DEVELOPMENT OF AN AUTOMATED ALL-TEFLON HPLC SYSTEM FOR THE ANALYSIS OF PRECIOUS GEOLOGICAL AND EXTRATERRESTRIAL MATERIALS. T. J. Ireland[1], N. Dauphas[1], and F.L.H. Tissot[1] [1]Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, USA (tireland@uchicago.edu)

Introduction: With the recent success of sample return missions such as Genesis (solar wind; *e.g.,* [1-2]), Stardust (cometary dust particles; *e.g.,* [3-5]) and Hayabusa (asteroid; *e.g.,* [6-7]), as well as the recently announced OSIRIS-REx mission (estimated to collect more than 60 g of asteroidal material), it is clear that a new frontier of solar system research has been entered. Given the precious nature of these samples, it is also apparent that laboratory techniques need to be made as efficient as possible in order to maximize the information that we can gain from these unique and invaluable specimens. To determine the chemical and isotopic compositions of these samples, it is often necessary to separate and purify elements of cosmochemical interest from the host rocks. A widely used method for the chemical separation of elements, following sample digestion, is through column chromatography techniques.

Traditional, open-column systems (flow induced by gravity) face several limitations, such as restrictions of overall column length and diffusion effects, which can severely compromise separation efficiencies. Many of these limitations can be overcome by using a pump or pressure medium to sustain flow. In addition, if the system is automated, the overall setup is often referred as a high-performance liquid chromatography (HPLC) system. HPLC systems offer many distinct advantages relative to traditional column layouts, which include: a clean, closed-system setup, pressure- or pump-driven elution, increased flexibility of column features (*e.g.,* length, diameter, temperature) and the ability to automate the whole process. In light of the great effort and expense involved in obtaining samples from return missions, refining column techniques will be a key factor in maximizing our use of these samples.

Here, we outline the development of a computer-controlled all-Teflon HPLC system, with several distinctive features. This system was designed to be as flexible as possible, in order to address a wide variety of column setups, as well as a multitude of geochemical and cosmochemical problems. The data that can be gathered from this device can be used to address fundamental questions about a sample, such as *what is the material composed of, when did it form,* and *how does this sample relate to other objects/events in the solar system?*

Description of the HPLC system: The use of automated HPLC systems is common in the biomedical field, where high sample throughput is desired and the column chemistry is easily repeatable. There have also been some previous applications in the geosciences, especially with respect to studies in environmental or low-temperature aqueous systems. However, for the elemental and isotopic systems that we are interested in, and for the cosmochemical problems that we are addressing, there are no suitable commercially available HPLC systems. Thus, we have put thorough and meticulous thought into designing an HPLC system to match our needs.

The most distinctive feature of the HPLC system is that all parts along the fluid flow path are made of Teflon. This characteristic is imperative in our design because our column procedures utilize a variety of concentrated acids and organic solvents, which could corrode metal, leach glass, or weaken other plastics. Teflon is the most resistant plastic with respect to these types of reagents.

The flow path begins with six liquid reservoirs (labeled A in Figure 1), which can be used to hold any combination of reagents required for a particular column chemistry (*e.g.,* water, hydrochloric acid, nitric acid, acetone, hydrogen peroxide, or any other liquid). These reservoirs are connected to six computer controlled self-priming solenoid pumps, which have Teflon-wetted interiors. These pumps feed into a custom designed mixing chamber (B; Figure 1, Figure 2). These solenoid pumps dispense liquid at a set volume, so that the total volume, as well as eluent molarities, can be accurately controlled. A benefit of these pumps is that we can slowly and incrementally increase the molarity of an eluent along a pre-defined gradient ramp. Fine-scale gradient ramps are difficult to achieve with traditional setups, since all reagents need to be pre-mixed.

The mixing chamber can be seen in detail in Figure 2. Distinctive features of this chamber include a computer monitored Teflon level sensor at the base to monitor liquid levels. This sensor sends a signal to the computer when it is covered/uncovered by liquid, which can be used to activate or close selected valves. A Teflon magnetic stirring bar will be present, just above the level sensor, to ensure that the liquids inside are thoroughly mixed and equilibrated prior to introduction on the column. The motor for the stirrer sits in a cavity on the side of the mixing chamber, but does not contact the fluid directly. After filling and mixing, the chamber will be pressurized via N_2 gas. A 3-way valve below the chamber will be activated to allow the mixed liquid to enter the column. Once the liquid level falls below the level sensor, the valve closes, the N_2 gas is vented, and a new stage of pumping commences. Additionally, the third port on the three-way valve serves as a sample introduction dock, through a luer-lock connection and a syringe. In this manner, the sample can be introduced directly to the column with no worry about contaminating the mixing chamber.

The column portion (C; Figure 1) of the HPLC system has the unique advantage of allowing us to vary the column length, depending on the demands of the elemental system being studied. In essence, the column in our system is a rigid piece of Teflon tubing, which is contained in a water jacket. By adding and removing pieces to this water jacket, and changing the length of the column tubing, we can manipulate the total column length. Ultimately, after passing through the column, the eluted volumes will drain through a solenoid manifold valve (D; Figure 1), that will direct the eluent to the appropriate collection vessel (thereby, allowing us to separate different column cuts).

A further enhancement of our HPLC system is that the whole system can be thermally controlled. Some studies indicate that higher temperatures can sharpen the elution peak of an element, thereby increasing the separation efficiency of a column [8-11]. Using a circulating water heater (E; Figure 1), we have designed an independent, closed loop water system that is in contact with all components. This loop consists of a water jacket surrounding the column, an insulating jacket that encompasses the mixing chamber and six Teflon coils that are isolated inside of the liquid reservoirs.

Lastly, the proposed system will be automated via an external computer running LabView software from National Instruments. Through this computer system, we will be able to specify mixing parameters, monitor the level sensor, and control all valves and pumps. In this manner, the whole column sequence can be preprogrammed and automated.

Application and Results: Currently, the HPLC system is still in development. However, prior to obtaining results for actual samples, careful consideration must be given to the calibration of the system. We are presently in the process of running several calibration tests for the separation of Ni (from matrix elements – especially Mg), to facilitate Ni isotopic analyses.

References: [1] Burnett et al. (2003) *Space Sci. Rev.* 105, 509-534. [2] Wiens et al. (2007) *Space Sci. Rev.* 130, 161-171. [3] Brownlee et al. (2003). *JGR*, 108, E10 8111. [4] McKeegan et al. (2006) *Science* 314, 1724-1728. [5] Zolensky et al. (2006) *Science* 314, 1735-1739. [6] Yano et al. (2006) *Science* 312, 1350-1353. [7] Tsuchiyama et al. (2011) *LPSC XLII* abstract #1788. [8] Cerrai and Testa (1963) *J. Inorganic Nuclear Chem.* 25, 1045-1050. [9] Siekerski and Sochacka (1964) *J. Chromatography* 16, 385-395. [10] Horwitz et al. (2006) *Sep. Sci. Tech.* 41, 2163-2182. [11] Pourmand and Dauphas (2010) *Talanta* 81, 741-753.

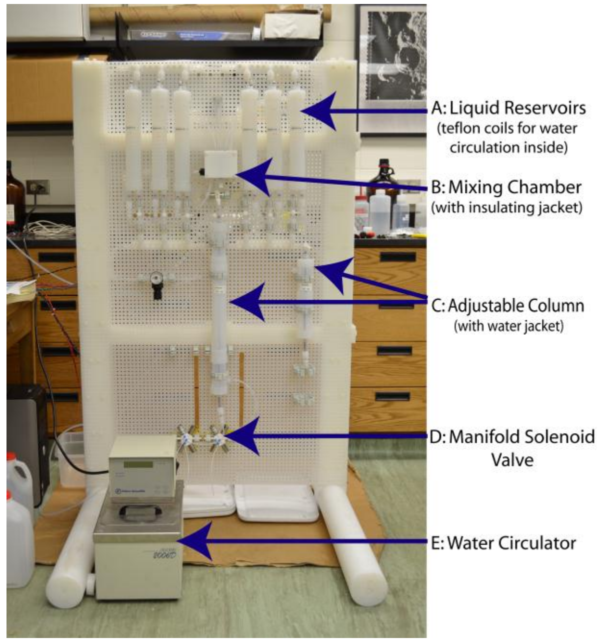

Figure 1: Overall design of the HPLC system. Please note the presence of the water circulator, which sustains water flow up through the water jacket of the column, through the insulating jacket of the mixing chamber, through the Teflon coils in the liquid reservoirs prior to returning to the circulator. Also note the possibility of several different column lengths.

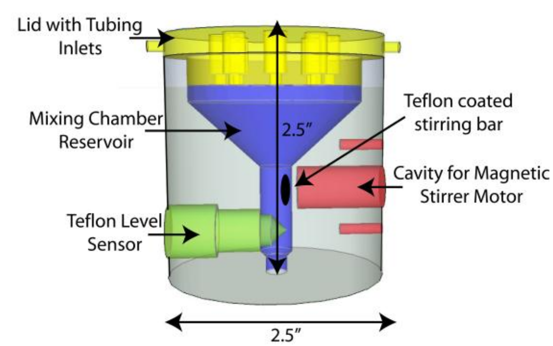

Figure 2: A 3-D rendering of the custom-designed mixing chamber with specific features labeled. The mixing chamber will feature a Teflon level sensor, a stirring bar, and ports for the introduction of up to six reagents. In addition, the chamber can be pressurized with N_2 to force the reagents into the column.