

CHARACTERIZATION OF THE RARE EARTH ELEMENTS IN MURCHISON LEACHATES: RELATIVE ABUNDANCES AND FUTURE PROSPECTS. T.J. Ireland¹, N. Dauphas¹, ¹Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, USA (tireland@uchicago.edu)

Introduction: Several studies of primitive, un-equilibrated meteorites have revealed the existence of isotopic variations of nucleosynthetic origin at both the bulk rock and internal (within-rock) scales [e.g., 1-11]. These isotopic variations are mainly attributable to the presence of pre-solar grains, which may have formed in different astrophysical environments and may record information about the p-, s- and r-nucleosynthetic processes. Generally, isotopic variations at the bulk meteorite scale are smaller (or, in some cases non-existent) than the within-rock (i.e., individual grains/components) scale. One technique to access the within-rock components is by sequential acid leaching, involving step-wise dissolution of a meteorite powder progressing from weaker to stronger acids.

In terms of the rare earth elements (REE) particular attention has been paid to Sm and Nd in both leachates and bulk meteorites [3-5, 9]. These two elements are of particular importance because of complementary decay schemes involving the decay of Sm to Nd ($^{147}\text{Sm} \rightarrow ^{143}\text{Nd}$ $t_{1/2}=106$ Gyr; $^{146}\text{Sm} \rightarrow ^{142}\text{Nd}$ $t_{1/2}=103$ Myr). However, isotopic data on the other REE are sparse. Obtaining precise isotopic data for all the multi-isotopic REE from the same sample can potentially shed additional light on the nucleosynthetic processes that produce the REE.

Here, we report REE abundance data for six leachates derived from the Murchison CM2 chondrite, along with some preliminary REE separation experiments. Previous studies of these leachates showed that large isotopic anomalies are present for both Os [7] and Cr [11]. The ultimate goal of this work is to develop a chromatographic separation technique for isotopic analysis of the individual REE to determine their carrier phases and to constrain the nucleosynthetic processes that produced the REE.

Methods: The six Murchison leachates were previously described in detail by Reisberg et al. [7] and involved the sequential dissolution of 16.57 g of the meteorite by the following steps:

- Step 1) 50 mL acetic acid + 50 mL H₂O, 1 day, 20 °C
- Step 2) 25 mL HNO₃ + 50 mL H₂O, 5 days, 20 °C
- Step 3) 30 mL HCl + 35 mL H₂O, 1 day, 75 °C
- Step 4) 30 mL HF + 15 mL HCl + 15 mL H₂O, 1 day, 75 °C
- Step 5) 10 mL HF + 10 mL HCl, 3 days, 150 °C
- Step 6) 1 mL HNO₃ + 3 mL HF, 170 °C, 5 days

Bulk REE Separation: Small aliquots of each leachate were dried down and re-dissolved in 3 mL of

3 M HNO₃. The leachate aliquots were then loaded onto a 2 mL Eichrom TODGA cartridge following the procedures outlined by Pourmand et al. [12]. After the removal of the matrix elements, the REE were eluted in 0.05 M HCl.

Ln-Resin Separation Experiments: Experiments for the separation of the individual REE were conducted using Eichrom Ln-resin, which uses di(2-ethylhexyl) orthophosphoric acid (HDEHP) as the extractant phase. On this particular resin, the affinity of the REE with HDEHP increases with atomic mass. Thus, the lighter REE, which have a lower affinity, can be eluted with weaker acids and the heavier REE with stronger acids [13]. Partition data exist for the REE in HNO₃ on this resin [13], but to our knowledge are lacking for HCl.

The partition coefficients of the REE on Ln-resin, as a function of HCl acid molarity, were determined by a series of batch equilibration experiments. Multi-element solutions that contained ~10 ppm of each REE were mixed at various HCl molarities ranging from 0.01 M to 10 M. About 5 mL of each HCl molarity were added to 300 mg of resin, and allowed to equilibrate over 8 hours with an agitation step every 2 hours. Following equilibration, the mixture was filtered to obtain the acid fractions [14].

Mass Spectrometry: All samples were dried down and re-dissolved in 3 mL of 3% HNO₃, in preparation for mass spectrometry. The REE were analyzed on a Thermo Neptune ICP-MS at the University of Chicago following the methods of Pourmand et al. [12].

Results and Discussion:

Bulk REE Separation on Leachates: CI-chondrite normalized REE data for each leachate are presented in Figure 1A, while Panel 1B shows the relative fraction of the REE in each leachate. The highest concentrations of REE were present in the final leachate step, which contains the most refractory and acid-resistant phases present in the meteorite. However, this leachate comprises a small overall percentage of the meteorite, so only contains ~10 to 20% of the REE. Leachate 1, on the other hand, possesses a lower concentration of REE, but represents a much larger percentage of the whole rock REE content (35 to 80%). Despite having different shapes, leachates 2 and 3 have similar REE concentrations and are characterized by a comparable overall percentage. Leachates 4 and 5 have very low REE abundances, and represent less than 0.3% of the whole rock REE budget.

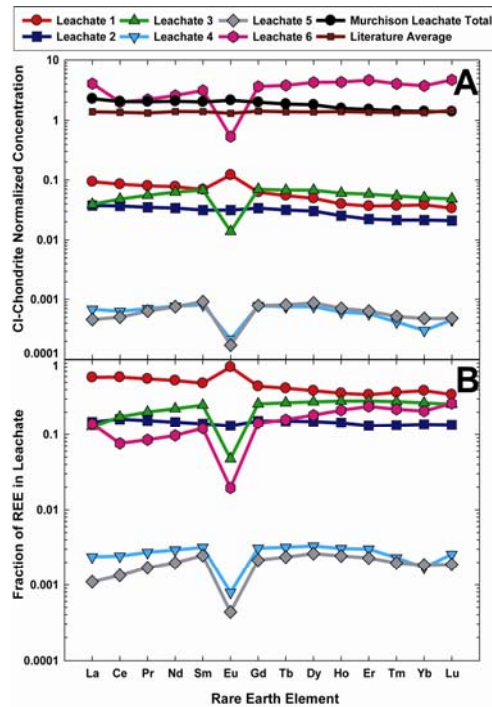


Figure 1: A) CI-chondrite normalized [15] REE data for each leachate step. The black line represents the sum of each leachate step, while the brown line is a compilation of literature values [16-17]. B) Fraction of the bulk-rock REE budget that is contained in each leachate.

Leachates 3-6 have similar REE patterns, with a common Eu depletion and a generally concave up configuration. Leachate 2 is essentially flat, but may have a slight HREE depletion. Leachate 1 contains the majority of the Eu present in the meteorite (~80%), and is slightly enriched in the LREE relative to the HREE.

There is a slight discrepancy in the overall abundances of the LREE to MREE, calculated by adding the leachate steps together, and previously reported REE data for Murchison [16-17], although the HREE show excellent agreement. The exact reason for this is unclear; however, it is apparent that leachate 1 can account for much of the disagreement. This interpretation is most clearly seen in the Eu abundance of leachate 1, as well as by the LREE abundances. Another factor to consider is that the leachates were generated from a larger sample size (16.57 g) than the previous studies.

Ln-resin Separation Experiments:

Partition coefficients for the REE on Ln-resin in HNO_3 have been previously published [13]; however, in several recent studies [18-19] the REE have been eluted in HCl. These studies indicate that separation

factors of the REE on Ln-resin may be greater in HCl than HNO_3 .

The data from the batch equilibrium experiments are presented in Figure 2. The partition coefficients (K_d) for each REE at each acid molarity was calculated based on the following formula [14]:

$$K_d = \frac{(C_B - C_A)/w}{C_A/V}$$

where C_B and C_A are the concentrations of REE before and after equilibration, w is the weight of resin and V is the volume of acid used in the equilibration experiment. The chromatographic technique that we are developing to separate the individual REE from each other will be based on these partition coefficient data.

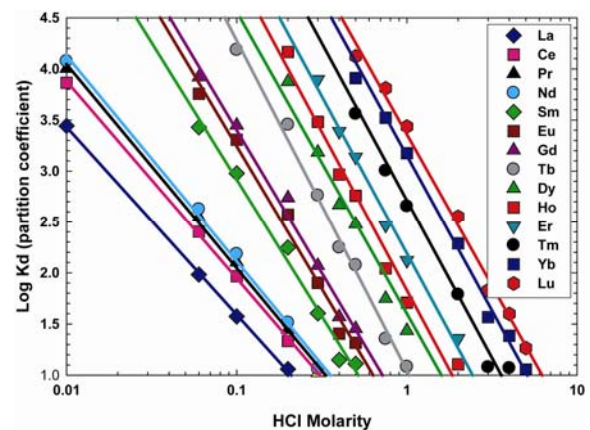


Figure 2: Partition coefficients of the REE on Ln-resin at various HCl molarities. The REE elute in order of atomic mass as acid molarity increases.

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