DEVELOPMENTS IN PF-HPLC (PNEUMATIC-FLUOROPOLYMER HIGH PERFORMANCE LIQUID CHROMATOGRAPHY). J.Y. Hu[1], F.L.H. Tissot[1], R. Yokochi[1,2], T.J. Ireland[1] and N. Dauphas[1], [1]Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago IL, [2]Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, IL.

Introduction:

Return missions are providing unique opportunities to deepen our knowledge of the formation and evolution of the solar system. The six Apollo missions have been critical in shaping our understanding of the Earth-Moon history [1], and the recent Genesis (solar wind; *e.g.*, [2]), Stardust (cometary dust from Wild 2; *e.g.*, [3,4]) and Hayabusa (dust from S-type asteroid from Itokawa; *e.g.*, [5]) missions brought in a wealth of data.

Because of the limited availability of such return samples, every step of the methodology – from sample preparation to isotopic analysis – must be optimized in order to maximize the amount of information extracted from the samples. If the latest generation of TIMS and MC-ICPMS offers unprecedented accuracy and precision in isotopic analysis (e.g., [6]), much progress remains to be done on the sample purification end. Indeed, isotope geochemistry techniques are often time-consuming, and rely on column chemistry techniques that have not evolved much in the last 40 years (*e.g.*, open-system, gravity driven column) [7].

One alternative to lengthy, laborious traditional column chromatography is High-Performance Liquid Chromatography (HPLC) [8]. The HPLC outperforms traditional chromatography in several aspects, which include: 1) close-system setups, 2) pressurization of the system which allows for longer columns and finer resins to be used leading to better separation, 3) possibility to automate the elution sequence, therefore removing the human error component [9]. Despite these merits, some drawbacks hinder use of HPLC in cosmochemistry. These drawbacks are mainly associated with the structure and materials used to build the systems. Metal and glass parts are commonly present in the liquid flow path and are prone to corrosion by concentrated acids and organic solvents, leading to possible contamination of the samples and damage to the system. Electronic parts spatially associated with the HPLC unit are also exposed to harsh chemical environments, thus shortening dramatically the lifespan of the instrument.

In an effort to provide the community with a robust and durable system that overcomes the drawbacks of common HPLC system, we developed the first PF-HPLC: a Pneumatic-Fluoropolymer High Performance Liquid Chromatography system. Below we review the main features of the system and detail the latest upgrades that we included.

Overview of PF-HPLC:

The PF-HPLC system was built at the Origins Lab of the University of Chicago and earlier versions of the system were described in [9,10].

The most distinctive features are:

1) The elution procedures are automated through computer control using a LabView software interface, so as to achieve (i) fresh mixing of reagents for each elution step, (ii) finely controlled gradient elutions. This improves the sample-to-sample reproducibility.

2) The system is temperature controlled to improve chemical separations.

3) A flexible modular design was adopted to enable quick change of resin types and column length depending on the separation schemes needed.

The diagram below (Fig. 1.) outlines the main components of the PF-HPLC. Ultra-pure reagents (*e.g.*, HF, HCl, HNO_3, H_2O_2, HIBA, or any other liquid) are stored in six Teflon reservoirs. The reagents a supplied

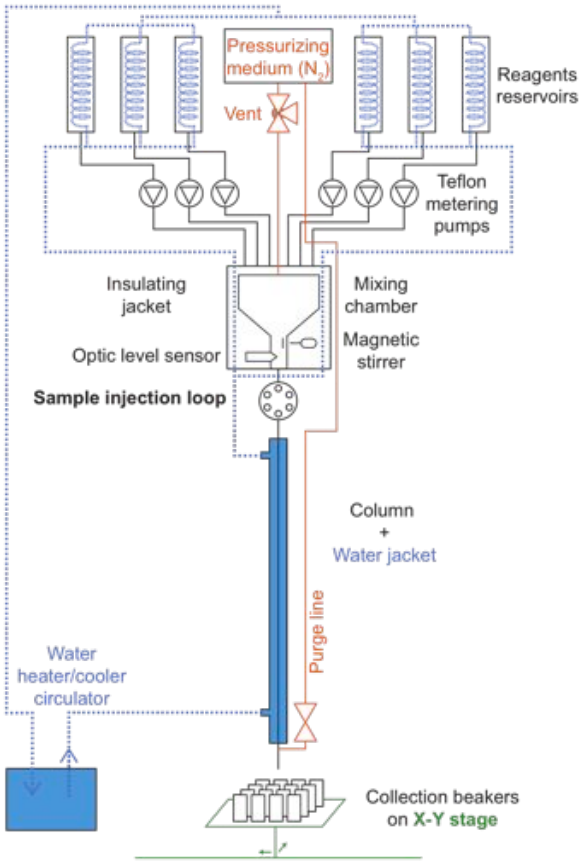

Fig. 1. *Schematic view of the PF-HPLC.*

to a mixing chamber via Teflon pumps (stroke volume 40 μL). A Teflon-coated stirring magnet is externally activated and mixes the reagents in the chamber. Between the chamber and column is a Teflon pneumatic sample injection loop (Fig. 2). When the loop is open, dry N_2 will pressurize the mixing chamber and force acids through the column (position 1). The loop can also introduce samples through the sample tubing (position 2). At the end of the column is a pneumatic X-Y stage with beakers on it. The X-Y stage can be controlled by computer and moved in 2 orthogonal directions to bring the beakers to the end of the column and collect the purified solutions. A gas line is used to purge the tube right below the column and reduce the dead volume of the system. Any solution left in the tube will be completely transferred to the beakers.

The water circulation system can control the temperature of the system over a wide range (0 to 80°C) to optimize the separation efficiency.

Upgrades:

The previous version of the PF-HPLC [11] was using a pneumatic 3-way valve for sample injection and a manifold to direct the various chemistry cuts into their assigned beakers. Because of dead volume problems, we decided to completely rethink these two major components of the system.

The connection between the mixing chamber and the column is now done through a typical HPLC sample injection loop (Fig. 2.). The inner part of the loop rotates to direct the liquid flow either (1) from the mixing chamber to the column, or (2) from the mixing chamber, through the sample tubing, to the column.

This design is very common in HPLC system. However, the part we designed is unique as it is entirely made out of highly resistant plastics (e.g., fluoropolymer, PVDF), and is pneumatically actuated.

The manifold at the bottom of the column has been removed and replaced by an all-plastic, pneumatic X-Y stage (Fig. 3.). A T-connector immediately below the column allows us to flush clean N_2 into the tubing leading from the end of the column to the collection vessel, solving any dead volume problem we had before. The stage is composed of 2 4-positions pistons placed at right angles, and can thus reach up to 16 positions, *i.e.*, collection of up to 16 different cuts is possible without tending to the instrument.

References: [1] Crawford et al (2014) *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 372*, #20130315. [2] Wiens et al (2007) *Space Sci. Rev.*, *130*, 161-171. [3] McKeegan, K. et al (2006) *Science*, *314*, 1724-1728. [4] Zolensky et al (2006) *Science*, *314*, 1735-1739. [5] Yano et al. (2006) *Science* 312, 1350-1353. [6] Dauphas, N. et al (2009) *Chemical Geology*, *267*, 175-184. [7] Martin et al (1941) *Biochemical Journal*, *35*, #1358. [8] Tachibana et al (2003) *AJL*, *588*, L41. [9] Ireland, T.J. (2013) *Chemical Geology*. *357*, 203-214. [10] Ireland, T.J. et al (2012) *LPSC* #2141. [11] Tissot, F.L.H. et al (2013) *LPSC* #2867.

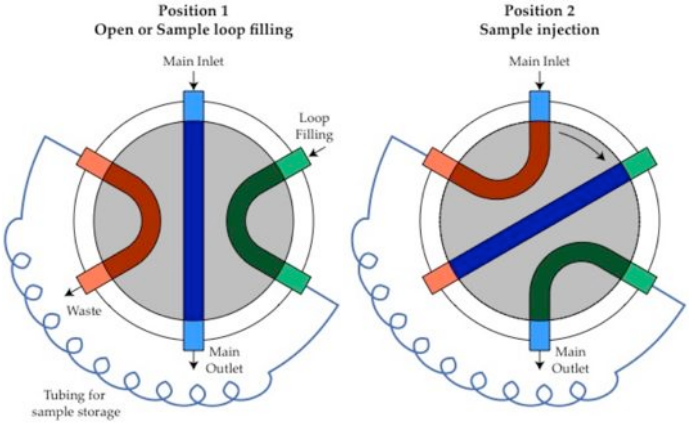

Fig. 2. *Schematic of the all-plastic pneumatic sample injection loop.*

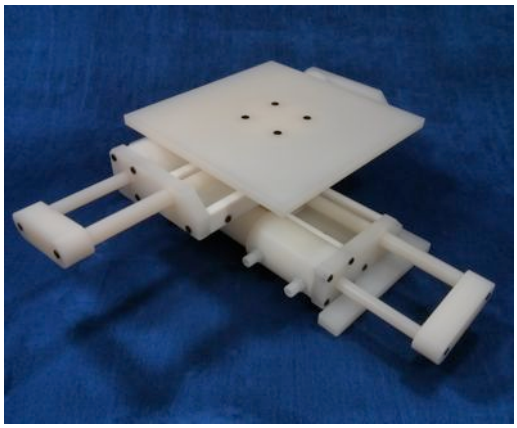

Fig. 3. *Picture of the pneumatic all plastic X-Y stage.*