RIMS WITH LASER ABLATION PROBES FOR TRACE ELEMENTAL ANALYSIS OF GENESIS SAMPLES: LESSONS LEARNED FOR RB AND SR. I. V. Veryovkin [1, 3] and C. E. Tripa[2, 3], [1] 18W079 71st St, Darien, IL 60561 (verigor@live.com), [2] 655 South Blvd, Apt. 301N, Oak Park, IL 60302 (etripa@hotmail.com). [3] Formerly: Department of Chemistry, University of Illinois at Chicago (UIC), 845 W. Taylor St., Chicago, IL 60607

Introduction: Improving accuracy and precision of solar elemental abundances was the main goal of Genesis sample return mission [1]. To this end, material directly related to the Sun's outer convective zone, the solar wind (SW), was collected. Analysis of elements with atomic masses between 80 and 100 has not been accomplished on Genesis SW collectors so far, and it was the focus of our efforts aiming at resolving two major cosmochemical issues: (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 [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, accurate quantitative measurements of SW fluences of Rb, Sr, Y, Zr and Se are required. This is a *major experimental challenge* because these elements are implanted in the SW collectors at fluences below 10^8 at/cm^2 [1] – i.e., at least, two orders of magnitude lower than SW measured to date by Secondary Ion Mass Spectrometry (SIMS) and Resonance Ionization Mass Spectrometry (RIMS). Here we summarize what we learned from our development of the RIMS to measure Rb and Sr and compare results from two standard reference materials, ion implants in Si and sapphire, replicating Genesis flight collectors.

Approach: To rise to the challenge mentioned above, the improved RIMS instrumentation must have its signal-to-noise ratio (SNR) considerably improved. RIMS is a combination of a time-of-flight mass spectrometer (TOF-MS) with Resonantly Enhanced Multi-Photon Ionization (REMPI) ion source where extraction of atoms from the solid sample can be done by either ion or laser beam acting as analysis probe. Each of these three "pillars" of RIMS, namely, the TOF-MS, the tunable laser system for REMPI, and the pulsed analysis probe, contribute to the SNR. Therefore, they must be fully optimized to yield best SNRs, and all the three "sweet spots" of alignment parameters must be efficiently overlapped for best overall SNR. To do this optimization, ion implant standards were used in this work conducted at UIC. The *first* pillar on which our RIMS approach rested was TOF-MS instrument with improved SNR. We equipped it with a mass analyzer based on the novel Right-Angle Ion Mirror-Prism (RAIMP) concept [6], which permits efficient control of the range of energies of ions that reach the detector and thus improves the SNR of our RIMS by efficiently eliminating secondary/direct ions causing noise counts. The *second* pillar supporting our RIMS approach was the system of tunable lasers for REMPI of laser–ablated neutral atoms. With optimal REMPI schemes these lasers improve SNR by maximizing atomic photo-ion signals. We built three tunable Ti:sapphire lasers and demonstrated [3, 4] that optimal focusing and positioning of REMPI beams helps improve discrimination between resonantly ionized atoms (i.e. useful signal) and matrix cluster photo-ions (effectively, noise), thus additionally improving the SNR. The *third* pillar of our RIMS development effort, the analysis probe, was chosen to be based on laser ablation. This choice was made because a single laser shot easily extracts for analysis more sample atoms than any ion beam pulse, thus effectively improving the SNR. And, in contrast to ion beams, lasers do not bring foreign atoms on analyzed surfaces. Moreover, using ultrafast lasers with femtosecond or picosecond pulse lengths enables sample material extraction in the "cold" ablation regime, which is free of ion beam mixing artifacts. We demonstrated that reshaping the laser ablation beam profile into flat-top instead of Gaussian, enables ultrahigh resolution depth profiling [4], which was exactly what is needed for efficient and accurate excavation of SW atoms implanted in Genesis samples and for clearly distinguishing them from atoms originating from the collector surface contamination. Another advantage of laser ablation probe for Genesis is that insulating collector materials (such as sapphire) can be analyzed without additional sample preparation steps (e.g. conductive coating deposition) that could result in extra surface contamination

Accomplishments: We have built all three pillars up and enabled and optimized RIMS operation using a RAIMP-equipped testbed TOF-MS instrument at UIC [3, 4]. We tried RIMS analyses of three different SW collector materials (Si, DOS and sapphire). Here we report on comparison between two types of laser ablation probes: 800 nm femtosecond laser (~75 fs) and 213 nm picosecond laser (~27 ps). The former one was operating with flat-top beam profile, allowing us to demonstrate sub-nm depth resolution on Rb and Sr ion implants in Si (Fig.1, [7]). Unfortunately, we found that

the fs infrared laser probe was incapable of performing depth profiling of sapphire – because low light absorption cross section of this material resulted in negligibly low material removal rates. As a result, we could not detect Rb and Sr signals from sapphire ablated by this infrared laser. Our interest in RIMS measurements on sapphire was driven by the need to identify the SW collector material, which had the least possible mass interferences from native matrix ions with the signals of Rb and Sr. Example of such interferences from Si clusters is shown in Fig.2. We hypothesized that no such clusters would be forming on sapphire because it is aluminum oxide. To test this hypothesis, we had to overcome the physical limitation of infrared laser ablation of sapphire. To this end, we used a new ps ultraviolet laser whose radiation was efficiently absorbed by sapphire. Fig. 3 shows RIMS mass spectra measured with this laser on Si and Fig.4 – on sapphire. Interestingly, Si ablated by the ps ultraviolet laser has

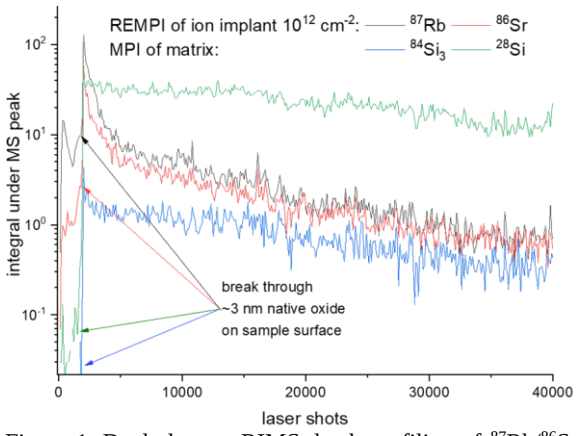

Figure 1. Dual-element RIMS depth profiling of $^{87}Rb/^{86}Sr$ ion implants in Si (90 keV @ 10^{12} cm^{-2}) with flat-top 800 nm fs laser probe. A distinction between the surface contamination + native oxide region (~3 nm thick) and the bulk of Si sample is very clearly visible. Sharp material interface detected here has no beam mixing artifacts that are typically observed with ion beam probes.

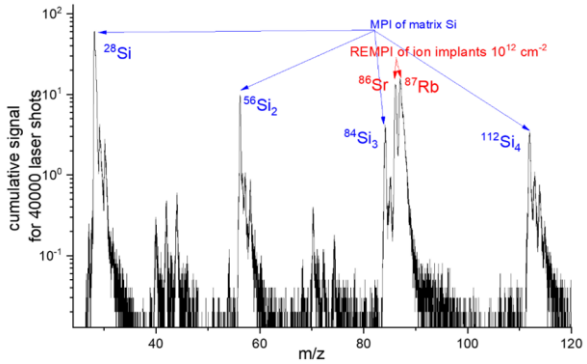

Figure 2. Mass spectra of photoions observed under fs 800 nm laser irradiation of Si. Direct/secondary ions were efficiently suppressed by the RAIMP ion optics. Note mass interference between Si_3 clusters and Sr/Rb peaks.

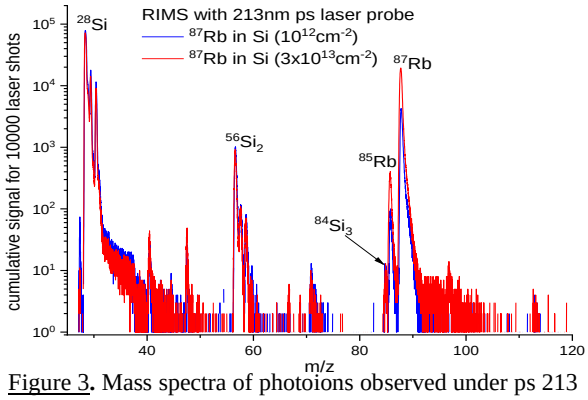

Figure 3. Mass spectra of photoions observed under ps 213 nm laser irradiation of Si. Note much less pronounced mass interference between Si_3 clusters and Sr/Rb peaks compared to fs 800 nm laser ablation.

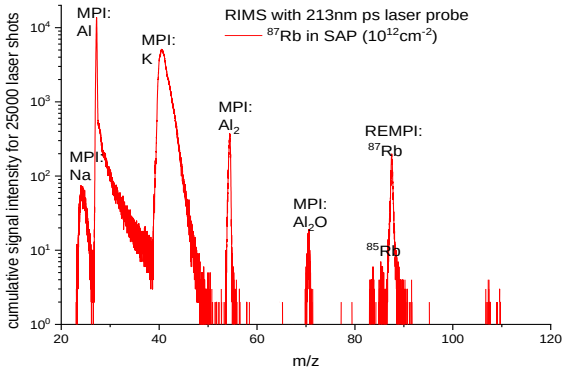

Figure 4. Mass spectra of photoions observed under ps 213 nm laser irradiation of sapphire. Note no visible mass interference between around Sr/Rb peaks. MPI is multiphoton (non-resonant ionization). Peaks of Na and K ions correspond to surface contamination. Small Al-containing ions come from the bulk and can be considered native matrix ions for sapphire.

noticeably fewer mass interferences compared to the case of the fs infrared laser probe. *But the main result here is clear demonstration that sapphire and 213 nm ps laser ablation probe are a perfect match in terms of mass interferences, thus enabling trace element RIMS analysis.* This should be the approach applied to real Genesis samples in the future.

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