TRACE ELEMENTAL ANALYSIS OF GENESIS SAMPLES: PROGRESS IN DEVELOPING RIMS WITH LASER ABLATION PROBE. I. V. Veryovkin[1], C. E. Tripa[1], J. M. Gross[1], L. Hanley[1], A. J. G. Jurewicz[2,3] and D. S. Burnett[4], [1] Department of Chemistry, University of Illinois at Chicago (UIC), 845 W. Taylor St., Chicago, IL 60607 (verigo@uic.edu), [2] Center for Meteorite Studies, Arizona State University, ASU m/c 6004, Tempe, AZ 85287 and [3] Dartmouth College, Hanover, NH 03755 (Amy.Jurewicz@asu.edu), [4] Division of Geological & Planetary Sciences, Caltech, Pasadena, CA 91125 (burnett@gps.caltech.edu)

Introduction: Improving the accuracy and precision of solar elemental abundances was a driver of Genesis sample return mission science [1]. Specifically, a major goal was to replace the current precise but indirect CI chondrite source of solar elemental composition with a source directly related to the Sun's outer convective zone (OCZ), the solar wind (SW). While many important objectives of the Genesis mission have been successfully met, analysis of elements in the mass range 80-100 has not yet been accomplished. It is the focus of our effort in order to addresses two major cosmochemical issues: (a) possible gas-dust fractionation during the 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 Rb, Sr, Y and Zr (to clarify why the clear *r*- and *s*-process double peak structure in the Solar System elemental abundance curve seen for the magic neutron numbers N=82 and 126 is not apparent for the N=50 region). To meet these goals, quantitative measurements for SW fluences of Rb, Sr, Y, Zr and Se are required.

Measuring Rb, Sr, Y, Zr and Se is a *major analytical challenge:* these elements are present in the SW sample at fluences below 10^8 at/cm^2 [1]; i.e., lower than SW measured to date by Secondary Ion Mass Spectrometry (SIMS) and Resonance Ionization Mass Spectrometry (RIMS) [3, 4] by two or more orders of magnitude.

The Approach: This work discusses the development of RIMS instrumentation with features allowing it to rise to the challenge mentioned above [5]. New approaches to increase the signal-to-noise ratio (SNR) of current RIMS analyses are based upon the following fundamentals. RIMS is a combination of a Time-of-Flight Mass Spectrometer (TOF-MS) with a laser post-ionization ion source. Extracted material must be atoms (not ions) from the solid sample produced by either an ion- or a laser beam acting as analysis probe. Each sub-system of the RIMS (the analysis probe, the TOF-MS, and the resonance post-ionization lasers) contributes to the SNR and therefore must be properly designed and optimized.

The RIMS under construction at UIC has an *analysis probe* based on "cold" laser ablation. A single laser shot can easily extract more atoms from the sample than any ion beam pulse, thus effectively improving the SNR for the analysis. Using ultrafast lasers with femtosecond or picosecond pulses dramatically reduces heating (a "cold" ablation regime) during extraction of material from the sample and is, in theory, free of ion beam mixing artifacts. In contrast to ion beams, lasers do not introduce foreign atoms on analyzed surfaces, but like ion beams, *flat craters* (Fig. 1) enabling high resolution depth profiling can be obtained with laser beams that have specially shaped power density profiles. Depth profiling will minimize the amount of matrix relative to SW in a given pit, and will allow the elimination of surface shots containing contaminants: which is what we need for efficient and accurate analysis of in Genesis samples. Another important benefit of using laser ablation probes for RIMS of Genesis samples is that insulating collector materials (such as sapphire) can be analyzed without extra sample preparation steps (e.g. conductive coating deposition) that could cause sample contamination.

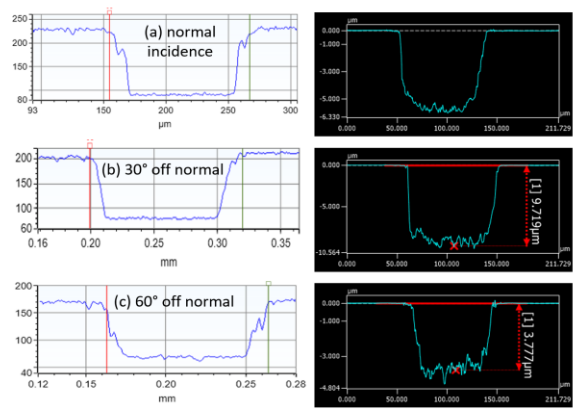

Figure 1. *Ablation of Si with flat-top laser probe.* (a), (b) and (c) – normal incidence, 30° and 60°, respectively. Characterization: Bruker-Nano Contour GT-K optical profilometer (LEFT) and Keyence VK-X1000 3D laser scanning confocal microscope (RIGHT). Crater depths for 20000 shots from ~6 µm for normal ablation to ~4 µm for 60° correspond to material removal rates from ~0.3 nm to ~0.2 nm per shot, respectively.

Another feature: we have equipped the *TOF-MS* with novel ion optics designed for improved SNR. Its mass analyzer is based on the novel Right-Angle Ion Mirror-Prism (RAIMP) concept [6], which features a special adjustable slit controlling the range of energies of ions reaching detector (Fig.2). This energy filtering

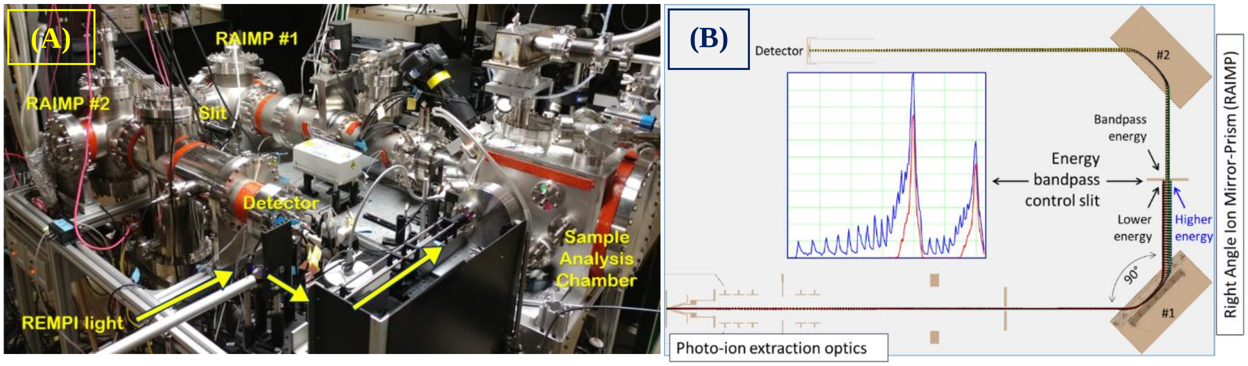

Figure 2. *The testbed RIMS at UIC: TOF-MS for RIMS operation with the RAIMP mass analyzer:* **(A)** The actual instrument after upgrade. **(B)** SIMION modeling of photo-ion trajectories. Inset: modeling of mass spectra of C_{60} ions with the energy bandpass slit open (blue) and partially closed (red). Closing the slit cuts off "tails" resulting from imperfect TOF-focusing of ions with higher energies (the situation typical for direct/secondary ions).

in conjunction with TOF focusing further improves the SNR of RIMS by efficiently eliminating secondary/direct ions that cause noise. Additionally, an efficient pulsed ion extraction optics optimized for operation with laser post-ionization improves SNR by increasing the detectable signal and suppressing secondary/direct ions such as direct atomic and cluster ions (e.g. matrix ions: Si_n from Si and C_n from DOS).

Finally, the new RIMS features three *tunable lasers* for Resonantly-Enhanced Multi-Photon Ionization (REMPI) of laser–ablated neutral atoms. With optimal REMPI schemes, these lasers increase the atomic photo-ion signals, improving SNR. Optimal focusing and positioning of REMPI beams helps improve discrimination between resonantly ionized atoms (i.e. useful signal) and matrix cluster photo-ions (i.e. noise).

Thus, all three sub-systems of the RIMS in development require optimized alignment parameters yielding best SNRs. Their status is described below.

Accomplishments: Combined operation of all three subsystems of RIMS at UIC is being optimized in a testbed instrument (Fig.2), which is applied to three different SW collector materials (Si, DOS and sapphire). We use ion implants standards in these experiments to understand the space of alignment parameters and learn how to find and overlap the "sweet SNR spots" of each sub-system. Our tunable lasers are currently set up for simultaneous RIMS of two trace elements (Rb and Sr) and one reference element Mg.

Fig.3 shows the progress in depth profiling with RIMS using 800 nm femtosecond laser probe: from June to November 2019 we improved dynamic range by optimizing the laser ablation probe. Note that the depth resolution of the laser probe was sufficient to resolve surface contamination from the ion implant.

Continuing and future effort: Our ongoing efforts using the testbed RIMS are focused on: (1) improvement of SNR by increasing RIMS signals and lowering noise baselines; to this end, we are implementing a new data acquisition system; (2) improvement of quality and accuracy of depth profiling using a different laser ablation probe (213 nm picosecond laser), especially on sapphire SW collectors, and achieving higher dynamic range with detection limits sufficient for trace element analysis.

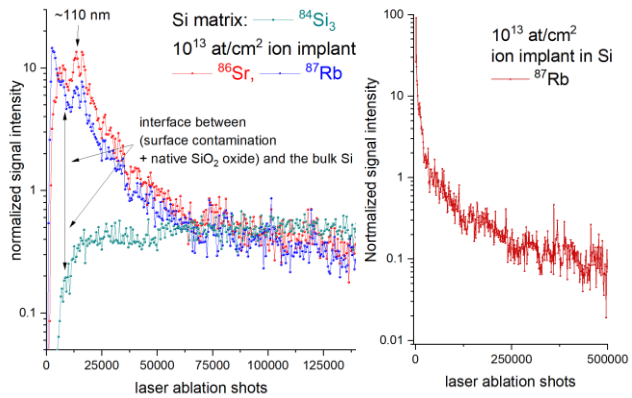

Figure 3. *Depth profiles* of Sr and Rb ion implants in Si measured at UIC by RIMS with flat-top laser ablation probe (800 nm fs laser). Left: two-element RIMS (06.2019), Right: single-element (Rb) RIMS (11.2019). Comparison reveals improved dynamic range of depth profiling resulting from laser probe optimization.

At the same time, we are constructing a dedicated RIMS for Genesis, which will incorporate all these thoroughly optimized hardware components and take advantage of all newly developed methods.

Results of these efforts will be presented at LPSC.

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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. (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] Veryovkin I. et al. (2019) *LPSC L*, Abstract #2432.