RATIO VARIATIONS OF REFRACTORY LITHOPHILE ELEMENTS IN CHONDRITES AND THEIR COMPONENTS: IMPLICATIONS FOR PLANETARY COMPOSITIONS.

T. Yoshizaki[1], W. F. McDonough[1,2,3] and R. D. Ash[2], [1]Department of Earth Science, Tohoku University, Sendai, Miyagi 980-8578, Japan (tacasy22@dc.tohoku.ac.jp), [2]Department of Geology, University of Maryland, College Park, MD 20742, USA, [3]Research Center for Neutrino Science, Tohoku University, Sendai 980-8578, Japan.

Introduction: Historically, relative abundances of refractory lithophile elements (RLEs) are considered to be nearly constant among all classes of chondrites and the solar photosphere, at least within about 10%. This had led to the assumption that the bulk RLE ratios of the terrestrial planets are chondritic [e.g., 1–3]. The REE+Y elements are recognized as having highly coherent geochemical behavior and show even less variations in RLE ratios. However, recent high-precision measurements suggested that there are meaningful variations in some RLE ratios (e.g., Nb/Ta, Y/Ho, Zr/Hf) between chondrite groups and terrestrial samples [e.g., 4–6]. Although these observations may guide us to a better understanding of the building blocks of the terrestrial planets, the detailed nature and the origin of such variations are unclear. Several processes can result in such variations: i) heterogeneity in the solar nebula; ii) chemical fractionation in the solar nebula; iii) asteroidal alteration and/or metamorphism; iv) formation of an incompatible-element-enriched reservoir that was hidden in the deep mantle or removed by collisional erosion; v) partitioning of RLEs into a (S-bearing) metallic core; and vi) terrestrial weathering.

Various stable isotope systems (e.g., O, Ti and Cr) in chondrites strongly suggest that isotopic composition of the solar nebula was not homogeneous when chondrite parent bodies accreted [e.g., 7], and enstatite chondrites (ECs) and the terrestrial samples are almost indistinguishable in most of these systems. Thus, it has been suggested that ECs can be the main building blocks of the Earth [e.g., 8].

Since chondritic components, such as chondrules, matrix and sulfides, formed in the solar nebula prior to a formation of chondrite parent bodies, they can provide snapshots of spatial and temporal heterogeneities of chemical composition in the solar nebula. Therefore, to reveal the variation in a variety of RLE ratios among solar system materials, and put constraints on its origin, we have performed a systematic analysis of RLE compositions of these EC components in a suite of primitive ECs. Understanding the variation in RLE ratios in the solar nebula can put further constraints on the building blocks of the terrestrial planets and the solar system abundance of elements.

The mineralogy of ECs suggests formation under the extremely reducing conditions [9]. Under such a low fO_2 condition, generally refractory lithophile elements, like Ca and REEs, show a chalcophile behavior, being partitioned into mostly oldhamite (CaS) at an enrichment factor of ~10-100×CI [e.g., 10]. However, several RLEs, such as Nb and Ti, are not enriched in oldhamite [e.g., 11] and their behaviors under EC forming conditions are not well constrained. We seek to understand the cosmochemical behavior of RLEs and further constrain RLE fractionation under reduced conditions.

Samples: In order to reduce potential contributions from parent body metamorphism and terrestrial weathering, we studied chondritic components of only unequilibrated enstatite chondrites from NASA Antarctic meteorite collection. The samples include three EH3s [Alan Hills (ALH) A77295, ALH 84170 and ALH 84206] and two EL3s (ALH 85119 and MacAlpine Hills 88136). We compare our new EC data to the RLE compositions of chondrules from carbonaceous (CCs) and ordinary chondrites (OCs) [12–14].

Methods: Petrology, mineralogy and major element chemistry of the samples were analyzed using a SEM and electron microprobes. Trace element compositions of the samples were determined using a New Wave frequency-quintupled Nd:YAG laser system coupled to a Thermo Finnigan Element2 single-collector ICP-MS at University of Maryland. Measurements were carried out in low-mass resolution mode (M/ΔM = 300), with 15-200 μm laser spot size and a fluence of ~2-3 J cm^{-2}. The mass spectrometer was tuned to maximize signal (based on ^{43}Ca and ^{232}Th spectra) and minimize oxide production (UO/U < 1.2%) to maximize sensitivity and reduce isobaric interferences. A dwell time of 5 to 15 ms was used depending on element concentrations. National Bureau of Standards (NIST) 610 glass was used as an external standard material for a measurement of chondrules and matrix (fine-grained materials filling a space between chondrules and metal-sulfide nodules). Internal standard was ^{29}Si, which had been determined using electron microprobe. The Si concentration used for the chondrules as some analyses were polymineralic. For sulfides, the group IIA iron meteorite Filomena (for siderophile elements) and NIST 610 glass (for lithophile elements) were used as reference materials. Count rates were normalized using ^{57}Fe (for Filomena) and ^{63}Cu (for NIST 610) as internal standards.

Results and Discussion: The EC chondrules show non-chondritic values with large variation in several RLE ratios. The most significant ones are ratios of Nb to other RLEs. Nb/Ta of chondrules show large variation in all types of chondrites and the mean Nb/Ta ratio of EH and EL chondrules [12.7 ± 1.7 (2se, $n = 56$) and 15.7 ± 2:6 (2se, $n = 31$)] are clearly lower than the recommended chondritic value [19.9 ± 0.3 (2se) [4]] (Fig. 1). EC chondrules also show significantly high Zr/Nb (reaching up to ~200) with a large variation, suggesting Nb-depletion in EC chondrules. EC chondrules also show subchondritic mean values in Ti/Sc and Zr/Hf ratios. Unlike the chondrules, matrices in ECs do not deviate significantly from chondritic Nb/Ta and Zr/Nb, and there is no clear complementarity between chondrules and matrix (Fig. 1). CC and OC chondrules show subchondritic and nearly chondritic Nb/Ta, respectively, and both of them have chondritic (12.6 [15]) ~subchondritic Zr/Nb (Fig.1). Although addition of group II CAIs with subchondritic Nb/Ta and Zr/Nb [3, 16] seem to have played important role to fractionate RLE composition of CC and OC chondrules from chondritic composition, EC chondrules do not show any evidence for addition or subtraction of the group II inclusions.

Most troilites in ECs have, on average, a factor of 5 enrichments in Ti, V and Nb relative to CI, whereas Zr and Ta abundances are 10 times less and Hf is undetected (Fig. 2). Therefore, the variations in RLE ratios in EC chondrules can be explained by subtraction of troilite from a chondritic reservoir before/during EC chondrule formation. Complementary RLE ratios between chondrules, sulfides and the matrix suggest that the bulk RLE ratios of ECs are not significantly fractionated from the chondritic values [4, 17].

RLE composition of EC sulfides (Fig. 2) shows that some RLEs including Nb, Zr and Ti are partitioned into troilite at low fO$_2$. Since their trace element chemistry is comparable to that of troilite from reduced iron meteorites [e.g., 18], it is suggested that EC sulfide formed by equilibrium processes and that they are not products of silicate sulfidation. Although Münker et al. [18] argued that the incorporation of Nb-rich cores of highly reduced asteroids into the Earth's core, and their concomitant Ta enriched silicate portion into the silicate Earth, caused subchondritic Nb/Ta of the bulk silicate Earth, there is abundant evidence (e.g., Al/Ti, Zr/Sm) that the silicate Earth has chondritic (Ti/RLE) and (Zr/RLE) ratios. Therefore, RLE fractionation in the silicate Earth by subtraction of the RLE-bearing sulfide is unlikely, leaving us an enigmatic state regarding the role of Nb during the core formation.

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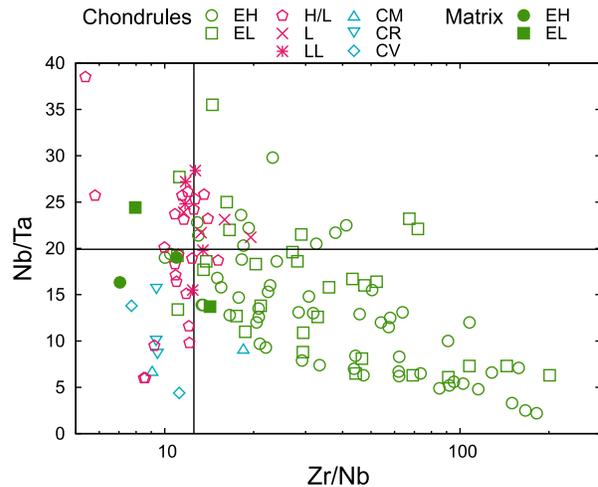

Fig. 1: Nb/Ta vs Zr/Nb of chondrules and matrix. Solid lines represent chondritic values [4, 15].
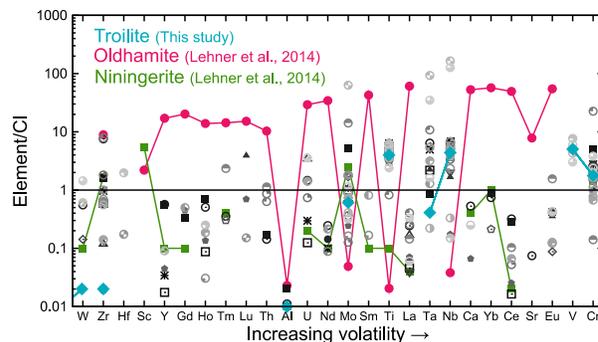

Fig. 2: Mean CI-normalized multi-element pattern of troilites from ECs. Gray plots show data for individual troilite samples. Elements are in order of condensation temperature [19]. Compositions of oldhamite and niningerite from an EH chondrite [11] are also shown.