REFRACTORY LITHOPHILE ABUNDANCE PATTERNS: THE DEVIL IS IN THULIUM. N. Dauphas[1], A. Pourmand[2], J.-A. Barrat[3], [1]Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago (dauphas@uchicago.edu), [2]Neptune Isotope Lab, Department of Marine Geosciences, University of Miami – RSMAS, Miami, [3]Université de Bretagne Occidentale, Institut Universitaire Européen de la Mer, CNRS UMR 6538, Plouzané, France

Introduction: Refractory lithophile element (RLE) abundances are often assumed to be in CI chondrite-porportions among different chondrite groups and planetary bodies. While this is demonstrably true at the ~10% level, discerning non-chondritic abundance patterns is challenging because planetary processes such as parent-body metamorphism, alteration, and igneous processes have oftern fractionated RLEs from one another. Testing this question has important ramifications as many refractory lithophile pairs, such as Sm-Nd and Lu-Hf, are decay systems routinely used to date early solar system events. In addition, fractionation of RLEs in bulk planetary bodies can provide clues on the nebular processes that governed the composition of planets. These processes could have involved decoupling between gas and dust after the most refractory elements had condensed.

A challenge to testing the assumption that RLEs are in constant proportions is that some chondrites contain large refractory inclusions that are heterogeneously distributed. Equally important is the redistribution of some of those elements among secondary phases that formed during parent-body aqueous alteration and metamorphism.

The rare earth elements (REEs) form a group of relatively uniform behavior during aqueous, metamorphic, and igneous processes. Exceptions are Ce and Eu, which also exist as 4+ and 2+ ions while other REEs maintain their 3+ state. Nebular processes can, however, fractionate REEs from one another in unique ways that do not necessarily follow any smooth trend with mass [1,2]. This is most clearly manifested in fine grained Calcium-Aluminum Inclusions (CAIs) with type II REE patterns. These objects show depletions in ultrarefractory heavy REEs (except Tm and Yb) and volatile REEs (Eu and Yb), while REEs of intermediate volatilities are a uniformly enriched (*i.e.,* Tm and light REEs except Eu). It remains uncertain what phase sequestered ultrarefractory REEs but it could have been hibonite of Ca,Ti-perovskite. it is also not clear whether such fractionations are present in bulk planetary bodies, in part because parent-body processes typically obliterate the fractionation signature associated with nebular processes [see *e.g.*, 3,4].

In order to test the assumption that RLEs are present in constant relative proportions in planetary bodies, we have measured at the University of Chicago, the University of Miami and Université de Bretagne Occidentale the REE abundance patterns of many chondrites, achondrites, and terrestrial rocks [5,6].

Methods: At the University of Chicago and Miami, the samples were fused with high-purity lithium metaborate flux. The REEs were then extracted from the rest of the matrix using the TODGA resin. The REE measurements were performed on a Thermo Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) [5 and references therein] in multi-collection, providing high precision on REE patterns including mono-isotopic REEs such as Tm. The abundances of mono-isotopic REEs had seldom been measured prior to the advent of ICPMS because these were not amenable to isotope dilution mass spectrometry (IDMS) techniques. The measurements at the Université de Bretagne Occidentale were done completely independently using a separate protocol [6 and references therein]. The samples were dissolved in acid and the measurements were then performed on a single collector high-resolution Thermo Element 2 ICPMS.

Results: There is very good agreement between the different techniques for the samples that were measured in all three labs. There is also good agreement between Lu measurements by bracketing with measurements performed earlier on the same samples by IDMS [7]. The results show significant variations in REE abundance patterns, even within one chondrite group. Eu/Eu* anomalies are also variable and tend to correlate with the extent of LREE/HREE fractionation. Tm/Tm* anomalies are constant within a group. All achondrites, terrestrial rocks, enstatite chondrites and ordinary chondrites display negative anomalies in Tm/Tm* of -3 to -5% relative to CI chondrites. Other carbonaceous chondrites show Tm/Tm* anomalies similar to CI or even larger, reaching +10% in the Allende CV chondrite.

The nugget effect: We focus our discussion below on ordinary chondrites, as they are characterized well. Nevertheless, similar issues exist for enstatite and carbonaceous chondrites as REEs tend to be concentrated in oldhamite and phosphate, respectively, in these meteorite groups. During metamorphism in ordinary chondrites, REEs that were initially in the chondrule mesostasis and other phases migrate into Ca-phosphate minerals, Ca-pyroxene, and plagioclase for Eu. In metamorphosed chondrites, Ca-phosphate show depletion in HREE because they are also partitioned into pyroxene [4]. Eu that is concentrated in plagioclase also

shows up as a negative anomaly in the Ca-phosphate pattern. Heterogeneous distribution of phosphates should thus be associated with a negative correlation between LREE/HREE fractionation and Eu/Eu* anomalies, as is observed. Using available data on the size and mode of phosphate grains in ordinary chondrites, we calculate that a 85 mg chondrite sample would only contain ~28 phosphate grains of 200 µm size, and the 95% confidence interval for this value is 18 to 39 grains. This nugget effect and the fact that phosphates have fractionated REE patterns explain much of the variations in REE patterns documented in ordinary chondrites. To evaluate this more quantitatively, we derived an equation that gives the dispersion (σ_R) on an elemental or isotopic ratio ($R=C_2/C_1$) arising from the nugget effect,

$$\sigma_R \simeq \frac{r(\rho_{nugget}/\rho_{matrix})}{[1+rf(\rho_{nugget}/\rho_{matrix})]^2}\sqrt{\frac{f\rho_{matrix}\pi d^3}{6m}}\left|R_{nugget}-R_{matrix}\right|,$$

where r is the ratio of concentrations $C_{1,nugget}/C_{1,matrix}$, m is the mass homogenized, and d is the size (diameter) of the nugget grains. We applied this equation to ordinary chondrite and found that it does explain the dispersion in La/Lu, $^{176}Hf/^{177}Hf$ and Eu/Eu* measured in ordinary chondrites, proving that a nugget effect associated with the presence of Ca-phosphate is responsible for the variations. A diagnostic signature of this effect is the presence of large and variable Eu/Eu* anomalies. To account for this, we have filtered all the data to retain patterns that have Eu/Eu* within 5% of the CI value. The patterns seen in all chondrite groups after such filtering are approximately parallel, demonstrating that to the first order, the REEs are present in chondritic proportions among planetary bodies (Fig. 1 [5]).

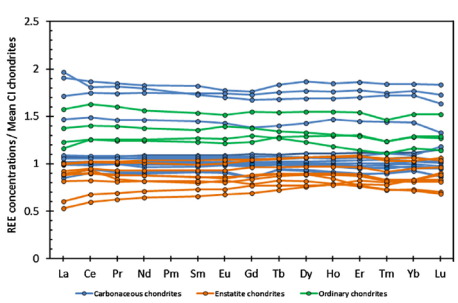

Fig. 1. REE patterns of all the chondrite samples with Eu/Eu* anomalies within 5% of the CI value [5].

Thullium anomalies: A characteristic feature of type II REE patterns most commonly found in fine grain CAIs is the presence of a large positive Tm anomaly. This arises from the fact that other REEs surrounding Tm are either more volatile (Yb) or more refractory (other HREEs) than Tm. ICPMS instruments allow one to measure the abundance of mono-isotopic Tm with a precision that was unachievable with previous techniques. Our results show that the Earth, Mars, the Moon, Vesta, ordinary chondrites, enstatite chondrites, and achondrites, all exhibit negative Tm/Tm* anomalies relative to CI. Carbonaceous chondrites show no or positive anomalies [5,6]. The measurements agree between Chicago, Miami, and Brest and they also agree with independent measurements by [8].

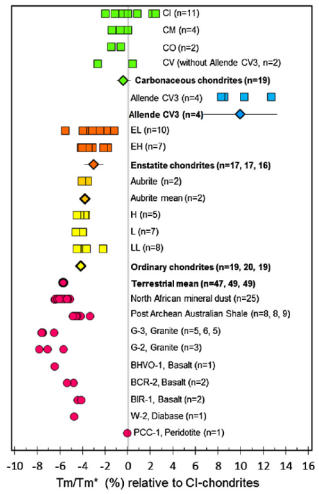

Fig. 2. Tm/Tm* anomalies in chondrites and terrestrial rocks [5]. Note that the variations in Tm/Tm* is explained by the fact that some of those rocks have strongly fractionated REE patterns, whose curvature introduce an artifact in the calculation of Tm/Tm*. Using a more sophisticated definition of Tm/Tm* removes this artifact [5,6].

This is interpreted to reflect the fact that CIs incorporated an extraneous 0.15% of refractory dust similar in composition to fine grain CAIs with the type II pattern. Allende, with its large +10% excess in Tm must have incorporated an extra 0.35% type II dust in addition to what CIs contained. These results demonstrate that at a fine level, all refractory lithophile elements are not present in CI proportions in all planetary bodies; the devil is in Tm.

References: [1] Boynton W. V. (1975) GCA 39, 569. [2] Davis A. M. and Grossman L. (1979) GCA 43, 1611–1632. [3] Murrell M. T. and Burnett D. S. (1983) GCA 47, 1999. [4] Crozaz G. et al. (1989). EPSL 93, 157. [5] Dauphas N., Pourmand A. (2015) GCA 163, 234. [6] Barrat J.A. et al. (2016) GCA 176, 1. [7] Dauphas N. and Pourmand A. (2011) Nature 473, 489. [8] endel V., Pack A. and O'Neill H. (2012) LPSC 43, #2578.