troilite, three grains are in metal-sulfide spherules and one grain is in a chondrule. Thus, there is no obvious correlation between $\delta^{48}\text{Ca}$ anomalies and either REE abundances or CaS occurrences.

From the observation that CaS in E3 chondrites and hibonite in carbonaceous chondrites exhibit Ca isotopic anomalies, we conclude that inhomogeneities also existed in the region of the solar nebula where enstatite chondrites formed. However, Ca isotopic anomalies are less common and much smaller in CaS than in hibonite where $\delta^{48}\text{Ca}$ ranges from -56‰ to +104‰ [4]. In hibonite, $\delta^{48}\text{Ca}$ can be positive or negative but only negative $\delta^{48}\text{Ca}$ values were observed in CaS. This does not preclude that positive $\delta^{48}\text{Ca}$ anomalies do exist in CaS but, perhaps, we have not yet sampled the right grains. In hibonite, the largest Ca isotopic anomalies correlate with Group III REE patterns [4,5]. In CaS, $\delta^{48}\text{Ca}$ and REE patterns are not correlated.

The isotopic heterogeneities in CaS occur on a small spatial scale. It is therefore unlikely that they were carried by a gas phase; the carriers were probably interstellar dust grains. There is no evidence for the presence of "trapped" carrier grains in CaS nor is there evidence that CaS grains are relict interstellar grains. We thus propose, as has been done before for hibonite [4], that the CaS precursors were dust aggregates with distinct isotopic compositions. These dust aggregates were then heated during local transient events and, upon cooling, CaS formed, trapping most of the REE and preserving the average Ca isotopic composition of the precursor dust aggregates.

References: [1] Lundberg *et al.* (1989) *Meteoritics* 24, 296-297. [2] Gao X. and Thiemens M. (1990) LPSC XXI, 401-402. [3] Floss *et al.* (1990) *Geochim. Cosmochim. Acta*, 54, 3553-3558. [4] Ireland T. (1990) *Geochim. Cosmochim. Acta* 54, 3219-3237. [5] Ireland T. (1988) *Geochim. Cosmochim. Acta* 52, 2827-2839.

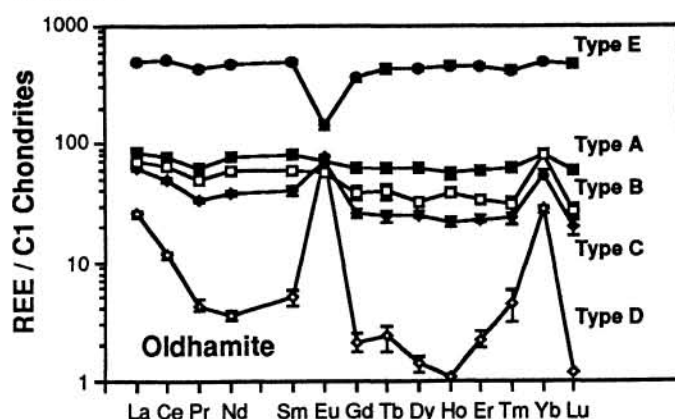
Figure 1

Table 1:	Meteorite	REE Patterns Observed
E3	Qingzhen (20)	A,B,C,D
	MAC88136 (10+3*)	A,B,C,E
	Yamato 691 (5*)	B,D
E3-4	ALHA77156 (9*)	A,B,C,E
E4	Indarch (13)	A,B

* weathered oldhamite