

A NOVEL TECHNIQUE FOR ACCURATE ANALYSIS OF LANTHANIDES, SC AND Y IN METEORITES: TOWARDS A REEVALUATION OF COSMIC ABUNDANCES. A. Pourmand^{1,2}, N. Dauthas², T. Ireland², ¹The University of Miami, RSMAS-MGG, 4600 Rickenbacker Causeway, Miami, FL 33149 (apourmand@rsmas.miami.edu), ²Origins Laboratory, Department of the Geophysical Sciences & Enrico Fermi Institute, The University of Chicago, 5734 South Ellis Avenue, Chicago, IL 60637.

Introduction: Over the last two decades, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has increasingly become the preferred method for determination of rare earth elements (REE) in geological material [1-3]. The use of Multi-Collector (MC) ICP-MS has been recently explored in conjunction with laser ablation and isotope dilution mass spectrometry to measure the concentration of a number of REEs [4-5]. Accurate and precise analysis of REEs requires: a) complete digestion of refractory phases, b) successful separation of interfering matrix elements, c) maintaining low procedural blanks, and d) elimination of molecular interferences prior to data acquisition. We present a novel procedure that takes advantage of high-purity borate fusion to achieve complete sample digestion, a single-stage extraction chromatography step for matrix separation, and MC-ICP-MS for measurement of multiple isotopes, including the concentration of mono-isotopic elements. The concentrations of 16 REEs (Lanthanides, Y and Sc) in standard materials are compared with literature values to examine the effectiveness of the proposed protocol. These improvements will help reexamine the cosmochemical behavior of lanthanides in meteorites. Measurements of Orgueil (CI1), Ivuna (CI1), Tagish Lake (C2-ungrouped), and Allende (CV3) reference powder are presented.

Sample digestion: Borate flux fusion is superior to other methods of sample dissolution (*e.g.*, HF Parr bomb and hotplate acid digestions) in its ability to rapidly achieve complete dissolution of refractory phases that commonly occur in meteorites. Nevertheless, acid dissolution is generally preferred due to higher procedural blanks associated with commercially manufactured borate fluxes. We have developed a straightforward purification scheme to reduce blank levels in commercial borate fluxes [6]. Following purification, approximately 15-60 mg of geostandard and meteorite powders were fused with LiBO₂ in high-purity graphite crucibles at a flux:sample ratio > 7 for 12 minutes. The melt was directly dissolved in 15 mL of 3 mol L⁻¹ HNO₃ for matrix separation.

TODGA chromatography: The flux solution was directly loaded to a 2-mL Eichrom TODGA cartridge. REEs were separated from the matrix following the procedure presented in figure. 1. The behavior of REEs in HNO₃ and HCl on the TODGA resin has been discussed in detail elsewhere [6].

MC-ICP-MS analysis: A Thermo Scientific Neptune MC-ICP-MS (Origins Laboratory, University of Chicago), interfaced with an Apex Q + Spiro TMD desolvating nebulizer, was used for the analysis of all elements. Representative isotopes, specifically selected to avoid isobaric interferences, were arranged in nine Faraday collectors and five cup configurations. A unique aspect of this collector arrangement is that ¹⁴⁹Sm and ¹⁶⁷Er isotopes are measured in all cup configurations to allow normalization of light REE and heavy REE to MREE (Sm-Er). As a result, the effect of signal instability caused by fluctuations in the plasma and the desolvating nebulizer is minimized. This is a major advantage over using single-collector ICP-MS for accurate determination of elemental ratios. The data acquisition consisted of 1 block of 5 cycles with 4.2 s integration time in dynamic mode. An idle time of 3 seconds was applied prior to making measurements in each collector configuration. Concentrations were measured by standard bracketing using a multi-element standard solution. Final concentrations are based on the mean of 2-3 analyses for each sample solution over the course of the run session. A total of 0.5 mL solution was consumed per sample analysis. Low-blank flux fusion, rapid matrix separation and the ability to measure elemental concentrations ratios of all 16 REEs *in a single solution* at pg g⁻¹ to ng g⁻¹ levels distinguish this method from previous sample digestion and MC-ICP-MS techniques [4-5].

Results and conclusions: *Blanks:* Mean procedural blanks (n=3) for Sm to Lu were < 81 pg. Higher blank levels were observed for Y (445 pg), Ce (305 pg) and Nd (268 pg). Blank corrections for all elements in BCR-2, BIR-1 and BHVO-1 were << 0.006 %. Corrections for PCC-1 were higher on average (8.4 %) due to much lower concentrations of REEs in the peridotite geostandard. Minor blank corrections were also implemented for Orgueil (0.31 %), Ivuna (0.4 %), Tagish Lake (0.86 %) and Allende (0.14 %).

Geostandards: REE concentrations normalized to the compiled values of Orgueil [7] for four geostandards are presented in figure 2. The REE patterns (including Y and Sc not shown) are in excellent agreement with recommended literature ratios at 95 % confidence interval, and demonstrate the effectiveness of the proposed analytical method.

Meteorites: The pattern of REEs in all meteorites relative to recommended Orgueil are presented in figure 3. The absolute REE concentrations of lantha-

nides in Orgueil are close to the values from literature compilation [7] within the uncertainties (5-7 %). Nevertheless, the REE pattern of Orgueil is not entirely flat and varying degrees of fractionation become evident from using different literature compilations for CI-chondrites. The REE pattern for Ivuna shows enrichment in light REE (La-Sm) and depletion in heavy REE (Gd-Lu). This raises some concern regarding the use of averaged CI-chondrite values as a representative for solar abundances. Although the origin of Tagish Lake is debated [8] and it remains ungrouped, its Orgueil-normalized REE pattern is similar to the observed pattern of Orgueil (Fig. 3). Previous REE patterns published for Tagish Lake, however, are not as smooth [8-9], which may have been the result of small sample size. The sample analyzed in this study came from a large amount of homogenized powder, and is therefore less prone to anomalies due to sample inhomogeneity. The results for Allende standard powder demonstrate group II-type REE patterns that have been associated with some Ca-Al-rich Inclusions (CAI) in CV3 chondrites [10-11]. Partial removal of refractory condensates and incomplete condensation of most volatile elements may be responsible for the fractionation observed in REE pattern in CV3 carbonaceous chondrites [e.g., 12].

Our group is currently analyzing the concentrations of additional meteorites. The results will be used to re-evaluate the cosmic abundances of REEs and constrain the cosmochemical behavior of these elements.

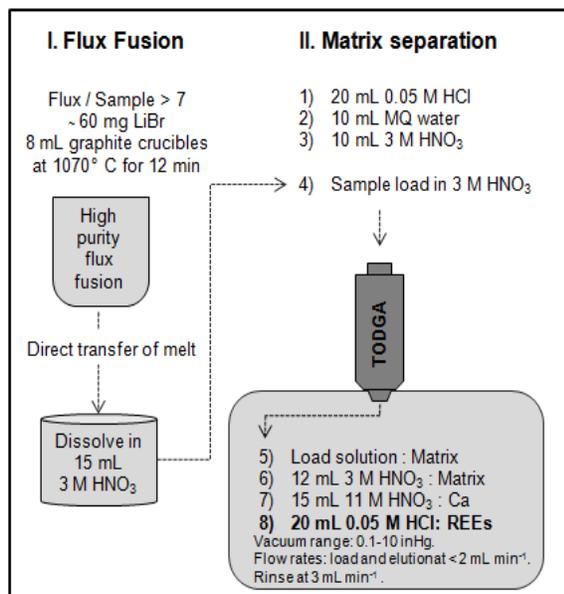


Figure 1. A rapid, high-purity borate fusion and TODGA cartridge chromatography protocol developed in this study for sample digestion and separation of REEs, Sc and Y from rock matrices.

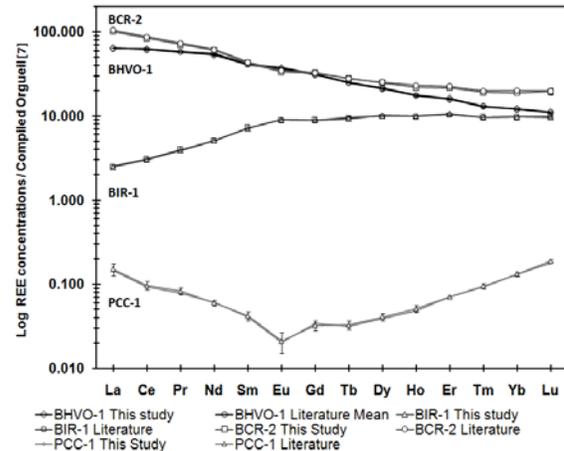


Figure 2. Concentrations of lanthanides in BCR-2, BHVO-1, BIR-1 and PCC-1 geostandards, normalized to compiled Orgueil values from literature [7], are in excellent agreement with recommended values for these geostandards within 95 % confidence interval.

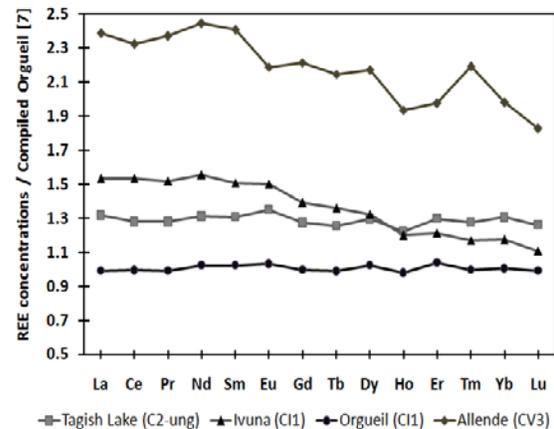


Figure 3. Concentrations of lanthanides in Allende standard powder, Ivuna, Tagish Lake and Orgueil, normalized to compiled Orgueil values [7]. Note the group II-type REE pattern in Allende. Tagish lake and Orgueil show similar patterns. Ivuna shows enrichment in LREE (La-Sm) and depletion in HREE (Gd-Lu). REE values in Allende, Ivuna and Orgueil are normalized to Lu concentrations determined by isotope dilution.

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