

INSIGHTS INTO EVAPORATION/CONDENSATION PROCESSES IN THE EARLY SOLAR SYSTEM FROM MASS-DEPENDENT FRACTIONATIONS OF REES IN TYPE II CAIS. J.Y. Hu¹, N. Dauphas¹, F.L.H. Tissot^{1,2}, R. Yokochi^{1,3} and T.J. Ireland¹, ¹Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago IL, ²The Isotoparium, Division of Geological and Planetary Science, Caltech, CA, ³Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, IL.

Introduction: Calcium-aluminum inclusions (CAIs) are the oldest solar system objects. Their extremely old ages, and unusual chemical and isotopic compositions provide a window into the processes that shaped the solar system in its earliest stage.

Some CAIs possess a highly fractionated REE pattern known as the Type II pattern, which is characterized by a relative depletion in the most refractory REEs (Gd-Lu except Tm and Yb), a uniform enrichment in moderately REEs (Tm and La-Sm), and a depletion in the most volatile REEs (Eu and Yb) [1,2]. This fractionation pattern is commonly interpreted to represent a snapshot of the condensation sequence, whereby the most refractory and most volatile REEs are depleted and only those of intermediate refractoriness are present in their full complement [3-5]. Those CAIs exemplify the kinds of thermal processing that affected the building blocks of planets.

If the simple interpretation of type II patterns representing a snapshot in the condensation sequence is correct, then one can make predictions as to how the stable isotopic compositions of the REEs should have been affected. At the temperatures relevant to CAI condensation, little equilibrium isotopic fractionation is expected and the most likely driver would be kinetic isotope effects. In the snapshot scenario, refractory REEs are depleted because they were sequestered in an ultra-refractory phase [3-5]. During condensation of that phase, kinetic isotope effects should have enriched the condensate in the light isotopes of the REEs, leaving behind a gas residue enriched in the heavy isotopes. We would thus expect the heavy, most refractory REEs (Gd, Dy, Er and Lu) to be isotopically unfractionated or heavy isotope enriched relative to solar. The light, moderately refractory REEs should show limited isotopic fractionation. The most volatile REEs Eu and Yb are depleted because they did not fully condense. If condensation took place in a supersaturated regime, then those elements should be enriched in the light isotopes. To summarize, Eu and Yb should have normal or light-isotope enriched compositions, light REE La, Ce, Nd, and Sm (Tm would behave the same but it has only one stable isotope) should have near normal isotopic compositions, and refractory heavy REEs Gd, Dy, Er, and Lu should have normal or heavy isotopic compositions. Measuring the stable isotopic composition of the REE provides a means of evaluating whether the snapshot scenario is correct.

We have analyzed the mass-dependent fractionations of 7 REEs including Ce, Nd, Sm, Eu, Gd, Dy and Yb in a group of 6 well characterized CAIs (5 with the type II and 1 with the type V pattern). We found that the REEs display diverse behaviors that are inconsistent with the simple condensation snapshot scenario.

Methodology: The CAIs that we have analyzed were selected from a group of well characterized samples from the Allende chondrite. The sampling and digestion procedures are described in details in [6] and only briefly summarized here. The CAIs were sampled from a few Allende slabs using a stainless-steel dental tool and then grounded to fine powder. They were then digested in mixtures of HF/HNO₃/HClO₄ and HCl/HNO₃ in several steps. The digested samples were passed through 2 U/TEVA columns for separation of U. After the U chemistry, a portion of the matrix that contained all the REEs was passed through a pre-packed TODGA column to extract the bulk of the REEs [7]. The extracted REEs of each CAI were then loaded onto a FluoroPolymer Liquid Chromatography system (FPLC) developed at the University of Chicago [8,9] for separation of the REEs from each other. After separation, the REEs were measured using a combination of an Apex Omega desolvating nebulizer and a Thermo Scientific MC-ICPMS upgraded to Neptune Plus specifications. To ensure that no artificial fractionation was introduced during the chemistry, a geostandard BCR-2 that was also used in U chemistry was purified and analyzed along with the CAIs. We measured several terrestrial samples using a double-spike approach and found that the procedure induced little (< 0.05 ‰/amu) isotopic fractionation with regard to the magnitude of the isotopic variations in CAIs (up to -3 ‰/amu). Because CAIs can also be affected by nucleosynthetic anomalies and for some elements cosmogenic effects, we decided to avoid applying the double-spike approach to those samples. Two different portions of the same CAI were also processed separately to test the reproducibility.

Results and Discussion: The isotopic variations of each REE span ranges of ~0.7 (for Yb) to ~3.1 ‰/amu (for Dy), with a typical external reproducibility of 0.05 ‰/amu, meaning that the isotopic variations are well resolved. The isotopic compositions of all 7 REEs in BCR-2 are consistent with earlier measurements using

the element addition and the double-spike method [10]. The two replicates of one CAI also yield the same results within errors.

The type V CAI with flat REE pattern displayed little isotopic fractionations relative to the terrestrial standard, except for a small heavy isotope enrichment in Ce. The type II CAIs show diverse isotopic fractionation patterns when they are plotted against their atomic numbers or the 50% condensation temperatures (see the results for type II CAI “AL3S5” in Fig. 1). The heavy REEs generally show negative isotopic fractionations while the light REEs and Eu showed both negative and positive fractionations, which is not consistent with the traditional view on the formation of the Type II REE pattern. Our measurement suggests that the simple “condensation snapshot” scenario is not

valid and more complex thermal processing must have been involved, which will be discussed at the time of the conference.

References: [1] Tanaka, T., & Masuda, A. (1973). *Icarus*, 19(4), 523-530. [2] Mason, B., & Taylor, S. R. (1982). Inclusions in the Allende meteorite. [3] Boynton, W. V. (1975). *GCA*, 39(5), 569-584. [4] Davis, A., & Grossman, L., (1979). *GCA*, 43(10), 1611-1632. [5] Kornacki, A. S., & Fegley, B. (1986)., *EPSL*, 79(3), 217-234. [6] Tissot, F. L., et al. (2016). *Science advances*, 2(3), e1501400. [7] Pourmand A., Dauphas N. and Ireland T.J. (2012). *Chem. Geol.* 291, 38-54. [8] Dauphas N. et al., Patent # US 9884266B2 [9] Ireland (2013) *Chem. Geol.* 357, 203-214 [10] Hu et al. (2018) LPSC #2083

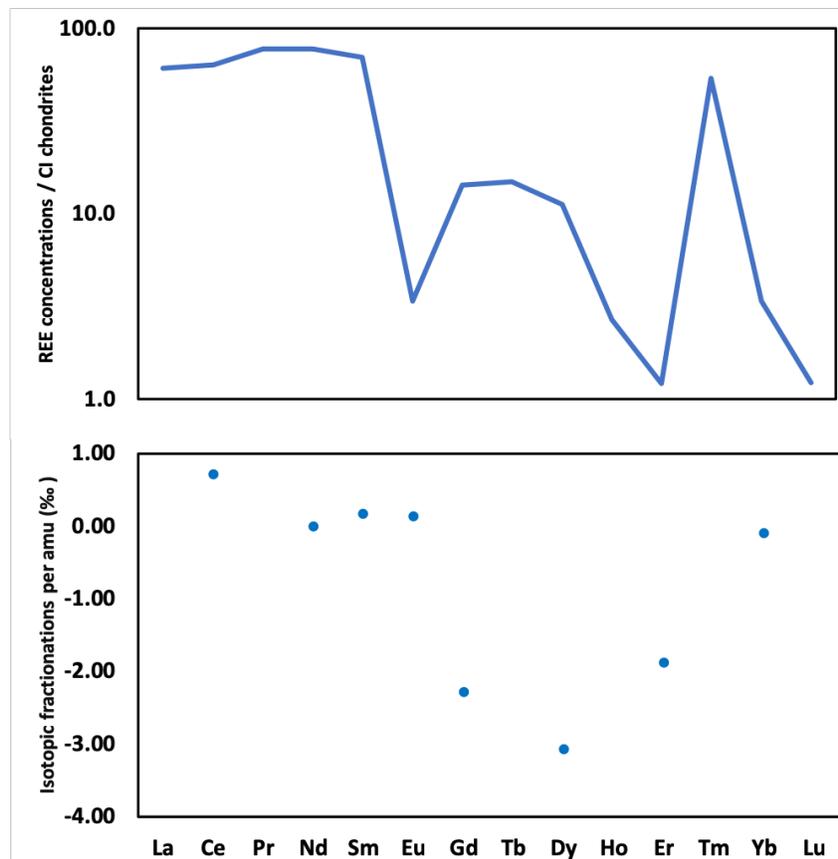


Fig. 1. REE patterns and isotopic compositions of 7 REEs of type II CAI “AL3S5”. The isotopic fractionations of the REEs (‰/amu) are normalized to the geostandard BCR-2.