HEAVY RARE EARTH ELEMENT ISOTOPICS FROM CHEMICAL SEPARATES OF THE MURCHISON METEORITE: IMPLICATIONS FOR SiC FORMATION.

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Introduction: The formation and evolution of the Solar System can be explored by examining the isotopic compositions of primitive chondrites and their components. For example, numerous studies have reported nucleosynthetic isotopic variation between bulk meteorite groups for elements like Zr, Mo, Ru, and Nd [*e.g.*, 1-5]. Furthermore, step-wise acid leaching to chemically isolate components of primitive chondrites reveals isotopic anomalies in elements such as Cr, Sr, Mo, Ba, Sm, Nd, Hf, W, and Os [*e.g.*, 6-9]. Such nucleosynthetic anomalies at both the bulk and component scales have been attributed to variable contributions of nucleosynthetically anomalous material such as presolar grains.

Studies employing chemical separation of meteoritic components via acid leaching are designed to concentrate presolar carrier phases. For example, [7] reported *s*-process excesses in the final leaching step for Ba, Nd, Sm, and Hf that were interpreted to reflect presolar SiC, a typical phase formed in outflows of AGB stars. Whereas many elements have been studied in bulk meteorites and acid leachates of primitive meteorites to better understand the *s*-process and its contributions to our stellar system, a knowledge gap exists for heavier isotopic systems ($62 < Z < 74$).

This work seeks to address this gap by examining the isotopic signatures of the heavy rare earth elements (HREEs), dysprosium (Dy, Z=66), erbium (Er, Z=68) and ytterbium (Yb, Z=70). Thus far, only Yb has been analyzed previously in bulk meteorites and no isotopic variations were found at the reported level of precision [10]. This outcome suggests that if isotopic anomalies in HREEs are present in bulk meteorites, they are not easily detected. As such, we present Dy, Er, and Yb isotopic compositions of a bulk dissolution of the primitive CM2 Murchison meteorite, but additionally from step-wise acid leachates of the same sample to 1) study the *s*-process in HREEs, 2) probe the presolar carriers of these REEs, and 3) examine the condensation history of SiC.

Methods: Approximately 6g of the Murchison meteorite (generously provided by the Field Museum Chicago) was processed through a similar acid leaching procedure as [8] by the following steps:

1) 25mL acetic acid + 25mL H_2O, 1 day, 20 ºC
2) 12.5mL HNO_3 + 25mL H_2O, 5 days, 20 ºC
3) 15mL HCl + 17.5mL H_2O, 1 day, 75 ºC
4) 15mL HF, 7.5mL HCl, 7.5mL H_2O, 1 day, 75 ºC
5) 7.5mL HF + 7.5mL HCl, 3 days, 150 ºC
6) 7mL HNO_3 + 14mL HF, 5 days, 200 ºC

Additionally, a matrix cut from a digestion of bulk Murchison was obtained for analysis from [11]. For all samples, the REEs were removed from the sample matrices following previously established methods [*e.g.*, 12]. Dysprosium, Er, and Yb were separated from the REE cuts, purified, and their isotopic compositions were measured on a Thermo Neptune*Plus* at the University of Münster using similar methods as [13]. Internal normalization was used to correct for instrumental mass bias for all isotope systems ($^{164}Dy/^{162}Dy = 1.107$, $^{166}Er/^{168}Er = 1.2414$, and $^{174}Yb/^{172}Yb = 1.4772$).

Results: The Dy, Er, and Yb isotopic compositions are presented below in ε-notation (parts per ten thousand deviation from the average isotopic compositions of terrestrial rock standards). The uncertainties shown represent the 2SD of replicate analyses of these standards run under similar conditions. Note that the fourth and fifth leaching steps are not presented below as these steps did not contain enough of the elements of interest to obtain meaningful data.

Selected Dy, Er, and Yb isotopic compositions of bulk Murchison and its leachates are shown in Fig. 1. These pairs of isotopes were selected as they allow for the clearest distinction between *s*- and *r*-process variations for each element. For Dy and Er, all leaching steps display resolved isotopic variations that plot along well-defined correlations (Fig. 1a/b), with the most anomalous steps being the first and last leachates, similar to previous observations for other elements [*e.g.*, 7]. In comparison, the leachates of Yb show much smaller isotopic variation (Fig. 1c). Additionally, whereas the leachates also define a correlation in Yb isotope space, leachate six—the most aggressive step that reportedly dissolves presolar SiC—is less anomalous than leachate three. This is in stark contrast to what is observed in Dy and Er, and other REEs [7].

Discussion: Acid leachates of the Murchison meteorite reveal Dy, Er, and Yb isotopic anomalies of varying magnitudes (Fig. 1). Similar to previous studies of other elements [*e.g.*, 7], the Dy, Er, and Yb data fit well to *s*-process models, indicating that the variations are caused by more or less of a certain material, likely SiC grains from AGB stars. Additionally, bulk Murchison plots in the direction of an *s*-deficit relative to the Earth (≡0), however, we note that the Dy, Er, and Yb anomalies are not all resolved from the terrestrial composition. Regardless, the observation that bulk Murchison may have formed from material with an *s*-deficit relative to the Earth is consistent with other elements such as Zr, Mo, Ru, and Nd [*e.g.*, 1-5].
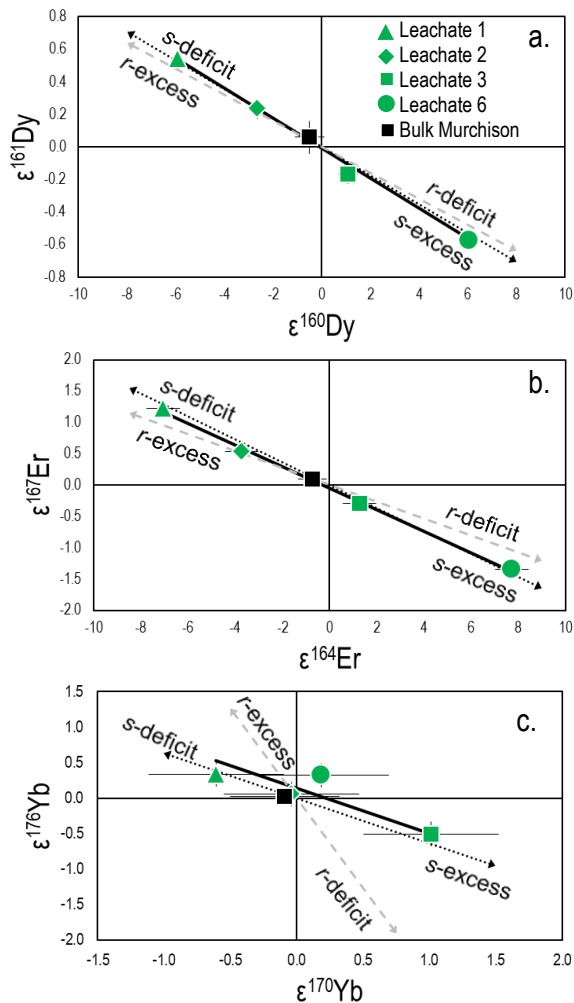
Fig. 1 – a) ε^{160}Dy v. ε^{161}Dy for Murchison leachates and bulk Murchison. The grey dashed (*r*-process) and black dotted (*s*-process) lines are mixing lines between terrestrial Dy and *p*-/*s*-/*r*-process Dy (*p*-, *s*-, and *r*-process contributions to each isotope were taken from [15]). Solid black line is a best fit through the leachates. b) Same as (a) but for ε^{164}Er v. ε^{167}Er. c) Same as (a) but for ε^{170}Yb v. ε^{176}Yb.

Due to the fact that Dy, Er, and Yb are all HREEs, they are expected to (geo-) chemically behave similarly. However, Yb anomalies in these leachates are markedly smaller than other REEs (Fig. 1), exhibiting approximately an order of magnitude lower *s*-process excess (the calculated difference in the amount of *s*-process derived material in a sample relative to Earth) in the same leachate compared to Dy and Er. We postulate that the reason for this isotopic incongruity is the relative concentrations of REEs in SiC grains. As shown by [14], the concentration of Yb in SiC is approximately an order of magnitude lower than other neighboring REEs, supporting what is seen in the isotopic data from multiple studies (Fig. 2). This indicates

a decoupling of Dy and Er (and other refractory REEs) from Yb during SiC formation that is likely due to their disparate condensation temperatures, shown in Table 1. This combined data shows that isotopically anomalous Dy and Er are condensing into the SiC while Yb remains in the gas phase, indicating that SiC forms between the condensation temperatures of Dy-Er and Yb. Because leachate six—the most chemically aggressive step—contains the highest *s*-process excess for Dy and Er, this suggests that the presolar carrier for the refractory REEs is indeed SiC. However, for Yb, the most *s*-process enriched phase is leachate three, suggesting a less refractory presolar phase as its carrier, such as a silicate or oxide.
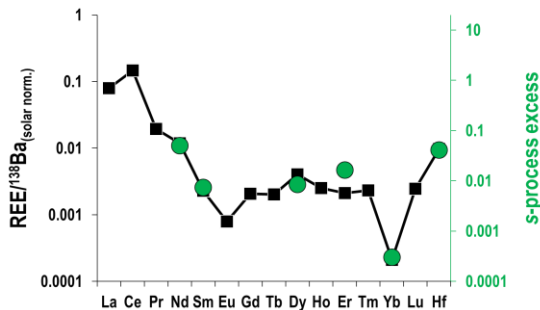
Fig. 2 – Select trace elements plotted against their concentration in SiC (left axis; black squares; data from [14] and their calculated *s*-process excess (in %, relative to terrestrial) in the most aggressive leachate step (this work; green circles; *s*- and *r*-process contributions to each isotope were taken from [15]). Nd and Sm isotopic data from [7]. Hf isotopic data measured in this work from the same Murchison leachates and in agreement with Hf data from [7].

Table 1 – 50% Condensation temperatures (T_c) of select elements from [16].

Element	~50% T_c
Nd, Sm	1590
Eu	1350
Gd, Dy, Er, Lu	1650
Yb	1475
Hf	1675

References: [1]Burkhardt et al. (2011) *EPSL*, **312**, 390. [2]Akram et al. (2015) *GCA*, **165**, 484. [3]Fischer-Gödde et al. (2015) *GCA*, **168**, 151. [4]Bouvier & Boyet (2016) *Nature*, **537**, 399. [5]Burkhardt et al. (2016) *Nature*, **537**, 394. [6]Dauphas et al. (2002) *ApJ*, **569**, L139. [7]Qin et al. (2011) *GCA*, **75**, 7806. [8]Reisberg et al. (2009) *EPSL*, **277**, 334. [9]Burkhardt & Schönbächler (2015) *GCA*, **165**, 361. [10]McCulloch et al. (1977) *GCA*, **41**, 1703. [11]Goldmann et al. (2015) *GCA*, **148**, 145. [12]Shollenberger et al. (2018) *GCA*, **228**, 62. [13]Shollenberger et al. (2018) *EPSL*, **495**, 12. [14]Ireland et al. (2018) *GCA*, **221**, 200. [15]Bisterzo et al. (2011) *Mon. Not. R. Astron. Soc.*, **418**, 284. [16]Lodders (2003) *ApJ*, **591**, 1220.