CLUES TO THE ISOTOPIC EVOLUTION OF THE SOLAR SYSTEM FROM Er AND Yb IN ALLENDE

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Introduction: Information about the earliest events that occurred in the Solar System is contained within calcium-aluminum-rich inclusions (CAIs), the first solids to form in the cooling protoplanetary disk. Relative to terrestrial standards, isotopic anomalies have been observed for many elements in normal (non-FUN) CAIs of different types (e.g., coarse- and fine-grained, group II and non-group II), as well as from various meteorites and meteorite classes [e.g., 1-6]. Interestingly, the isotopic compositions of normal CAIs, (hereafter called CAIs) suggest that they formed in a region that was isotopically homogeneous, yet clearly distinct from later formed objects in the Solar System [1]. Previous work has suggested that the isotopic difference between the CAI reservoir and terrestrial standards was caused by a late addition of supernova material after CAIs condensed [1]. Thus, the goal of this work is to better understand the origin of the reservoirs present at the start of the Solar System and why the isotopic composition of materials from these reservoirs apparently changed during evolution.

This study seeks to build on previous work that has characterized nucleosynthetic anomalies of the CAI-forming region. We have utilized a well-studied sample set of CAIs from the Allende meteorite that has been analyzed for Mg, Ti, Cr, Sr, Zr, Mo, Te, Ba, Nd, Sm, Gd, Dy, and U isotopic compositions [1,5,7-9]. To continue this comprehensive study, the heavy rare earth elements (REEs), erbium (Er, Z=68) and ytterbium (Yb, Z=70) were selected for analysis. Both elements have multiple stable isotopes that are produced by the *p*-, *s*-, and *r*-process nucleosynthesis, making them ideal for this investigation. In order to further define the isotopic character of the CAI-forming region, we present the first Er and Yb isotopic compositions determined for CAIs.

Samples and Methods: Previously purified rare earth element (REE) aliquots from four Allende CAIs (CAI 164, CAI 165, CAI 168, and CAI 174) [9] were obtained for Er and Yb isotopic measurement. In order to further purify both Er and Yb, a new chemical separation procedure was developed utilizing LN-Spec resin and various volumes of 1.25M, 2.15M, and 3.5M HCl to isolate individual heavy REEs. Analysis of multiple geologic rock standards demonstrate that column yields of >90% are achieved for both elements. Following two passes through this chemistry, Er and Yb are sufficiently pure for high-precision isotope analysis.

Isotopic measurement: The Er and Yb isotopic compositions of the samples and standards were measured on a Thermo Neptune*Plus* at the University of Münster. Internal normalization was used to correct for instrumental mass bias for both isotope systems ($^{166}Er/^{168}Er = 1.2414$ and $^{174}Yb/^{172}Yb = 1.4772$).

Results: The Allende CAIs analyzed in this study are isotopically indistinguishable from one another for both Er and Yb, yet are distinct from terrestrial standards (Figs. 1 and 2). The CAI data is presented as the average of the four CAIs measured, with the uncertainty given as the 2SD of the four samples. The uncertainties presented for the terrestrial standards represent the 2SD of the long-term reproducibility of that standard over the measurement campaign.

Erbium Isotopes: Relative to the terrestrial standards, the CAIs have an average ^{170}Er deficit of -21±5 parts per million (ppm). No resolvable anomaly was detected in other Er isotopes at our current level of precision. Like previously measured isotopes in these CAIs, the Er isotopic composition can be compared to an *r*-process abundance model. Such a model adjusts the amount of *r*-process atoms in the material of interest. The data and best fit to the data are shown in Fig. 1. It is noted that no uncertainties are taken into account for the model, possibly explaining the mismatch with ^{167}Er.
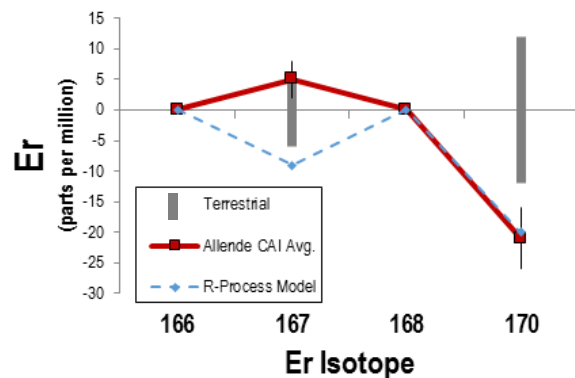

Fig. 1 – The average Er isotopic composition of four Allende CAIs. The y-axis shows the deviation from the terrestrial standards in ppm and the isotopes of Er are given on the x-axis. The dashed blue line is the "best fit" *r*-process deficit model based on *r*-process abundances from [10].

Ytterbium Isotopes: The CAIs measured in this study have an average ^{176}Yb deficit of -56±5 ppm relative to the terrestrial standards. No resolvable anomaly was detected in ^{173}Yb at our current level of precision. Like the Er isotopic data described above, the Yb data

can be compared to an *r*-process abundance model. Both the data and model are shown in Fig. 2. Similar to Er, the Yb data is not a perfect fit to the model, however the misfit of [173]Yb could again be due to uncertainty in the model which is not taken into account.
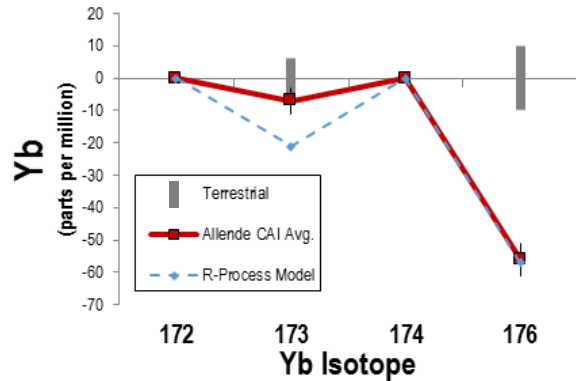

Fig. 2 – The average Yb isotopic composition of four Allende CAIs. The y-axis shows the deviation from the terrestrial standards in ppm and the isotopes of Yb are given on the x-axis. The dashed blue line is the "best fit" *r*-process deficit model based on *r*-process abundances from [10].

Discussion and Conclusions: The stable isotope compositions of almost all elements studied in CAIs, regardless of petrology or group, and including new isotopic data for Er and Yb, strongly supports an isotopically homogeneous CAI reservoir [1-6]. The vast majority of non-radiogenic isotopic differences between CAIs and terrestrial standards can be attributed to excesses or depletions in the amount of *r*-process derived material in the samples, regardless of minor mismatches with the *r*-process model. For the elements Sr to Ba (Z=38 to 56), CAIs are relatively enriched in *r*-process material, trending uniformly with the mass of the element towards the terrestrial value, from ~90 to ~10 ppm (Fig. 3) [1]. Interestingly, the studied REEs (Z=60 to 70) in CAIs have a relative deficit in *r*-process derived material compared to terrestrial standards. The previously observed systematic trend of decreasing *r*-process derived material with element mass in earlier versions of Fig. 3 [1, 5] is slightly disrupted by the addition of Er and Yb isotopic compositions. Whereas the significance of this trend remains unknown, its disruption may simply be a lack of understanding of the nucleosynthetic processes creating certain isotopes and/or the omission of uncertainties from both the nucleosynthetic model and the isotopic measurements generating Fig. 3.

For elements heavier than Yb (not shown in Fig. 3), the interpretation is less straightforward. Data from Hf isotopes in CAIs appears to be mostly consistent with a large *r*-process deficit [11]; however the existing dataset is insufficient to allow definitive statements about the homogeneity of the CAI-forming region for Hf. Additionally, large variations in the stable W isotope compositions of fine-grained CAIs are suggestive of large *r*-process excesses, whereas coarse-grained CAIs show little to no W isotope anomalies [12]. The reason for this variation is unknown, however it is possible that the difference is a function of the primary carrier phase of the studied elements in CAIs, as W is a siderophile element whereas many of the other elements studied are primarily lithophile under most conditions.
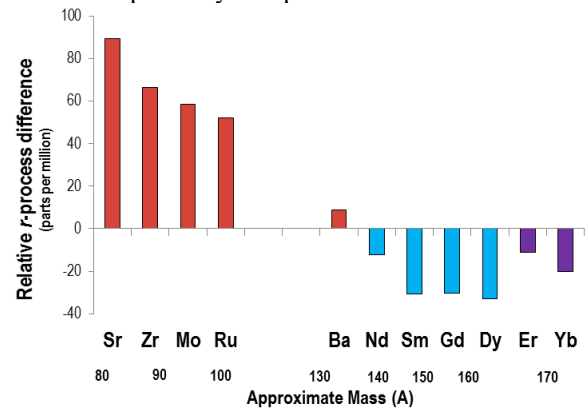

Fig. 3 – The relative *r*-process difference between CAIs and terrestrial standards (in ppm) on the y-axis plotted against elements of increasing mass. The terrestrial composition is defined as zero for each element. Figure modified from [1,5] with the addition of Er and Yb (in purple) from this study.

Regardless of the current uncertainties in a few individual elements, the isotopic character of the CAI-forming region is clearly defined by *r*-process enrichments and depletions of varying magnitudes, depending on the element investigated. The transition between the isotopic character of the CAI reservoir (defined in Fig. 3) to the isotopic character of later formed phases may be evidence for the late addition of supernova material with a reciprocal isotopic composition not incorporated into the CAI-forming region [1].

References: [1] Brennecka et al. (2013) *PNAS*, *110*, 17241. [2] Burkhardt et al. (2011) *EPSL*, *312*, 390. [3] Moynier et al. (2012) *Astrophys J*, *785*, 45. [4] Hans et al. (2013) *EPSL*, *374*, 204. [5] Brennecka et al. (2014) *LPS 45,* #2280. [6] Shollenberger et al. (2015) *LPS 46*, #2593. [7] Mercer et al. (2015) *LPS 46*, #2920. [8] Brennecka et al. (2015) *Goldschmidt 2015*, #385. [9] Brennecka et al. (2010) *Science,* 327, 449. [10] Bisterzo et al. (2011) *Mon. Not. R. Astron. Soc.*, *418*, 284. [11] Akram et al. (2013) ApJ 777, 169. [12] Kruijer et al. (2014) *EPSL*, 403, 317.