INTRODUCING TEFLON-HPLC.

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Introduction: With increasingly ambitious sample return missions and instrumentation of ever-increasing sensitivity and precision, column chromatography appears to be the neglected step-child of isotope geochemistry and little improvement has been brought to it in the past few decades. Traditional column chromatography (*i.e.*, open-system, gravity driven) techniques suffer from significant limitations pertaining to the overall length of column, resin size and diffusion effects, which can severely compromise separation efficiencies. Furthermore, some fine-scale separations still require complicated multi-step, highly time-consuming protocols (*e.g.* Ni-Mg, [1]). High-performance liquid chromatography (HPLC), while overcoming many of these limitations (*e.g.* a closed-system setup; the ability to pressurize the system, hence longer columns and better separation; a semi-automated set-up), is not immune to severe drawbacks. Mainly, 1) the liquid flow path often contains glass or metal parts which are easily corroded/dissolved by concentrated acids or organic solvents, leading to contamination of the samples, and 2) the electronic controls and housing are often spatially associated with the HPLC unit, drastically shortening the lifespan of the apparatus as the metallic parts rapidly corrode in these harsh chemical environments [*e.g.* 2].

Here, we address these issues in order to enable high precision analysis of precious (*i.e.* small size) samples acquired through elaborate sample return missions by introducing the first Teflon-HPLC (T-HPLC) system. We demonstrate in one practical example the type of improvement T-HPLC can bring to the community, and what future developments we will pursue.

T-HPLC Overview:

The T-HPLC was constructed at the Origins Lab at the University of Chicago and a detailed description of its distinctive features can be found in [3,4].

The key features are:

1) fully automated elution schemes controlled through LabView software interface, which enables for (i) fresh mixing of reagents for each elution steps and (ii) gradient/ramp elutions, while removing the human error/non-reproducibility component,

2) temperature control of the system (up to 80°C) for enhanced chemical separations,

3) a modular design making the system adaptable to a variety of separation schemes by quick and inexpensive change of the resin type or column length.

The system (Fig. 1) is composed of six Teflon reservoirs (for reagent storage), connected to a mixing chamber via Teflon pumps. The pumps deliver 40 μL of liquid per stroke, allowing for very precise mixing proportions (*i.e.* molarities) to be achieved. The mixing chamber is custom made in 25% carbon filled Teflon. A Teflon coated stirring magnet is externally activated and mixes the reagents in the chamber. When the reagents are mixed, the chamber is pressurized with dry N_2 which forces the liquid through the column. At the bottom of the column, a manifold distributes the liquid into various beakers, allowing for the system to run unattended. A liquid level sensor at the base of the chamber sends a signal when the chamber is empty, which triggers a valve below the chamber to close (thus isolating the column) and for the chamber to be vented before the next reagent mixture is prepared.

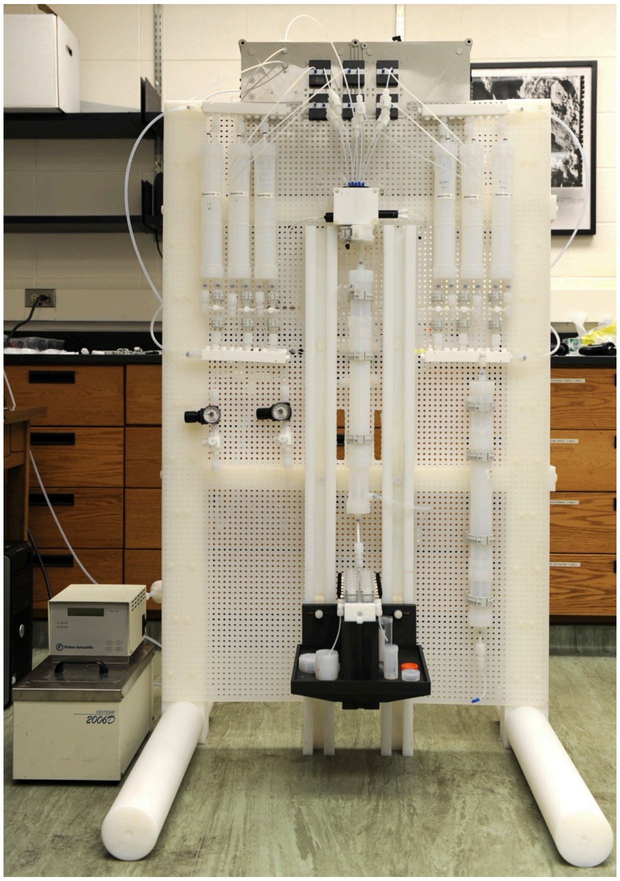

Fig. 1. *Picture of the Teflon-HPLC developed at the Origins Lab (University of Chicago). See text for details.*

Separation of Individual Rare Earth Elements

The REE comprise a suite of 14 elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) known for their similar partitioning characteristics. As such, they have proven to be very challenging to separate from one another [5]. To date, the separation of all the individual REE from each other has not been successful – only studies focused on subsets of the REE have been reported in the literature [6-9].

We tested the performance of the T-HPLC by trying to separate individual REE from each other in one column pass. We used a multi-element REE solution (REE + Sc + Y, 10 mg/g), and a 70 cm long column (ø=0.3 cm) filled with Ln-resin (25-50 μm resin bead size). The experimental temperature was set at 70 ^{o}C and the pressure adjusted to provide a flow rate of ~0.5 mL/minute. The resin was cleaned with 10 M HCl, and conditioned with 0.05 M HCl. The standard solution was loaded in 10 mL of 0.05 M HCl. Utilizing an elution curve simulation program we developed to optimize our separation, we devised an elution scheme that slowly increases HCl molarity along a convex ramp starting at 0.10 M HCl and increasing to 10 M HCl. The total elution volume was 700 ml. The elution parameters were read by the LabView program as a single file, and the automatic elution scheme was successfully completed.

The eluted solution was collected in small fractions (2 to 4 mL increments) later evaporated and picked up in 3% nitric acid for analysis on the Neptune ICP-MS.

The results of the elution are plotted in Fig. 2. In general, there is excellent separation of the multi-isotopic REE from each other. Some overlap of mono-isotopic REE (Pr, Tb, Ho) with neighbouring multi-isotopic REE remains but that is not a big concern since there are no isobaric interferences between these isotopes. This result (Fig.2.) demonstrates the effectiveness of our system and its great potential to tackle even the most difficult of column chromatography techniques.

Future Improvement of the T-HPLC:

Since these first results, the T-HPLC system was upgraded (Fig .1) to pneumatically actuated valves and pumps, as the acid fumes were sufficient to corrode and damage the electronics of our initial setup. These new components tend to have a longer lifetime (*i.e.,* more actuations) and are made almost entirely out of Teflon. The electronics, which control the gas flows to the pneumatic pumps and valves, are enclosed in a positively pressurized case, and is thus further isolated from acid fumes. Lastly, we are trying to improve on the presented separation of REE. Some tailing exists (only visible on a log scale elution curve) and account for up to 0.75% of overlap between neighboring REEs. Tests are currently being conducted to reduce this tailing, including the use of other extractant phases such as alpha-hydroxyisobutyric (α-HIBA) acid.

References: [1] Tang et al. (2012) EPSL 359-360, 248-263. [2] Sivaraman et al. (2002) J. Rad. Nucl. Chem. 252, 491-495. [3] Ireland et al. (2012) LPSC # 2141. [4] Ireland et al. (In prep) [5] Nash et al. (2001) Sep. Sci. Tech. 36, 1257-1282. [6] Hidaka et al. (1995) Anal. Chem. 67, 1437-1441 [7] Pin et al. (1997) Anal. Chim. Act. 339, 79-89. [8] Bouvier et al. (2008) EPSL, 273, 48-57. [9] Hidaka et al. (2009) EPSL 295, 173-178

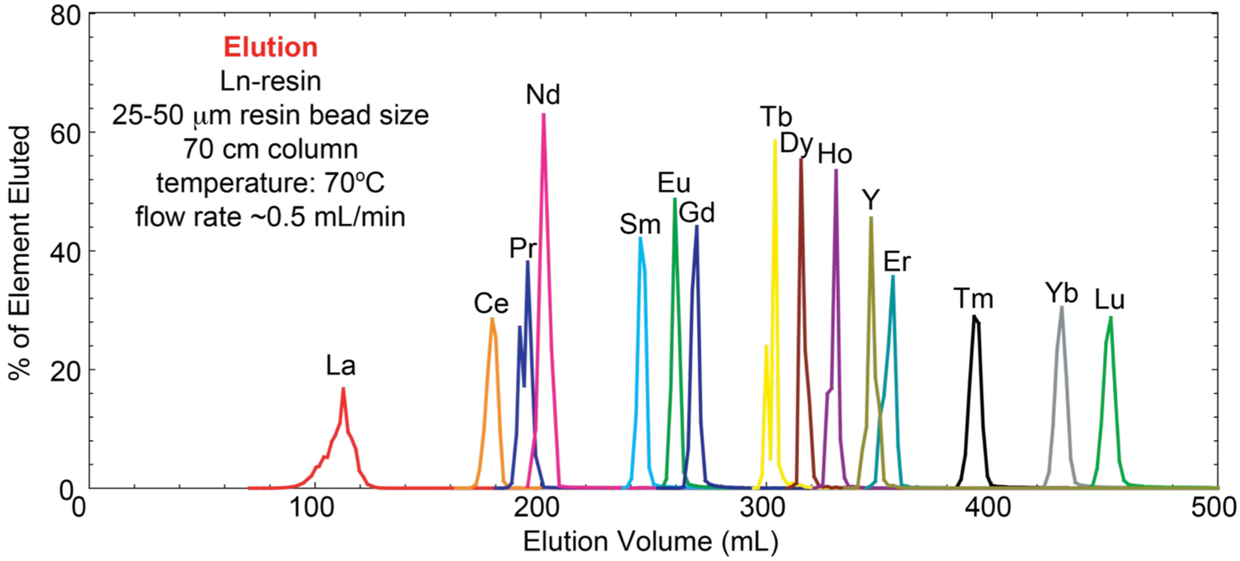

Fig. 2. *Elution curve for the separation of the REE. There is excellent separation of all the multi-isotopic REE (La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, and Lu) from each other, demonstrating the effectiveness of our T-HPLC system. The column was 70 cm long (0.3 cm diameter) and utilized Ln-resin at 25-50 mesh size, at a temperature of 70°C.*