THE REE ISOTOPIC COMPOSITIONS OF THE EARTH. J.Y. Hu[1], N. Dauphas[1], F.L.H. Tissot[1,2], R. Yokochi[1,3] and T.J. Ireland[1], [1]Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago IL, [2]Department of the Earth, Atmospheric and Planetary Sciences, MIT, Cambridge, MA, [3]Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, IL.

Introduction: Lanthanides are a group of 14 naturally occurring elements with atomic numbers ranging from 57 (La) to 74 (Lu), which are also known as rare earth elements (REE). REEs are ubiquitous in minerals and rocks. The chemical properties of REEs vary as smooth functions of their atomic numbers, a phenomenon known as the contraction of the lanthanides. This is the main control behind REE fractionation in minerals and rocks. The relative abundance of REEs is usually presented as the REE pattern by normalizing the concentrations in the sample to those in reference materials such as chondrites and shales.

REEs exhibit a significant range in terms of volatilities, with 50% condensation temperatures between 1647 and 1356 K at a total pressure of 10^{-4} bar according to condensation calculations [1]. Highly fractionated type II REE patterns are reported in CAIs and likely to be related to the condensation and evaporation processes that happen in the earliest stage of the solar system. Such process may induce significant isotopic fractionation on individual REEs, which is suggested by Tm abundance anomalies and Ca MDFs in CAIs. The Isotopic signature of CAIs may also be inherited in chondrites and cause planetary isotopic variations. Studying the isotopic fractionation of the REEs will shed light on the processes that occur in the early solar system.

Here we present the first systematic study on MDF of 7 REEs including Ce, Nd, Sm, Eu, Gd, Dy and Yb. The samples that we have analyzed are geostandards and span from high temperature igneous rocks to low temperature samples such as manganese nodules. Based on the samples we have measured, we estimate the isotopic composition of the bulk silicate earth.

Methodology: The samples we have studied here are geostandards which span from high to low temperature including 4 basalts (BCR-2, BHVO-2, BIR-1a, W-2), 1 andesite (AGV-2*), 1 granite (G3), 1 carbonatite (COQ-1), 1 shale (SDC1), 1 limestone (CCH-1) and 2 manganese nodules (NODA-1, NODP-1). To ensure accurate measurement, we have developed an all-Teflon, pneumatically actuated, high performance liquid chromatography system (FPLC) to purify individual REE from one another [2]. Every sample is first passed through a pre-packed TODGA column to extract REEs from the matrix [3]. The REEs of each sample are then loaded on the FPLC for separation, after which purified REEs are measured on a Thermo Scientific MC-ICPMS upgraded to Neptune Plus specifications with the addition of an OnTool Booster pump. REEs with 4 or more isotopes (Ce, Nd, Sm, Gd, Dy and Yb) are measured via double-spike technique while Eu is analyzed by Dy doping to guarantee that the precision is high enough to distinguish natural isotopic fractionation. All the REE MDFs are reported based on the in-lab isotopic standards that are prepared in the Origins Lab and available upon request.

Results and Discussion: The typical external reproducibility of the REE isotopic analyses is approximately 0.02‰ per amu (Fig. 1). For the samples that have been measured, the natural fractionations of each REE are generally homogeneous, ranging from 0.10 to 0.25‰ per amu. The ranges of fractionations are most prominent for Sm and Eu while heavy REEs do not show large fractionations. No strong relationship is observed between Ce/Eu anomalies and MDFs after considering the curvature of the REE patterns. Two manganese nodules (NODP-1 and NODA-1) show the heaviest Ce isotope composition, which are consistent with the previous study [4]. The estimated average isotopic composition of the bulk silicate earth is -0.02‰ for $\delta^{142/140}$Ce, -0.02‰ for $\delta^{146/145}$Nd, -0.18‰ for $\delta^{149/147}$Sm, +0.34‰ for $\delta^{153/151}$Eu, +0.06‰ for $\delta^{157/155}$Gd, 0.00‰ for $\delta^{163/162}$Dy and +0.02‰ for $\delta^{174/173}$Yb.

References: [1] Lodders, K. (2003). The Astrophysical Journal, 591(2), 1220. [2] Ireland (2013) Chemical Geology. 357, 203-214. [3] Pourmand A., Dauphas N. and Ireland T.J. (2012). Chem. Geol. 291, 38-54. [4] Nakada, R., Takahashi, Y., & Tanimizu, M. (2016). Geochimica et Cosmochimica Acta, 181, 89-100.
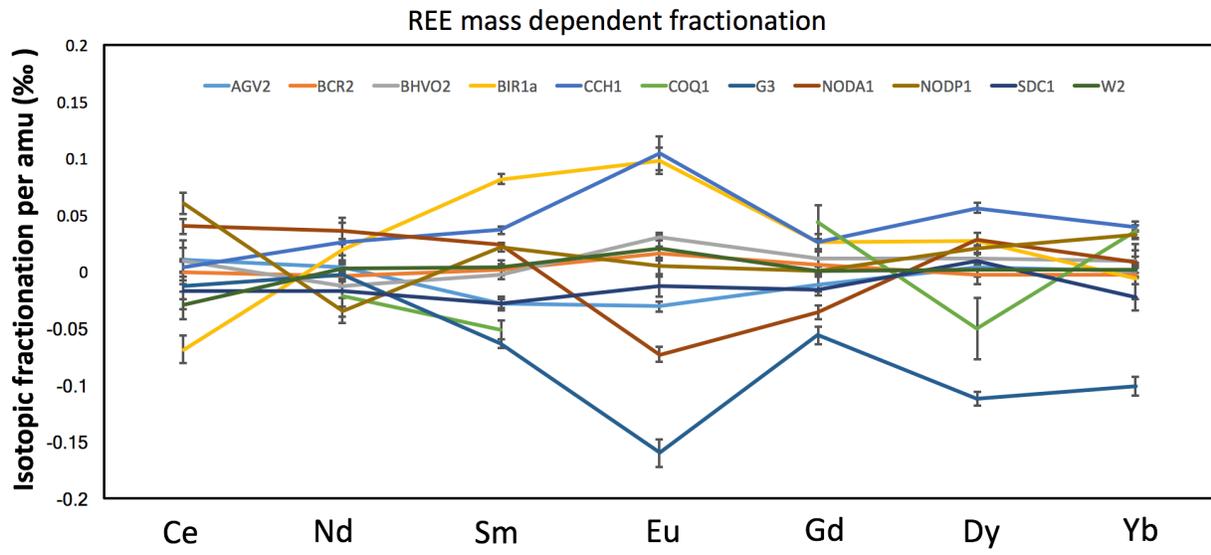
Fig. 1. Isotopic compositions of 7 REEs of geostandards. Y-axis is the isotopic fractionation of REEs per amu after renormalizing to the average of all geostandards.