TOWARDS RIMS MEASUREMENTS OF ULTRA-LOW ELEMENTAL ABUNDANCES IN GENESIS SOLAR WIND COLLECTORS.

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Introduction: While many important objectives of the Genesis mission [1] have been successfully met, a specific objective awaiting to be addressed is the analysis of elements in the mass range 80-100. This objective is the focus of our collaborative effort whose goal is to address two major cosmochemical issues. These are: (a) a possible gas-dust fractionation in solar accretion process (addressed by comparing abundances of non-volatile Rb, Sr and Se with the volatile Kr, as proposed in Ref. [2]), and (b) determining structure in the distribution of elemental abundances in the N=50 closed shell region using Sr, Y and Zr (addressing why the clear *r*- and *s*-process double peak structure in the Solar System element abundance curve associated with the magic neutron numbers N=82 and 126 is not apparent for the N=50 region). To meet this goal, we ultimately require quantitative RIMS measurements of SW fluences of Rb, Sr, Y, Zr and Se as well as a reference element (Mg). Analyses of Rb, Sr, Y, Zr and Se are difficult because these elements are implanted in the Genesis solar wind (SW) collectors at fluences below 10^8 at/cm^2 [1] – at least, two orders of magnitude lower than SW measured to date by Secondary Ion Mass Spectrometry (SIMS) and Resonance Ionization Mass Spectrometry (RIMS) [3, 4].

This work discusses progress in development of the improved RIMS instrumentation capable of meeting this challenge [5]. Our plan is to analyze three elements simultaneously: two of the listed trace elements and Mg. To do this, the instrument design features an analytical probe based on ultrafast laser ablation, which has a potential for higher signal-to-noise ratio, high resolution depth profiling, and the ability to analyze insulating Genesis samples (such as sapphire). The instrument also features novel ion optics designed for improved signal-to-noise ratio. Although being designed for Genesis samples, it will be useful for other planetary materials, many of which are insulators.

Accomplishments thus far: We have developed and tested a laser ablation probe well suitable for ultra-trace analysis of Genesis collectors. Its most important advantage, compared to ion sputtering, is a higher number of sample atoms volatilized in a single analysis shot, which leads to improved signal-to-noise ratio. This probe is based on a fs 800 nm laser whose beam is conditioned using special refractive optics enabling a flat-top power density profile [6]. Irradiating solids with such a laser beam can lead to formation of flat-bottomed craters with nearly-cylindrical shapes (Fig.1), resulting from layer-by-layer ablation of sample material. Key strengths of this approach are: (a) "cold" material ablation without damaging underlying layers, minimizing ion mixing artifacts (theoretically, even if analysis begins on a contaminated surface), and (b) minimized sampling of the surface contamination from the crater rim (because its diameter grows negligibly with increasing numbers of laser ablation shots). Importantly, the flat-top power density profile of the laser probe is stable over a broad range of spot sizes (from a few µm to ~100 µm) and can be selected by using a suitable objective lens [6].

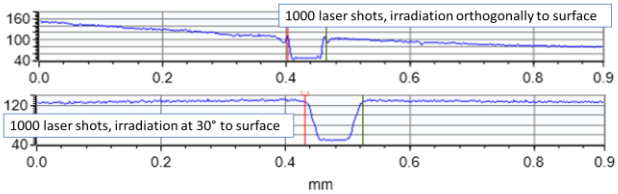

Figure 1. Optical profilometry of laser ablation craters made on Si by fs 800 nm beam with flat-top profile, 1000 shots at 25 mW power. Top: orthogonal irradiation, crater depth ~11 µm; Bottom: irradiation at 30° from surface normal, crater depth ~ 7 µm. Crater diameters ~ 80 µm.

For better suppression of noise originating from secondary/direct ions, we have developed and tested an improved time-of-flight (TOF) mass analyzer. It is based on the novel Right-Angle Ion Mirror-Prism (RAIMP) concept [5,7], which features a special adjustable slit controlling the range of energies of ions reaching detector (Fig.2, insert A on the bottom left). This energy filtering in conjunction with TOF focusing has a potential to eliminate secondary/direct ions causing noise counts and thus to further improve the signal-to-noise ratio in RIMS analyses. We constructed the new TOF mass analyzer system comprised of two RAIMPs and installed it for tests on an operational home-made TOF mass spectrometer (MS) equipped with the described above ultrafast laser ablation probe and optimized for laser post-ionization (Fig.2). Currently, this instrument is undergoing tests in RIMS mode using ion implanted standards made from the same materials as Genesis collectors: Si, diamond-on-Si (DOS) and sapphire.

To enable the RIMS operation, we have developed and constructed three tunable Ti:sapphire laser systems that are currently set up for Rb, Sr and Mg. The initial RIMS tests were conducted with ^{87}Rb ion implants (10^{13} at/cm^2 @ 180 keV), and succeeded in finding the instrumental alignments with efficient suppression of direct/secondary ions (Fig.2, insert B on the bottom right – for Si and DOS). These “noise ions” formed in fs laser ablation included direct atomic ions and matrix cluster ions (Si$_n$ from Si and C$_n$ from DOS), detected as direct and photo- ions. “Noise ion” suppression was confirmed for all three tested Genesis substrates.

Continuing and future effort: Our ongoing efforts are focused on: (1) optimization of RIMS signals and signal-to-noise ratios, (2) testing depth profiling with flat-top laser ablation probe, and (3) constructing the optical beamline to collinearly overlap multiple beams from working tunable lasers and thus add Sr and Mg to the list of analyzed elements. RIMS depth profiling experiments are in progress and all results will be reported at the LPSC.

While the RAIMP-upgraded UIC TOF-MS (Fig.2) is a well-suitable testbed for all the newly developed hardware and experimental procedures, most of actual RIMS analyses of Genesis (Rb, Sr, Y, Zr and Se, plus Mg) need to be conducted using a dedicated RIMS instrument operating under ultrahigh vacuum (~10^{-10} Torr or better) for best precision of results. Construction of this instrument is underway, and it will incorporate all the described above new hardware.

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References: [1] Burnett D. S. et al. (2003) *Space Sci. Rev. 105,* 509–534. [2] Wiens R. et al. (1991) *Geophys. Res. Lett. 18* (2), 207–210. [3] Burnett D. S. and Genesis Science Team (2011) *PNAS 108* (48), 19147-19151. [4] Veryovkin I. V. et al. (2014) *LPSC XLV*, Abstract #2795. [5] Veryovkin I. V. et al. (2018) *LPSC XLIX*, Abstract #2824. [6] Laskin A. (2013) *Laser Technik Journal* 10 (1) 37-40. [7] Veryovkin I. V. and Hanley L., (2017) *Proc. 65th ASMS Conf. Mass Spectrom. and Allied Topics*, Citation ID 288660/ThP 373

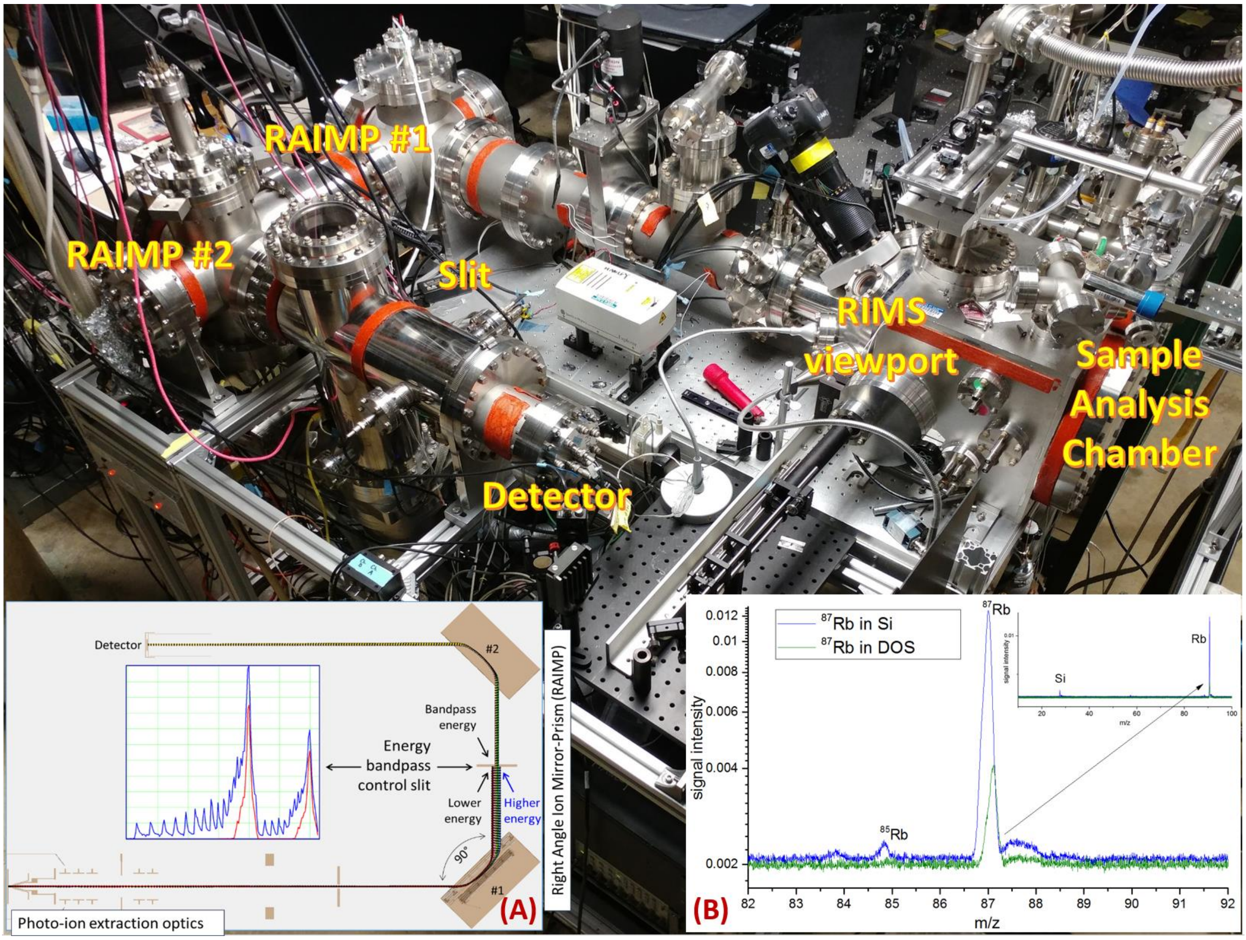

Figure 2. TOF-MS instrument at UIC used to test the described hardware. This instrument operating under high vacuum conditions (~5×10^{-9} **T**orr) is optimized for a combination of the fs laser probe with laser post-ionization, including Resonance Ionization. Insert (A) – layout of he instrument ion optics modelled by SIMION (Inset: the effect on mass spectra when the energy bandpass control slit is closing, m/z 720 and 721); Insert (B) – RIMS spectra measured on ^{87}Rb ion implants in Si and DOS (Inset: the entire mass spectral range illustrating the efficiency of direct/secondary ion suppression).