Teflon-HPLC: A novel chromatographic system for application to isotope geochemistry and other industries

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A B S T R A C T
Traditional column chromatography techniques are restricted by several factors, including limitations on column length, resin grain size, elution time, and a general inability to slowly ramp up or down reagent concentrations along a gradient. Likewise, most existing high-performance liquid chromatography (HPLC) systems are not amenable to certain column chromatography techniques that require highly concentrated acids.

Here, we outline the development of a Teflon HPLC (T-HPLC) system for application to a wide variety of chromatography problems. The primary factors that set the T-HPLC system apart from any currently available chromatography procedure are the following: 1) a fluid flow path enclosed entirely by Teflon, 2) fully automated elution schemes controlled by computer software, which allows for fresh mixing of reagents for each elution step, and fine scale gradient/ramp elutions, 3) temperature control of the entire system (up to 80 °C) for enhanced chemical separations and, 4) a modular design making the system easily adaptable to a variety of separation schemes.

The effectiveness of the T-HPLC system is tested on two column techniques that are of particular interest to the geochemistry/cosmochemistry communities. The first application involves the separation of Ni from Mg, which is required for high precision Ni isotopic studies and for investigating the abundance of the extinct 60 Fe radionuclide. The T-HPLC system greatly simplifies and improves upon the classical technique. In a single pass on an 80 cm long column, we achieve excellent separation of Ni from Mg, with a much improved time frame (10 h versus 70 h). The second application is the separation of the individual rare earth elements from each other. The isotopic compositions of the multi-isotopic REEs (La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb and Lu) may hold important information about nucleosynthetic processes, cosmic-ray exposure effects in meteorites and airless bodies, and mass fractionation effects. For this application, we also developed a computer simulation that uses experimentally determined partition coefficients to simulate an elution curve in order to optimize the actual column elution scheme. Overall, we were able to achieve excellent separation of the multi-isotopic REEs from each other.

Although the two applications that we explore are in the fields of geochemistry/cosmochemistry, the modular design and adaptability make the T-HPLC system useful to a wide array of scientific fields and industries.

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1. Introduction

Column chromatography techniques have proven to be an invaluable tool in the geosciences, as well as in other scientific fields and industries, and are commonly employed in a wide variety of geological applications. In particular, open-system, gravity-driven column chromatography has been established as an essential step in many isotope geochemistry methods, which require high purity separations of the elements of interest from matrix elements. These well-established traditional column techniques are undoubtedly useful, but their application to challenging and new problems in isotope geochemistry can be limited and some fine-scale separations still require complicated multi-step and time-consuming protocols. The chief limitations of traditional columns pertain to the overall length of column, resin size and lack of temperature control, which can severely compromise separation efficiencies.

In contrast to traditional column chromatography techniques, high-performance liquid chromatography (HPLC) systems have evolved considerably. HPLC systems offer several advantages over traditional columns, which include: 1) a closed-system setup, 2) the ability to pressurize the system, which allows for longer columns and finer resin, resulting in better separation, and 3) automation of the elution sequence. There are several HPLC systems that have been used for bulk geochemical analyses such as the Dionex DX-500, which can be used for measuring transition metals and REE concentrations in rock
and seawater samples (Dionex, 1992; Tachibana and Hsu, 2003). However, despite these advantages, HPLC systems have not been widely applied to radiogenic and non-traditional stable isotope geochemistry. As stated above, part of the reason for this trend is because of well-established traditional methods for many elements of interest — there has been no impetus to change. Another reason is that most commercially available HPLC systems suffer from significant limitations as well. These drawbacks are typically associated with the materials used in the construction of these systems. For example, many HPLC systems are designed to work with dilute acids and organic solvents, and may contain parts in the reagent flow path that can be corroded, dissolved or leached with the use of concentrated acids or certain organic solvents that are commonly used for separating elements of geochemical relevance. PEEK (polyether ketone tetrafluoroethylene) is often used in HPLC systems (including the Dionex DX-500 mentioned above) to avoid contamination with metals, but even at 20 °C, this material is not recommended for use with hydrobromic, hydrofluoric, nitric, and sulphuric acids (Pritchard, 1995). Another related issue is that the electronic controls and housing are often spatially associated with the HPLC unit, so metallic parts rapidly corrode upon exposure to harsh chemicals and vapors, thereby limiting the lifespan of the apparatus. For example, Sivaramam et al. (2002) changed their chemical approach for a HPLC system due to concerns over the potential corrosion of components in their system by high molarity acids. For these reasons, application of HPLC systems to radiogenic and non-traditional stable isotope geochemistry is rare. Given the advantages of HPLC systems, it is unfortunate that these systems have not yet been widely adapted to the world of isotope geochemistry.

Here, we bring the benefits of HPLC to isotope geochemistry, by outlining the development of a Teflon-HPLC (T-HPLC) system that we have constructed at the University of Chicago. This development was made possible by the availability of Teflon-made components used in the semi-conductor industry. Teflon has not been traditionally used in HPLC because of high costs, difficulties in machining to tight tolerances and concerns about porosity. However, in isotope geochemistry where low analytical blanks and system integrity are critical, the advantages of Teflon outweigh its drawbacks. Another aspect of our effort has been to isolate the electronic controls from exposure to corrosive fumes.

The T-HPLC system has several distinctive features that improve upon existing technologies and allow it to be easily modified for applications to a wide variety of geochemical and cosmochemical problems, which include: 1) a fluid path that is entirely enclosed in Teflon, 2) fully automated elution systems controlled through LabView software, which allows for fresh mixing of reagents for each elution step, and fine scale gradient/ramp elutions. This automation should also improve reproducibility, 3) temperature control of the entire system (up to 80 °C) for enhanced chemical separations, and 4) a modular design making the system easily adaptable to a variety of separation schemes. These features of the system can facilitate high element yields through the column and efficient separation of the analyte(s) of interest. Following a detailed description of our T-HPLC system, we will discuss a couple of focused applications that are of particular interest in isotope geochemistry, cosmochemistry, and nuclear chemistry.

The first application involves the separation of Ni from Mg, which is important for studying the abundance of extinct radionuclide $^{60}$Fe ($^{60}$Fe $\rightarrow$ $^{60}$Ni; $t_{1/2} = 2.62$ Myr; Rugel et al., 2008) in the early solar system. Tang and Dauphas (2012) demonstrated that up to five repetitions of a 14-hour long column chemistry procedure were needed to adequately separate Ni from Mg, with chemical reagents having to be constantly mixed due to acetone evaporation. Our goal is to improve upon the efficiency of this elution procedure. Our second major focus is the separation of individual rare-earth elements (REEs) from each other. The REEs comprise a suite of geochemically and cosmochemically important elements known for similar partitioning characteristics; hence, these elements have proven to be very challenging to separate from one another (Nash and Jensen, 2001). The isotopic composition of the multi-isotopic REEs may hold important information about nucleosynthetic processes (McCulloch and Wasserburg, 1978a; McCulloch and Wasserburg, 1978b; Andersen and Sharma, 2006, 2007; Carlson et al., 2007; Gannoun et al., 2011; Qin et al., 2011), neutron capture and cosmic-ray exposure effects on meteorites (Eugster et al., 1970a; Eugster et al., 1970b; Burnett et al., 1971; Lugmair and Marti, 1971; Russ et al., 1971; Bogard et al., 1995; Hidaka et al., 2000a; Hidaka et al., 2000b; Hidaka and Yoneda, 2007; Hidaka et al., 2009) and mass fractionation effects (Albalat et al., 2012). Several previous studies have reported moderate success in separating the individual REE by HPLC (Sisson et al., 1972; Yoshida and Haraguchi, 1984; Cassidy and Chauvel, 1989; Meisel et al., 2001; Sivaraman et al., 2002; Haley and Klinkhammer, 2003; Verma and Santoyo, 2007), but these analytical developments have not yet transitioned into isotope geochemistry due to the lack of suitable HPLC systems that meet the stringent standards of this field.

Although our focus is on radiogenic and non-traditional stable isotope geochemistry, we want to emphasize that this novel T-HPLC system is easily adaptable to many chromatographic problems and can be extremely useful in a vast array of industries.

2. Description of the T-HPLC system

2.1. Brief background on column chromatography

In general, column chromatography techniques take advantage of the differing affinities of certain elements on specific resins, in order to isolate the elements of interest and remove any potential interfering or undesired elements. The partitioning behavior of an element on a resin is related to the resin properties, as well as to the liquid phase added to the column. This behavior can be changed by varying the properties of this liquid phase (e.g., changing reagent molarity or reagent type). To achieve quantitative separation of an element from other matrix elements, careful determination of elemental partitioning on the resin being used is essential. Several factors can impact the efficiency of element separation on a column. These factors include the length of column, size of resin beads (thus, the porosity of the column and the height of a theoretical plate), interconnectivity of resin, temperature, and the type/concentration of liquid used during elution. Gravity-driven column chromatography techniques, for example, are primarily restricted by the mesh-size of the resin, as well as the overall length of the column, which can have a prohibitive effect on elution time. Smaller resin mesh-sizes and longer column lengths will both cause an increase in elution time, or potentially halt elution. An increased elution time may be accompanied by diffusion within the column, which is a detrimental problem that will ultimately offset any gain obtained by using longer columns. Column systems that use a pump or pressurization medium can mitigate most of these diffusion effects. Pump or pressure-driven columns also allow one to use a finer resin mesh size, as well as narrower or longer columns, which may increase column efficiency by increasing the reactive surface area. In addition, elution flow rates can be more precisely controlled by varying pump speeds or pressures.

Further, traditional column setups are generally run at room temperature; thus, open systems are not amenable to temperature control because it is difficult to ensure that all parts of the column are at the same temperature and that reagents are not lost by evaporation. However, increased temperatures may have a significant effect on separation factors and the sharpness of an elution peak (Cerrai and Testa, 1963; Siekerski and Sochacka, 1964; Horwitz et al., 2006; Pourmand and Dauphas, 2010). Another impediment of traditional column setups is the difficulty involved to achieve small-step gradient ramps in eluent concentration as the eluents need to be pre-mixed prior to column chemistry. Due to limitations on the amount of different eluents being used, generally only coarse steps are utilized. Lastly, some reagents used in elutions can be unstable and may break down over time. For example, H$_2$O$_2$ or acetone is occasionally used in certain column chemistries (Strelow, 1988; Munkers et al., 2001). Over a relatively short time, H$_2$O$_2$ will break down to H$_2$O, or acetone will evaporate. The challenges
outlined above can be addressed effectively by our proposed T-HPLC system.

A distinct advantage of column chromatography systems, especially with respect to precious samples, is that numerous elements can be separated from a single sample digestion through the meticulous selection of resins and a thorough collection of all material that passes through a column. For example, Pourmand and Dauphas (2010) outlined a method for the separation of Ca, U, Hf, and Lu from meteoritic material that used two different types of resin (TODGA and Ln-resins) and several elution steps to separate and collect the desired elements. In this manner, the amount of sample digested is minimized and a large amount of chemical and isotopic data may be acquired.

2.2. Description of the T-HPLC system

HPLC systems have the power to overcome several of the limitations posed by traditional column setups. However, as stated previously, current commercially available systems are unsuitable for the harsh chemicals and reagents required for some geochemical separations. The answer to this problem is to create a closed HPLC system with a flow path entirely made of Teflon (the material of choice in isotope geochemistry for the last 40 years), where the electronic controls are isolated from the corrosive chemicals and fumes used in the purification unit. Due to its superior material properties (i.e., chemically inert and resistant), Teflon is the most suitable substance for the wide variety of reagents that may be used. In addition to this innovative flow path, it is desirable to have an HPLC system capable of separating a large range of chemical elements, adept at easily switching from one application to another quickly and inexpensively, and able to provide a high degree of separation of elements in a single pass through the column. The key aspects to our T-HPLC are as follows:

1) A flow path entirely made of Teflon (PTFE/PFA);
2) six reagent reservoirs;
3) a custom-designed mixing chamber for reagent mixing;
4) a modular and adjustable chromatographic column setup (both in diameter and length);
5) control over the thermal state of the entire system (up to 80 °C); and
6) complete automation using LabView software and a code we designed.

The flow path begins with the reagent reservoirs (labeled A in Fig. 1), which can hold up to 300 mL of each reagent. There are six such reservoirs that can be used for any combination of water, bases, acids (e.g., HNO₃, HCl, HF, H₂SO₄, oxalic acid), organic solvents (e.g., acetone) or any other reagent required for a particular column chemistry. Inside each of these reservoirs is a coiled Teflon tube that allows for water to flow through the reservoirs to maintain the reagents at a set temperature. These reservoirs are connected to six computer-controlled self-priming solenoid pumps (Cole-Parmer Part 73120-40), which have Teflon-wetted interiors. These pumps deliver reagents into a custom-designed mixing chamber (B in Fig. 1) at a rate of 40 μL per stroke. Since the volumes of acid, water and organic solvents introduced to the mixing chamber are carefully regulated, we can very accurately control the eluent molarity (as demonstrated in Fig. 5). The main advantage of this setup is the ability to vary acid molarities discretely on a smooth ramp in a procedure known as gradient elution in HPLC, rather than jumping from one acid molarity to another. A gradient elution typically provides better separation of elements.

![Fig. 1. i) Schematic diagram of the T-HPLC system showing the important design elements involved in the system. ii) Photograph showing the overall setup of the T-HPLC system, denoting key sections of the instrument. A) Six reagent reservoirs that can store any combination of reagents required for a particular column chemistry. There are Teflon coils inside these reservoirs that allow for water to circulate and maintain the temperature of the reagents. B) A custom-designed mixing chamber ensures that reagents are well-mixed prior to passing onto the column. An insulating jacket surrounds the mixing chamber to preserve a constant temperature. C) The column itself consists of a rigid length of Teflon tubing in a water jacket. The column length and/or diameter can be easily adapted to any elemental system we are interested in. D) Two manifold solenoid valves are present at the base of the column, which can direct discrete elution cuts to different collection vessels. E) A water circulator pumps water up through the system to maintain the system temperature. The water can be heated to a temperature of 80 °C. The water flow path proceeds from the water jacket surrounding the column, to the insulating jacket around the mixing chamber, before circulating through the Teflon coils hosted inside the reagent reservoirs, before returning to the circulator.](image-url)
The custom-designed mixing chamber has a couple of key distinguishing features. First, a computer-monitored Teflon level sensor, close to the base of the chamber, monitors the liquid level. The volume below this sensor marks the limit of the smallest liquid pulse out of the chamber and is on the order of 150–200 μL. Second, a Teflon magnetic stirring bar is placed just above the level sensor to ensure that reagents inside the chamber are thoroughly mixed and equilibrated prior to introduction on the column. The motor for the magnetic stirrer sits in a cavity on the side of the mixing chamber, but is not in contact with any liquid directly. Once the pumps finish filling the mixing chamber reservoir and the reagents are thoroughly mixed, the chamber is pressurized via dry N₂ gas and a three-way solenoid valve (Cole-Parmer Part 01540-11) just below the chamber opens, allowing the liquid to enter the column. The advantages of using gas to push the liquid are that it is extremely clean, offers constant pressure with time, is robust against corrosion, and minimizes the dead volume between the mixing chamber and column. A drawback is that the gas dissolved in the mixing chamber can potentially form bubbles in the column if there is a drop in pressure or an increase in temperature in the column relative to the mixing chamber. The issue of bubble formation is minimized by maintaining the mixing chamber at the same temperature as the column. In the elutions that we performed, we did not find any noticeable bubble formation that could hamper the flow. Another restriction in the current systems is that the maximum column pressure that can be reached is currently limited to the tolerance of the mixing chamber (~80 psi N₂ in our system). Once the liquid level passes the level sensor, the valve between the mixing chamber and column closes, the N₂ gas is vented and a new stage of pumping begins. The mixing chamber is designed to hold pressures up to ~80 psi, with the lid fitting snugly against a Teflon O-ring. The system is further sealed through an insulating jacket, which closely fits around the mixing chamber. This insulating jacket also has a pathway for water flow to keep the mixing chamber at the same temperature as the rest of the system.

The three-way solenoid valve at the base of the mixing chamber serves a couple of important functions. The first, as outlined above, is to provide a barrier from the mixing chamber to the column during reagent mixing, which can then be opened for the injection of the mobile phase to the column. The second function, and use of the third port on the valve, is for sample introduction through a Luer lock connection and syringe. In this manner, the sample can be introduced directly to the column without any concern about contaminating the mixing chamber.

The column portion of the T-HPLC system represents another innovation (C in Fig. 1). Our design includes the capability of varying the column length, depending on the demands of the elemental system being studied. In essence, the column in our system is a piece of Teflon tubing contained in a water jacket. Thus, by adding or removing pieces from the water jacket, and changing the length of Teflon tubing, we can easily adapt the column length and the column diameter to any elemental system of interest. The column is filled with the desired resin prior to attachment to the system, utilizing a vacuum box to ensure that the resin is tightly packed. Ultimately, after passing through the column, the eluted volumes are collected in Teflon beakers distributed through computer-controlled manifold solenoid valves (D in Fig. 1). The use of two solenoid manifolds, with 6 outlets each, allows us to independently collect a large number of elution cuts without the need of tending to changing vials.

A further enhancement is that the whole system can be thermally controlled. Using a circulating water heater (E in Fig. 1), we have designed an independent, closed loop water system that is in contact with all of the components of the HPLC system and can support temperatures of up to 80 °C. The circulation path goes from the circulating water heater through the water jacket surrounding the column, up to the insulating jacket that surrounds the mixing chamber (B in Fig. 1), to the six Teflon coils that are isolated inside of the reagent reservoirs (A in Fig. 1), before the water is re-circulated back to the water heater.

Lastly, the proposed system is controlled via an external computer, running LabView software from National Instruments. LabView uses a graphical programming interface that enables the control of electric components, as well as the ability to program additional commands. Through this computer system we are able to specify an elution scheme (i.e., the mixing parameters, including the types of reagents, volumes and molarities desired), from which the program calculates the amount of liquid needed from each liquid reservoir for each step. From there, the computer program controls the pumping of the solenoid pumps, the mixing of reagents, the monitoring of the liquid level in the mixing chamber, the opening/closing of the valve that leads from the mixing chamber to the column, the N₂ pressurization of the mixing chamber, and the distribution of eluted volumes from the solenoid manifolds at the end. In this manner, a complex elution can be completely automated.

2.3. Future improvements

We are currently exploring the option of upgrading to pneumatically actuated valves and pumps, whereby these components are operated via a compressed gas pressure instead of through electronics. These types of valves and pumps tend to have a longer lifetime (i.e., more actuations) and can be made almost entirely out of Teflon (the solenoid valves used here have an important metal component). In this manner, the electronics, which would control the gas flows to the pneumatic pumps and valves, can be even further isolated from the HPLC system. An additional improvement involves housing all the electronic components inside an enclosure with positive N₂ pressure, which is designed to isolate the electronics from potentially corrosive fumes.

An important limitation of the existing T-HPLC system is that only one separation can be performed at a time. With traditional columns, several samples can be separated concurrently from multiple columns. Thus, the gain in efficiency in a single separation can be offset by the lack of throughput. For some complex separations (i.e., the REE as discussed in Section 4), this is a fair tradeoff. To address this issue, we are considering the potential of hooking up multiple columns to the system in the future.

3. Applications of T-HPLC to Ni–Mg separation

3.1. Brief background on Ni isotope measurements for cosmochemical applications

The study of Ni isotopic anomalies and Ni stable isotope variations by TIMS (thermo-ionization mass spectrometry) and MC-ICP-MS (multi-collector inductively coupled plasma mass spectrometry) has been a very active area of research in cosmochemistry and isotopic geochemistry (Birck and Lugmair, 1988; Shukolyukov and Lugmair, 1993a; Shukolyukov and Lugmaír, 1993b; Quitté et al., 2007; Dauphas et al., 2008; Regelous et al., 2008; Quitté et al., 2010, 2011; Steele et al., 2011; Tang and Dauphas, 2012). In particular, discussions about the prevalence of ⁶⁰⁶⁰Fe, an extinct radionuclide that decays to ⁶⁰⁶⁰Ni (T₁/₂ = 2.62 Myr; Rugel et al., 2009), at the time of solar system formation have been quite intense (Shukolyukov and Lugmair, 1993a; Tachibana and Huss, 2003; Mostefaoui et al., 2004; Guan et al., 2007; Marhas and Mishra, 2012; Tang and Dauphas, 2012). This debate is centered around substantial differences (almost 2 orders of magnitude) in the estimate of the ⁶⁰⁶⁰Fe / ⁶⁰⁶⁰Fe ratio at the time of solar system formation, a parameter that has significant bearing on the astrophysical context of solar system birth. To resolve this problem, Tang and Dauphas (2012) measured the Ni isotopic composition of several meteorite samples, including angrites, HEDs and unequilibrated ordinary chondrites. Tang and Dauphas (2012) developed a 3-step column chromatography process for the purification of Ni from matrix elements in these samples — in the next section we outline the second step of this procedure, which represents a significant time impediment to the overall process.
3.2. Difficulties with current methodology

A major difficulty faced by analysts in order to generate precise and accurate measurements of Ni isotopes for application to 60Fe–60Ni extinct radionuclide systematics is to separate Ni from Mg in silicate rocks (where the Mg/Ni ratio is high). One reason that a high degree of separation between Ni and Mg is required is due to the presence of an argide interference produced on 24Mg (24Mg40Ar), which can interfere with the low abundance isotope 64Ni. In addition, measurement precision on the other Ni isotopes (58Ni, 60Ni, 61Ni and 62Ni) decreases with increasing matrix concentrations. To ensure a negligible matrix effect, a ratio of Cmatrix/CNi < 0.5 is required.

The separation of Ni from Mg is achieved by using a 40 cm long (0.3 cm ID) Teflon column filled with Bio-Rad AG50-X12 200–400 mesh hydrogen-form cation exchange resin, which is attached to a vacuum box to facilitate the elution. The elution scheme is as follows (adapted from Strelof et al., 1971):

1) Condition column with 10 mL of 20% 10 M HCl–80% acetone mixture.
2) Load sample in 5 mL of 20% 10 M HCl–80% acetone mixture.
3) Rinse column with 30 mL of 20% 10 M HCl–80% acetone mixture.
4) Collect Ni with 150 mL of 20% 10 M HCl–80% acetone mixture.
5) Repeat procedure 5 times to ensure adequate separation of Ni (10 to 100 ppm level) from Mg (% level).

This separation scheme was used by Tang and Dauphas (2012) as high-precision measurement of Ni isotopes was crucial for their work, making it essential to remove all matrix elements from the solution. This procedure represents a significant time inefficiency in the Ni separation process. Each elution lasts about 14 h – so the whole second step of the 3-step Ni purification technique takes a total of about a week's worth of time. In addition to the time inefficiency, the HCl–acetone mixture becomes unstable over the course of an elution and acetone would evaporate, so it needs to be freshly mixed every half hour.

3.3. Application of T-HPLC system to the separation of Ni from Mg

Two experiments were conducted to ascertain how well our T-HPLC system functions in terms of separating Ni from Mg and the results are shown in Fig. 2. Both experiments had the same loading solution, which contained 1 μg/g of Fe, Ni and Mg respectively, in a solution of 20% 10 M HCl and 80% acetone. The rinsing and collection solutions paralleled the 3-step Ni purification process. Each elution lasts about 14 h — so the whole second step of the 3-step Ni purification technique takes a total of about a week's worth of time. In addition to the time inefficiency, the HCl–acetone mixture becomes unstable over the course of an elution and acetone will evaporate, so it needs to be freshly mixed every half hour.

4. Applications of T-HPLC to the separation of the REE

4.1. Brief background on REE separation for cosmochemical applications

As stated in the introduction, the REEs comprise a suite of geochemically and cosmochemically important elements known to have similar partitioning characteristics. Thus, the REEs are of particular interest to geochemists and cosmochemists, but are also challenging to separate from each other at the level required for isotope geochemistry work. Several well-established methods have been employed for the bulk separation of REEs for geochemical applications by traditional column chemistry (e.g., Gast et al., 1970; Strelof and Jackson, 1974; Hooker et al., 1975; Walsh et al., 1981; Crock et al., 1984; Henderson and Pankhurst, 1984; Balaram, 1996; Baker et al., 2002; Pourmand et al., 2012) or by HPLC (see review by Verma and Santoyo, 2007). These methods are effective for obtaining bulk concentration data and chondrite-normalized REE patterns, which are often used to provide insight into a sample's history. However, these bulk methods are not suitable for high-precision isotopic analyses of the individual REEs because of isobaric, oxide and molecular interferences that may be present during ICP-MS analysis.

Fig. 2. Elution curves generated from two experiments involving the separation of Ni from Mg on the T-HPLC system. A) A 40 cm long column (diameter 0.3 cm) at room temperature shows that there is significant overlap between the elution curves for Ni and Mg. B) A 80 cm long column (diameter of 0.3 cm) at an elevated temperature (65 °C) demonstrates that the elution peaks sharpen, and that there is excellent separation of Ni from Mg.
Over the past several years, it has become increasingly important in geochemistry/cosmochemistry to address various questions involving REE isotope systematics (e.g., Caro et al., 2003; Boyet and Carlson, 2005; Andreasen and Sharma, 2006; Andreasen and Sharma, 2007; Bennett et al., 2007; Carlson et al., 2007; O'Neil et al., 2008; Thrane et al., 2010; Gannoun et al., 2011; Albalat et al., 2012). For instance, in the geologic community, a lot of attention has been centered on separations of REEs from a single sample digestion and column procedure could be a significant leap forward in terms of how we analyze these elements, with implications for nucleosynthetic processes (McCulloch and Wasserburg, 1978a; McCulloch and Wasserburg, 1978b; Andreasen and Sharma, 2006, 2007; Carlson et al., 2007; Gannoun et al., 2011; Qin et al., 2011), neutron capture and cosmic-ray exposure effects on meteorites (Eugster et al., 1970a; Eugster et al., 1970b; Burnett et al., 1971; Lugmair and Marti, 1971; Russ et al., 1971; Bogard et al., 1995; Hidaka et al., 2000a; Hidaka et al., 2000b; Hidaka and Yoneda, 2007; Hidaka et al., 2009) and mass fractionation effects (Albalat et al., 2012).

Methods of separating the individual REEs using α-HIBA (alpha-hydroxyisobutyric acid; e.g., Hidaka et al., 1995; Rehkämper et al., 1996; Meisel et al., 2001; Carlson et al., 2007) or Ln-resin (which uses HDEHP as the extractant phase; e.g., Pin and Zaldegui, 1997; Horwitz et al., 2006; Bouvier et al., 2008; Hidaka et al., 2008) have been refined over the years, but these studies have mainly focused on a small subset of the REEs or have not provided enough resolution between REE to allow for high-precision isotopic analysis. Although Ln-resin is a powerful method for separating REEs, α-HIBA has been favored in HPLC systems because the HDEHP chemistry requires the use of high molarity and corrosive acids that cannot be handled by commercial HPLC systems. This is most clearly expressed by Sivaraman et al. (2002) who considered the feasibility of using a HDEHP coated column in a HPLC system, but decided against this approach because of concern that the high molarity acids would damage the system.

A thorough study of REE separation using Ln-resin and the T-HPLC system was conducted to assess the effectiveness of this novel chromatographic technique. This study involved the determination of partition coefficients of the REEs on Ln-resin using both HCl and HNO₃ molarity at varying acid molarities, a computer simulation of the elution curve (using the appropriate resin and column properties) in order to optimize the gradient elution scheme that was utilized, and the actual REE elution itself. Through this study, it is shown that the designed T-HPLC system is effective at addressing a very complex elution scheme and has a remarkable potential to improve or facilitate other chromatographic problems.

### 4.2. Determination of REE partition coefficients on Ln-resin

Several previous studies have used Ln-resin for partial REE separation (e.g., LREE: Pin and Zaldegui, 1997; Sm and Gd: Hidaka et al., 2009). On resins using HDEHP as an extractant phase, 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 (Pierce et al., 1963; Horwitz and Bloomquist, 1975). This elution sequence, from light to heavy REE, is opposite to that of α-HIBA (Rehkämper et al., 1996). To optimize the elution sequence, we ran elution simulations using plate theory (Martin and Synge, 1941), which requires the partition coefficient as an input parameter.

The partition coefficients (Kᵟᵣ, i.e., the affinity of an element for a particular resin) of the REE on Ln-resin, as a function of HCl and HNO₃ molarity, were determined by a series of batch equilibration experiments following the procedure outlined by Pourmand and Dauphas (2010) conducted at room temperature. In brief, a series of 10 μg/g bulk REE standards were generated from commercially available mono-elemental solutions, which were evaporated to dryness and subsequently re-dissolved in 5 mL of various HCl or HNO₃ molarities (ranging from 0.01 to 5 M) in clean 15 mL PFA beakers. For each respective molarity step, approximately 300 mg of dry Ln-resin was collected from 2 mL pre-packed cartridges (50-100 μm bead size), which are available from Eichrom. The resin was added to the PFA beakers, and the mixture was agitated by placing on a vortex shaker for 5–10 min every 2 h. After 10 h of equilibration, the resulting mixtures were passed through 2 mL Bio-Rad columns fitted with frits, to separate the acid phase from the resin. To prepare for mass spectrometry, the acid phases were dried down and re-dissolved in 0.46 M HNO₃.

The concentrations of the REE in each solution were determined by sample-standard bracketing on a Thermo Neptune MC-ICP-MS at the Origins Lab of the University of Chicago, following the procedures of Pourmand et al. (2012). An Apex-Q + Spiro desolvating nebulizer was used for sample introduction to the ICP-MS, which helps to reduce oxide production in the plasma. Oxide interferences are a potential problem with bulk REE analyses, as oxide production on the light REE can interfere with the heavier REE.

The Kᵟᵣ (concentration in mol/g of element in solid divided by the concentration in mol/L of element in liquid) for each REE in the various acid molarities was calculated by the following equation:

\[
Kᵟᵣ = \frac{(C_B-C_A)V}{w} \frac{1}{C_A}
\]

where Cᵦ and Cᵦ are the concentrations of REE in solution before and after equilibration, w is the weight of dry resin and V is volume of acid used in the equilibration experiment.

The results of the Kᵟᵣ experiments are shown in Fig. 3 and the linear regression statistics for each curve (slope and intercept) are given in Table 1. These data are consistent with the observations of Pierce et al. (1963), Horwitz and Bloomquist (1975) and Pin and Zaldegui (1997), who also noted similar linear trends for comparable experiments. A greater spread of Kᵟᵣ (i.e. higher separation factors) was observed for HCl relative to HNO₃, which may reflect slight complication of the REEs at elevated HNO₃ molarities.

### 4.3. Computer simulation of elution curve

As the REEs have very similar partitioning characteristics, minor changes in the elution scheme will result in drastically different separation patterns. To avoid a lengthy and potentially unsuccessful trial and error approach, it was important to optimize the elution scheme beforehand. Thus, we developed a chromatography simulation code (see Mathematica code in the Supplemental materials) based on plate theory (Martin and Synge, 1941) and an earlier program written by one of the authors (Dauphas, 2002).

The plate theory of chromatography states that a chromatographic column can be divided into a finite number of theoretical plates of defined height. Within each plate, and at any point in time, equilibrium between the liquid phase and the solid phase is achieved. Let’s note Cᵦ and Cᵦ as the concentration of the element in the solid phase (in mol/g) and the liquid phase (in mol/L), respectively. The affinity of an element for a particular resin is given by the partition coefficient, Kᵟᵣ, which is defined as:

\[
Kᵟᵣ = \frac{Cᵦ}{Cᵦ}
\]
As the liquid moves down into the column from theoretical plate to theoretical plate, it equilibrates with the solid in the next plate. When the liquid in plate \( i - 1 \) moves down into plate \( i \), the distribution of the element contained in the liquid (from plate \( i - 1 \)) and in the solid (from plate \( i \)) is not at equilibrium anymore (i.e. \( K_{d,i} \neq C_i / C_l \)). The distribution of the element between the liquid and the solid phase changes accordingly to the \( K_{d,i} \) value imposed by the reagent type and molarity. The following mass balance equation can be written to describe this process:

\[
m_i^l + m_i^s = m_{eq}^i + m_{eq}^s
\]  

(2)

where the exponents refer to the plate, \( m_i \) and \( m_l \) to the mass of element, respectively, in the solid phase and the liquid phase, and the subscript \( eq \) to values after equilibrium has been reached (i.e. \( K_{d,i} = C_i / C_l \)). This equation can be rewritten as:

\[
dC_i^lV_i^l + C_i^sV_i^s = dC_i^lV_i^l + C_i^lV_i^l
\]  

(3)

where \( d \) refers to the density of extractant-loaded beads, and \( V_i \) and \( V_s \), respectively, to the volume of liquid and solid in the plate. The volumes of liquid and solid are the same in each plate, and can be expressed as a function of the porosity of the resin (\( \phi \)) and the volume of the plate \( V_i^l \), as:

\[
V_i^l = V_i^l \times \phi
\]  

(4)

Table 1: Linear regression statistics for determination of \( K_{d,i} \) as a function of acid molarity at room temperature.

<table>
<thead>
<tr>
<th>Element</th>
<th>Equation (log form)</th>
<th>Slope</th>
<th>Err slope</th>
<th>y-int</th>
<th>Err y-int</th>
<th>( r^2 )</th>
<th>( K_{d,i} ) conversion factor for 70 °C*</th>
</tr>
</thead>
<tbody>
<tr>
<td>For HCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>( y = -1.841 \log(x) - 0.250 )</td>
<td>-1.841</td>
<td>0.026</td>
<td>-0.250</td>
<td>0.034</td>
<td>1.000</td>
<td>1.38</td>
</tr>
<tr>
<td>Ce</td>
<td>( y = -1.933 \log(x) + 0.013 )</td>
<td>-1.933</td>
<td>0.035</td>
<td>0.013</td>
<td>0.046</td>
<td>0.999</td>
<td>1.20</td>
</tr>
<tr>
<td>Pr</td>
<td>( y = -2.000 \log(x) + 0.047 )</td>
<td>-2.000</td>
<td>0.056</td>
<td>0.047</td>
<td>0.067</td>
<td>0.998</td>
<td>1.06</td>
</tr>
<tr>
<td>Nd</td>
<td>( y = -2.017 \log(x) + 0.096 )</td>
<td>-2.017</td>
<td>0.071</td>
<td>0.096</td>
<td>0.086</td>
<td>0.996</td>
<td>1.05</td>
</tr>
<tr>
<td>Sm</td>
<td>( y = -2.681 \log(x) + 0.236 )</td>
<td>-2.681</td>
<td>0.151</td>
<td>0.235</td>
<td>0.116</td>
<td>0.987</td>
<td>0.93</td>
</tr>
<tr>
<td>Eu</td>
<td>( y = -2.796 \log(x) + 0.446 )</td>
<td>-2.796</td>
<td>0.164</td>
<td>0.446</td>
<td>0.126</td>
<td>0.986</td>
<td>0.90</td>
</tr>
<tr>
<td>Gd</td>
<td>( y = -2.800 \log(x) + 0.600 )</td>
<td>-2.800</td>
<td>0.160</td>
<td>0.600</td>
<td>0.122</td>
<td>0.987</td>
<td>0.90</td>
</tr>
<tr>
<td>Tb</td>
<td>( y = -3.231 \log(x) + 1.046 )</td>
<td>-3.231</td>
<td>0.122</td>
<td>1.046</td>
<td>0.065</td>
<td>0.993</td>
<td>0.90</td>
</tr>
<tr>
<td>Dy</td>
<td>( y = -2.958 \log(x) + 1.602 )</td>
<td>-2.958</td>
<td>0.249</td>
<td>1.602</td>
<td>0.100</td>
<td>0.966</td>
<td>0.83</td>
</tr>
<tr>
<td>Ho</td>
<td>( y = -3.109 \log(x) + 1.830 )</td>
<td>-3.109</td>
<td>0.194</td>
<td>1.830</td>
<td>0.077</td>
<td>0.981</td>
<td>0.84</td>
</tr>
<tr>
<td>Er</td>
<td>( y = -3.084 \log(x) + 2.191 )</td>
<td>-3.084</td>
<td>0.143</td>
<td>2.191</td>
<td>0.046</td>
<td>0.991</td>
<td>0.82</td>
</tr>
<tr>
<td>Tm</td>
<td>( y = -3.084 \log(x) + 2.712 )</td>
<td>-3.084</td>
<td>0.126</td>
<td>2.712</td>
<td>0.049</td>
<td>0.990</td>
<td>0.83</td>
</tr>
<tr>
<td>Yb</td>
<td>( y = -3.038 \log(x) + 3.151 )</td>
<td>-3.038</td>
<td>0.097</td>
<td>3.151</td>
<td>0.041</td>
<td>0.994</td>
<td>0.84</td>
</tr>
<tr>
<td>Lu</td>
<td>( y = -2.967 \log(x) + 3.360 )</td>
<td>-2.967</td>
<td>0.108</td>
<td>3.360</td>
<td>0.046</td>
<td>0.993</td>
<td>0.83</td>
</tr>
<tr>
<td>For HNO(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>( y = -1.709 \log(x) - 0.717 )</td>
<td>-1.709</td>
<td>0.051</td>
<td>-0.717</td>
<td>0.067</td>
<td>0.998</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>( y = -1.960 \log(x) - 0.870 )</td>
<td>-1.969</td>
<td>0.030</td>
<td>-0.870</td>
<td>0.040</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Pr</td>
<td>( y = -2.049 \log(x) - 0.889 )</td>
<td>-2.049</td>
<td>0.028</td>
<td>-0.869</td>
<td>0.036</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>( y = -2.105 \log(x) - 0.849 )</td>
<td>-2.105</td>
<td>0.082</td>
<td>-0.849</td>
<td>0.108</td>
<td>0.997</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>( y = -2.316 \log(x) - 0.508 )</td>
<td>-2.316</td>
<td>0.045</td>
<td>-0.508</td>
<td>0.059</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>( y = -3.120 \log(x) - 0.951 )</td>
<td>-3.120</td>
<td>0.249</td>
<td>-0.951</td>
<td>0.224</td>
<td>0.987</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>( y = -3.128 \log(x) - 0.696 )</td>
<td>-3.128</td>
<td>0.423</td>
<td>-0.696</td>
<td>0.421</td>
<td>0.982</td>
<td></td>
</tr>
<tr>
<td>Tb</td>
<td>( y = -3.707 \log(x) - 0.612 )</td>
<td>-3.707</td>
<td>0.071</td>
<td>-0.612</td>
<td>0.054</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>( y = -3.577 \log(x) - 0.111 )</td>
<td>-3.577</td>
<td>0.111</td>
<td>-0.111</td>
<td>0.100</td>
<td>0.995</td>
<td></td>
</tr>
<tr>
<td>Ho</td>
<td>( y = -3.926 \log(x) - 0.159 )</td>
<td>-3.926</td>
<td>0.282</td>
<td>-0.159</td>
<td>0.115</td>
<td>0.984</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>( y = -3.975 \log(x) - 0.566 )</td>
<td>-3.975</td>
<td>0.251</td>
<td>-0.566</td>
<td>0.103</td>
<td>0.984</td>
<td></td>
</tr>
<tr>
<td>Tm</td>
<td>( y = -3.957 \log(x) - 1.105 )</td>
<td>-3.957</td>
<td>0.230</td>
<td>-1.105</td>
<td>0.094</td>
<td>0.987</td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>( y = -3.648 \log(x) - 1.846 )</td>
<td>-3.646</td>
<td>0.198</td>
<td>-1.846</td>
<td>0.081</td>
<td>0.988</td>
<td></td>
</tr>
<tr>
<td>Lu</td>
<td>( y = -3.520 \log(x) - 1.939 )</td>
<td>-3.520</td>
<td>0.161</td>
<td>-1.939</td>
<td>0.066</td>
<td>0.992</td>
<td></td>
</tr>
</tbody>
</table>

* Conversion factor calculated from taking the center of the peak volume at 70 °C (from Fig. 6) divided by the centers of the peak volume at room temperature (from Fig. 4).
and

\[ V'_j = V_j \times (1 - \phi). \]  

(5)

By substituting Eqs. (1), (4) and (5) into Eq. (3), one can calculate the equilibrium concentration of the element in the liquid moving down into the column in each plate as:

\[ C_i = \frac{d(1-\phi)C_i + \phi C_i^{-1}}{d(1-\phi)K_d + \phi}. \]  

(6)

And the corresponding equilibrium concentration of the element in the solid becomes:

\[ C_{eq} = K_d \times C_i. \]  

(7)

Eqs. (6) and (7) are used in the chromatography simulation code to calculate the equilibrium condition within each plate in the column throughout the entire elution.

The input parameters to the simulation code are: 1) the column length and the parameters needed to calculate the volume of resin in each theoretical plate (i.e., column radius, porosity, and the HETP [height equivalent to a theoretical plate]), 2) the volume of each elution step, 3) the density of the extractant-loaded beads and 4) the partition coefficient of the element(s) for the resin during each elution step (i.e., \( K_d \) corresponding to the reagent type and molarity). Determination of the HETP for Ln-resin (\( \sim 0.35 \pm 0.05 \text{ cm} \)) was evaluated using the \( K_d \) values measured for this study, and by adjusting the HETP value until simulated elution patterns fit published elution curves obtained on Ln-resin (Pourmand and Dauphas, 2010; Ali and Srinivasan, 2011).

Using the above value of HETP, the \( K_d \) values of the REEs, a resin density of 1.15 g/mL, and a porosity of 67% (also called FCV — free column volume — and equal to the free volume in mL per mL of packed resin, Horwitz et al., 2006) we simulated the elution patterns of the REE for various ramps of HCl molarity (see Fig. 4 caption for detail on the ramps). Fig. 4 shows a set of molarity ramps (left panels) and their corresponding simulated elution of the 14 REE + Yttrium (right panels). The bottom panels show the best optimized elution ramp and separation pattern. This elution scheme was implemented to test the T-HPLC (see next section). It is worth noting that the chromatography simulation code provided in this publication is applicable to any elution scheme on any resin, provided that the appropriate input parameters are known.

4.4. Application of the T-HPLC system to the separation of the REEs

To test the performance of our T-HPLC system, we prepared a multi-element REE solution, containing 10 µg/g of eachREE, as well as Sc and Y (which behave similarly to the REEs). A 70 cm long column (diameter of 0.3 cm) was filled with Ln-resin with 25–50 µm resin bead size (the finest mesh size commercially available). The experiment was conducted at 70 °C with the pressure adjusted to provide a flow rate of ~0.5 mL/min. The resin was initially cleaned using 50 mL of 10 M HCl and then conditioned with 30 mL of 0.05 M HCl. The standard solution was loaded onto the column in a 10 mL volume in 0.05 M HCl. Utilizing the elution curve simulation program to optimize our separation, we devised an elution scheme that would slowly increase HCl molarity along a pre-defined ramp starting at 0.1 M HCl and increasing to 10 M HCl over 183 steps. Fig. 5 shows a plot of the desired molarity ramp as defined by the elution curve simulation, along with the calculated molarity from the steps in the LabView program and several intervals where we titrated the eluted solution to check its molarity. This figure demonstrates that the T-HPLC system is very effective and accurate at controlling reagent mixing and molarities.

The gradient ramp was programmed into the LabView program and the whole elution scheme was automated. Each mixing step involved a total of 4 mL of reagents, and the eluted solution was collected in either 2 mL or 4 mL increments, depending on when elements were predicted to elute. In total, 680 mL of solution were collected over a period of ~15 h. These solutions were subsequently evaporated to near-dryness and then picked up in 0.46 M nitric acid for analysis on the Neptune MC-ICP-MS. Admittedly, this is a long amount of time for a single column; however, most of the procedure is done automatically and the quality of the separation would be difficult to achieve using a traditional column setup.

The results of the elution are plotted in Fig. 6. There is some overlap of mono-isotopic REEs with neighboring multi-isotopic REEs (e.g., Pr overlaps with Nd), but this is not a big concern since there are no isobaric interferences between these isotopes. In addition, there is some dissimilarity between the elution curve from Fig. 6 and the simulated elution curve from Fig. 4, although the broad shapes of each curve, and the relative placement of the elution peaks, are consistent with each other. The slight discrepancy may be attributed to uncertainties in the experimentally determined \( K_d \)'s and/or because the \( K_d \)'s used in the simulation were determined at room temperature, while the T-HPLC experiment was run at 70 °C. Conversion factors for the differences between the \( K_d \) at 70 °C versus those at room temperature are given in Table 1, and range from 1.38 for La to ~0.83 for Dy to Lu.

Most importantly, however, the T-HPLC system achieved excellent separation of the multi-isotopic REEs (La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb and Lu) from each other — a result that is difficult to obtain with current techniques. Of particular note, there is strong separation of Nd from both Ce and Sm, which is a key factor for studies concerned with the Sm–Nd isotopic systems. With some necessary refinement (see Section 4.6), this result represents a major breakthrough for measuring REE isotopic abundances. All multi-isotopic REEs can now potentially be separated and analyzed from a single sample digestion, helping to elucidate various processes that affect the REE, while using minimal amounts of sample. Overall, this result demonstrates the effectiveness of our system and its great potential to tackle even the most difficult of column chromatography techniques.

4.5. Blank

A major concern with any new geochemical method, especially those that require large volumes of reagents, is the analytical blank. There are two main potential sources of blank contamination in a HPLC setup — the first from the reagents being used, and the second from the resin. To minimize the blank from reagents, only acid that had been distilled multiple times through quartz and Teflon stills was utilized. Additionally, purified water from a Milli-Q system, with a resistivity of 18.2 MΩ/cm, was used as the diluent. This careful preparation of reagents, as well as the internal monitoring of blank levels over time, can help ensure that there is a minimal contribution from these sources.

To address the potential blank contribution from the resin, a couple of cleaning steps were implemented prior to the column chemistry. Firstly, loose resin (~25 to 50 g) was poured into a 1 L pre-cleaned PFA bottle, containing 6 M HCl. This solution was shaken vigorously throughout the day, and allowed to settle overnight. The following morning, the acid was decanted, the resin was rinsed with MQ water, and the process was repeated. After this step, the resin was stored in MQ until ready for use. After loading the resin into a column, an additional cleaning step was employed (see Section 4.4) — 50 mL of 10 M HCl was eluted through the system, which should remove any REE that may still be present because the \( K_d \) of the REE on Ln-resin at high HCl molarities is very low (e.g., Fig. 3).

A complete system blank was evaluated by running the elution scheme outlined in Section 4.4 through the T-HPLC system, without a loading step. In this manner, a total of 670 mL of solution was collected, and was subsequently evaporated to near-dryness and picked up in 0.46 M HNO₃ for analysis on the ICP-MS. Table 2 shows the
concentration of REE blanks measured on the T-HPLC system, and a comparison of this blank with REE levels in CI chondrites (Pourmand et al., 2012). The measured system blanks range from 100 pg for Nd up to a high of 1481 pg for Ce, although blanks for individual elution steps would be reduced. We should be able to improve upon these blanks in the future by cleaning further the reagents and decreasing the diameter of the column to reduce the volume of acids and resin used. If 1 g of an average CI chondrite is dissolved and run through the T-HPLC system, this system blank would represent less than 0.5% for most of the REE.

4.6. Concern with Ln-resin and future efforts with REE separation

A noted concern with utilizing Ln-resin is a tailing effect of elution peaks that can often be observed as acid molarity is increased (Rehkämper et al., 1996; Pin and Zaldegui, 1997; Makishima et al., 2008; Hirahara et al., 2012). The small-step gradient ramp employed with the T-HPLC system reduced this tailing significantly, compared to our previous attempts using an open system column with broad molarity steps, but did not eliminate it. When the elution percent axis is viewed on a log scale, this tailing effect is readily apparent. The last

---

**Fig. 4.** Results of simulated elution of the REE on Ln-Spec resin obtained using various ramp of HCl molarity. The molarity ramps are calculated using the following arbitrary function: $D(v) = M_r \times \left[ 1 - \frac{v}{V_f} \right]^{-\frac{1}{p}} + M_i$ where $V_f$ is the total elution volume, $M_r$ the range of molarity spanned during the elution, $M_i$ the initial molarity of the ramp, and $V$ the eluted volume. $p$ is a curvature parameter that can vary from 0 to $\infty$. Elution curves are computed using a Mathematica code based on plate theory (Martin and Synge, 1941). The left panels show the curvature of the ramp as a function of the value of $p$, while the right panels show the corresponding simulated elution of the 14 REE + Yttrium. As can be seen, when separating the REE, the elution scheme (i.e. shape of the ramp) is a crucial parameter to optimize in order to obtain the best separation of the elements in the minimum volume of elution. Such a result is achieved on the bottom panel for $M_i = 0.1$, $M_r = 10$, $V_f = 700$ mL and $p = 4$ (bottom panels).
-0.25 to 0.75% of each REE has a long drawn-out tail that intersects the elution peaks of the other REE (Fig. 7). Whether this is a problem during isotopic analysis remains to be tested. Note that the α-HIBA chemistry elutes REEs in the opposite order to Ln-resin (from heavy to light on α-HIBA; Lugmair et al., 1975; Rehkämper et al., 1996), so a second pass of the REE cuts on cation-exchange resin using α-HIBA would very effectively remove the tailing problem.

5. Conclusions

Here, we have developed and tested a novel T-HPLC system for use in addressing a wide variety of geological and cosmochemical problems. Our new T-HPLC system represents an advancement over traditional column chromatographic techniques in a variety of ways:

1) All Teflon fluid flow path;
2) fully automated elution schemes allowing for fresh mixing of reagents for each elution step and the ability to perform gradient/ramp elutions;
3) A modular design with the ability to vary column length, resin type, and flow rate;
4) temperature control over the entire system (up to 80 °C); and
5) separation of electronic components from the HPLC system.

We tested our system on two separation schemes that are of particular interest to the geochemical and cosmochemical communities. In the first test, we established that the separation of Ni from Mg is much more efficient and effective using a long column at elevated temperature. Using these conditions, we effectively separated Ni from Mg in one column pass, as opposed to five passes that were utilized in prior traditional column chromatographic schemes.

In the second test, we demonstrated that individual REEs can be effectively separated from each other, using a long column and elevated temperatures. This result may have important ramifications for how REE isotopic studies are performed in the future. While some challenges still remain (i.e., tailing of the REEs), we are confident that our T-HPLC system will be able to address these obstacles.

The distinct attributes of the T-HPLC system gives the user much more power over the separation method and greatly simplifies the complex chemistry that is required for some separations. In addition, this system not only saves the user valuable time, but it also eliminates many of the potential issues with conventional column chemistry (e.g., inability to achieve fine-scale gradient ramps, human error). Our major point of emphasis is that this T-HPLC system is readily adaptable.
to address a wide variety of chromatographic techniques across several scientific fields and industries.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2013.08.001.

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Fig. 7. The same elution curve from Fig. 6 with the x-axis in log scale. Note the long tails of each REE, which intercept the elution curves of the other REE. This tailing accounts for 0.25 to 0.75% of each element. Similar tailing behavior has been documented for the REEs on Ln-resin (e.g., Rehkämper et al., 1996; Pin and Zaldegui, 1997; Makishima et al., 2008; Hirabara et al., 2012).

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