RARE EARTH ELEMENTS IN BULK CHONDRITES AND CHONDRITE COMPONENTS

V. Bendel[1]*, A. Patzer[2], A. Pack[1], D. C. Hezel[3] and C. Münker[4], [1]Georg-August-Universität Göttingen, Geoscience Center, Department of Isotope Geology, Goldschmidtstrasse 1, D-37077 Göttingen, Germany (*vbendel@uni-goettingen.de), [2]Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN 37996, [3]Department of Mineralogy, Natural History Museum, Cromwell Road, SW7 5BD, London, UK, [4]Universität zu Köln, Institute for Geology and Mineralogy, Zülpicher Strasse 49b, D-50937 Köln, Germany

Introduction: Rare earth elements (REE) are important indicators for high-T fractional condensation and evaporation processes in the early solar system [1-4]. A major controlling factor for REE fractionation (i.e. deviation from a CI1 pattern) is their different volatilities [2]. Fractionated REEs are well-known for CAIs. Here we examine REE patterns in a large set of bulk chondrites and some terrestrial samples in order to identify volatility-controlled fractionations on the asteroidal and planetary scale. We apply a new sample preparation technique for laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) [5]. As reference material we use the Orgueil (CI1) meteorite, which is taken as the solar system reference [6]. In order to trace the origin of fractionated REEs in bulk chondrites, we have analyzed REEs in CAIs, chondrules and matrix of the CV3 chondrite Leoville.

Materials and Methods: Bulk carbonaceous, ordinary and enstatite chondrites and a few terrestrial samples were prepared for LA-ICPMS and electron probe microanalysis (EPMA) following the method described in [5] and applied by [7] and [8]. Samples were ground to powder in an agate mortar. Metal-bearing meteorite samples were oxidized in a muffle furnace before grinding. The powder was briefly fused with a 50 W CO_2 laser in a reducing atmosphere of a mixture of Ar and H_2 (7 vol.%). The spheres were then put on top of a vertical gas stream, briefly fused for 2 or 3 times and homogenized. The samples were quenched by switching off the laser. The spheres were then embedded in resin and polished for EPMA and LA-ICPMS.

A polished piece of 2.02 cm^2 of Leoville was used for EPMA and LA-ICPMS analyses.

Major elements were analyzed by means of EPMA. LA-ICPMS was conducted at ANU (Canberra) employing a 193 nm excimer laser and an Agilent 7500S ICP-MS. LA-ICPMS allows to measure all REEs, including the monoisotopic elements Pr, Tb, Ho and Tm, which are important to identify volatility-controlled fractionation. These elements are not accessible by isotope dilution mass spectrometry.

The concentrations of REEs were calculated using NIST SRM 612 and BCR-2G as external standards (concentration values from [9] and [10] respectively). The Ca concentrations obtained from EPMA were used for internal normalization. The precision of our LA-ICPMS measurements of REEs is usually better than ±5% (1σ, SD).

Results: *Chondrites.* The CI1 chondrite Orgueil was analyzed and used as a reference for the solar system. The precision of REE concentrations in Orgueil is better than ±2 – 3%.

Chondrites usually do *not* have unfractionated (i.e. flat) Orgueil-normalized REE patterns. The fractionations are volatility-controlled. The relative REE fractionations in most chondrites are, with Orgueil as a reference, whithin ±10%.

The carbonaceous chondrite Murchison (CM2) shows a fractionation with a 6 – 7% enrichment of heavy REE (HREE) over light REE (LREE). Two carbonaceous chondrites of the CV3 group (Allende and Mokoia) show highly fractionated REEs with a strong enrichment of LREE over HREE and a strong positive anomaly in Tm and Yb. Such patterns are typical for group-II CAIs, which are present in both, Allende and Mokoia. We analyzed different aliquots (200 to 300 mg) of Allende. Aliquots with a large amount of CAIs show more pronounced REE fractionations. The amount of CAIs is reflected in the Ca/Si and Al/Si concentration ratios.

Most of the analyzed ordinary chondrites show a slight fractionation with enriched HREEs but with a slight depletion of Tm and Yb.

The REE patterns of our two analyzed enstatite chondrites resemble those of the ordinary chondrites. They have enriched HREEs and a small depletion in Tm and Yb. Additionally, they are strongly depleted in Eu, the most volatile REE.

Bulk Earth. The terrestrial samples (European shale composite (Fig. 1), lherzolithe and Columbia River Basalt) have smooth Orgueil-normalized REE patterns. They show a REE fractionation due to the ionic radius, which is tipical for differentiated terrestrial samples. The samples show a slight depletion of Tm (≈4.5%) and Yb (≈2.5%) from the smooth trend which was quantified by fitting the HREEs with a third order polynomial.

Leoville. In order to identify the carriers of fractionated REEs, we have analyzed all components of a Leoville (CV3) section. The CAIs have fractionated REEs with group-II patterns. Most of the chondrules show flat REE patterns (except for Eu which is depleted in about half of the chondrules). However, four out of 22 analyzed chondrules show fractionated REEs with REE group-II like patterns.

The matrix was analyzed by nine independent measurements at different locations (Fig. 2). Four of these analyses have flat REE patterns. The other five analyses show a relative enrichment of LREEs over HREEs of about 20%. Tm and Yb are enriched by about 15% relative to the other HREEs. All analyses of the matrix show a strong enrichment of Eu (≈30% on average). For more information about REEs in the Leoville chondrite see also [11].

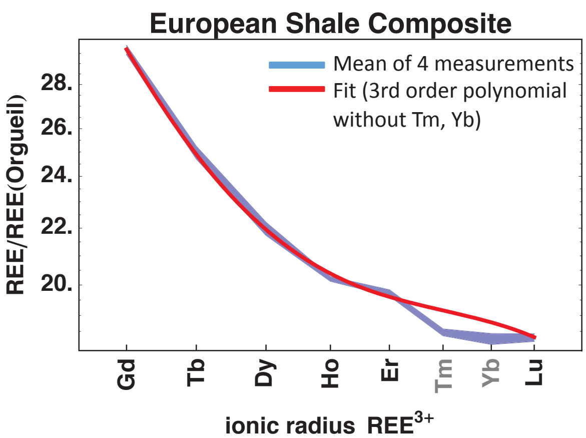

Fig. 1: Plot of the Orgueil-normalized HREEs in a European Shale Composite. Note the discontinuous depletions in Tm and Yb.

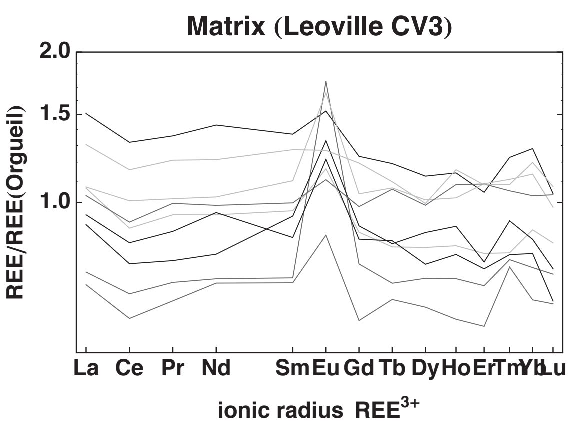

Fig. 2: REEs in the matrix of Leoville normalized to Orgueil (CI1).

Discussion: *Chondrites.* Murchison has an ultrarefractory REE pattern which is typical of the very first condensates forming in a cooling solar nebula.

The fractionated REE patterns of the CV3 chondrites are, compared to Orgueil, either depleted in an ultrarefractory component or enriched in a refractory component. Refractory and ultrarefractory condensates are rich in Al and Ca. As the CV3 chondrites have high Ca/Si ratios it is more likely that a refractory component (with REE group-II like patterns) was added to the reservoir where CV3 chondrites formed.

Most of the REE patterns of ordinary and enstatite chondrites are complementary to REE group II patterns. Ordinary and enstatite chondrites have low Ca/Si ratios. Therefore it is likely that a refractory component was removed from the spatial region where they formed. This can have happened through a bipolar outflow as discussed in [12].

Bulk Earth. By normalizing the REE concentrations of our terrestrial samples to Orgueil, the depletion of Tm an Yb is distinct. This means that the Earth might be either enriched in an ultrarefractory component or depleted in a refractory component with group-II REE patterns. This would imply that high-T fractional condensation occurred not only on asteroidal, but also on planetary scale. Such a process would require the transport of large amounts of gas and dust.

By normalizing the REE concentrations to Murchison, the relative depletion of Tm would become more pronounced (5%). The depletion of Yb, however, would become less pronounced (2% for the European shale composite and <1% for the other two samples).

We will conduct more analyses, including isotope dilution mass spectrometry, to verify this observation.

Leoville. The CAIs have typical REE group-II patterns as they are known from other CV3 chondrites. Four of the analyzed chondrules show also group-II patterns. This indicates that these chondrules had fractionated material in their precursers. However, the majority of the chondrules has flat REE patterns, suggesting that they did not contain a fractionated component in their precursers. The REE patterns of the matrix indicate that also the matrix contains a small amount of such a fractionated component.

The distribution of Eu between matrix (positive anomaly) and chondrules (negative anomaly) could be volatility-controlled. Eu is the most volatile REE and thus evaporates at lower temperatures during heating events. Assuming that chondrules and matrix formed from the same reservoir, as discussed by some authors [e.g. 13], would explain that Eu is depleted in some chondrules and enriched in the residual matrix.

Another possibility is that the precursers of the matrix contain more feldspar (with a positive anomaly in Eu) than the precursers of the chondrules.

References: [1] Pack A. et al. (2004) *Science*, *303*, 997-1000. [2] Boynton W. V. (1975) *GCA*, *39*, 569-584. [3] Boynton W. V. and Frazier R. M. (1980) *LPS XI*, 103-105. [4] Boynton W. V. (1989) *Min. Soc. of America*, 1-24. [5] Pack A. et al. (2010) *Geochem Trans.*, *11*. [6] Lodders K. (2003) *ApJ*, *591*, 1220-1247. [7] Pack A. et al. (2007), *GCA*, *71*, 4592-4608. [8] Patzer et al. (2010) *Meteorit. Planet. Sci.*, *45*, 1136-1153. [9] Pearce et al. (1997) *Geostandards Newsletter*, *21*, 115-144. [10] Jochum K. P. and Nohl U. (2008) *Chemical Geology*, *253*, 50-53. [11] Patzer A. et al. (2011), *this volume*. [12] Shu F. H. (1996) *Science*, *271(5255)*, 1545-1552. [13] Hezel D. C. and Palme H. (2010) *EPSL*, *294*, 85-93.